INTERFACE FORMATION BETWEEN HIGH DIELLECTRIC
PERMITTIVITY FILMS AND III-V COMPOUND
SEMICONDUCTORS USING HF CHEMISTRIES AND
ATOMIC LAYER DEPOSITION

by
Fee Li Lie

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2011
As members of the Dissertation Committee, we certify that we have read the dissertation prepared by Fee Li Lie entitled Interface Formation between High Dielectric Permittivity Films and III-V Compound Semiconductors using HF Chemistries and Atomic Layer Deposition and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

___________________________________________________ Date: 4/4/2011
Anthony J. Muscat

___________________________________________________ Date: 4/4/2011
James C. Baygents

___________________________________________________ Date: 4/4/2011
Ara Philipossian

___________________________________________________ Date: 4/4/2011
Supapan Seraphin

Final approval and acceptance of this dissertation is contingent upon the candidate’s submission of the final copies of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

___________________________________________________ Date: 4/4/2011
Dissertation Director: Anthony J. Muscat
STATEMENT BY AUTHOR

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Signed: Fee Li Lie
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# Table of Contents

**List of Figures** .................................................. 7

**List of Tables** .................................................. 12

**Abstract** ......................................................... 13

**Chapter 1. Introduction** ........................................ 16
  1.1. Background .................................................. 16
  1.2. Native oxide removal ....................................... 21
  1.3. Reaction between atomic layer deposition precursors and III-V surfaces 24
  1.4. Nature of III-V surface defects ............................ 26
  1.5. Explanation of dissertation format .......................... 28

**Chapter 2. Present Study** ......................................... 30
  2.1. In_{0.53}Ga_{0.47}As(100) native oxide removal by liquid and gas phase HF/H_{2}O chemistries .................................................. 30
  2.2. Controlled oxide removal and surface morphology of InSb(100) native oxide using gas phase HF etching ........................................ 31
  2.3. ALD of Al_{2}O_{3} films on gas phase HF etched InSb and InAs(100) .................................................. 33
  2.4. Interaction of TiCl_{4} with native oxide-covered InSb(100) .................................................. 35
  2.5. Passivation of InGaAs interface by atomic layer deposition of Al_{2}O_{3} and post deposition annealing .................................................. 36
  2.6. Effect of Deep-Level Defects on Surface Recombination Velocity at the Interface Between Silicon and Dielectric Films .................................................. 37
  2.7. Characterization of defect states at n-type In_{0.53}Ga_{0.47}As and Al_{2}O_{3} interfaces using surface recombination velocity .................................................. 38
  2.8. Future work .................................................. 39

**References** ....................................................... 46

**Appendix A. InGaAs(100) native oxide removal by liquid and gas phase HF/H_{2}O chemistries** .................................................. 48

**Appendix B. Controlled oxide removal and surface morphology of InSb(100) native oxide using gas phase HF etching** .................................................. 62

**Appendix C. A comparison of liquid and gas phase surface preparation of III-V compound semiconductors for atomic layer deposition** .................................................. 81
Table of Contents—Continued

APPENDIX D. Oxide removal and selective etching of In from InSb(100) with TiCl_4 ................................................................. 92
D.1. Introduction ........................................................................ 93
D.2. Experimental ...................................................................... 97
D.3. Results and Discussion .......................................................... 99
D.4. Conclusion ........................................................................ 112
   D.4.1. Acknowledgement .......................................................... 113

REFERENCES ........................................................................ 114

APPENDIX E. Passivation of InGaAs interface by atomic layer deposition of Al_2O_3 and post deposition annealing ............ 118
E.1. Experimental ...................................................................... 119
E.2. Results ............................................................................. 122
   E.2.1. Solvent cleaned surface ............................................... 122
   E.2.2. Liquid phase HF etched surface .................................. 129
   E.2.3. Correlating chemical and electrical characterization ....... 134
   E.2.4. Acknowledgement ........................................................ 135

REFERENCES ........................................................................ 137

APPENDIX F. Effect of Deep-Level Defects on Surface Recombina-

   tion Velocity at the Interface Between Silicon and Dielectric Films .......................................................... 139

APPENDIX G. Characterization of defect states at n-type Ga_{0.47}In_{0.53}As and Al_2O_3 interfaces using surface recombination velocity . . 155
G.1. Introduction ...................................................................... 156
G.2. Device Fabrication and Experimental Setup ..................... 159
G.3. Results ............................................................................ 163
G.4. Discussion ........................................................................ 169
G.5. Summary and Conclusion .................................................. 179
   G.5.1. Acknowledgment ........................................................ 182
   G.5.2. Definition of Variables ............................................... 183

REFERENCES ........................................................................ 185
LIST OF FIGURES

Figure 1.1. Plot of electron mobility (cm$^2$V$^{-1}$s$^{-1}$) versus band gap (eV) generated from literature data.  

Figure 1.2. Schematic cross section of InSb quantum well field effect transistor (QWFET) with an Al$_x$In$_{1-x}$Sb barrier layers. A buffer layer consisting of an Al$_x$In$_{1-x}$Sb film with graded composition and GaAs was inserted between the InSb and the Si substrate to enable integration of InSb onto Si. Reproduced with permission from Electronics Letters, Vol 43, Issue no. 14, 2007, Copyright the Institution of Engineering and Technology.  

Figure 1.3. Supply voltage ($V_{CC}$) versus physical gate length of n-channel field effect transistors (FETs) and Si MOSFETs. The horizontal lines are the $V_{CC}$ values used in the Si industry.  

Figure 1.4. Intrinsic gate delay versus physical gate length of n-channel field effect transistors (FETs) and Si MOSFETs. The dashed line indicates the projected intrinsic gate delay in the absence of source and drain parasitic resistances.  

Figure 1.5. Calculated density of states (DOS) for a GaAs(100) surface affected by oxidation. A characteristic semiconductor band gap with no states within the band gap (0 - 1.35 eV) is shown for a clean (2×4) reconstructed GaAs(100) surface. The addition of one to three monolayers (ML) of oxides on top of the (2×4)GaAs(100) generated states within the band gap. Reproduced from Microelectronic Engineering, Vol 86, M. Caymax, G. Brammertz, A. Delabie, S. Sioncke, D. Lin, M. Scarrozza, G. Pourtois, W-E. Wang, M. Meuris, M. Heyns, Copyright 2009, with permission from Elsevier.  

Figure 2.1. Core-level XPS spectra with the fitted components for an InGaAs(100) sample after gas phase HF etching at $P_{HF}$:$P_{H_2O}$ 1.23, 29°C, 100 Torr and subsequent 1 to 20 ALD cycles of Al$_2$O$_3$.  

Figure 2.2. F 1s, O 1s, and Al 2p core-level XPS spectra for an InGaAs(100) sample after gas phase HF etching at $P_{HF}$:$P_{H_2O}$ 1.23, 29°C, 100 Torr and subsequent TMA and H$_2$O pulses.  

Figure 2.3. Core-level XPS spectra for an InGaAs(100) sample after gas phase HF etching at $P_{HF}$:$P_{H_2O}$ 1.23, 29°C, 100 Torr and subsequent TMA and H$_2$O pulses.  

Figure D.1. Sb 3d and In 3d core-level XPS spectra taken at a 50 eV pass energy for InSb(100) samples (a) solvent cleaned, and annealed at (b) 500 K, (c) 550 K, (d) 600 K, and (e) 650 K in vacuum for 5 min at a base pressure of $10^{-10}$ Torr.
LIST OF FIGURES—Continued

Figure D.2. SEM topographical image of an InSb(100) surface after solvent cleaning and annealing in vacuum at 650 K for 5 min at a base pressure of \(10^{-10}\) Torr. Image (a) was taken at a grazing angle with a scale bar of 2.5 \(\mu\)m and image (b) was taken perpendicular to the surface with a scale bar of 500 nm.

Figure D.3. Sb 3d, In 3d, and Ti 2p core-level XPS spectra taken at 50 eV pass energy for InSb(100) (a) solvent cleaned, (b) exposed to TiCl\(_4\) at 298 K for 3 min and annealed to 500 K for 1 min, (c) exposed to TiCl\(_4\) at 470-530 K for 3 min, and (d) exposed to TiCl\(_4\) at 500-560 K for 3 min. The (b-a) spectrum is a difference, and the difference in the In 3d range was magnified \(\times 4\) for clarity. The In 3d spectra in (c) and (d) were magnified by \(\times 8\). Component states are shown by solid lines below each of the spectra in (c) and (d).

Figure D.4. Cl 2p core-level spectra taken at 200 eV pass energy for InSb(100) samples (○) exposed to TiCl\(_4\) at 298 K for 3 min and annealed at 500 K for 1 min, (—) exposed to TiCl\(_4\) at 470-530 K for 3 min, and (−−) exposed to TiCl\(_4\) at 500-560 K for 3 min.

Figure D.5. SEM topographical image of an InSb(100) surface after solvent cleaning and exposed to TiCl\(_4\) at 500-560 K for 3 min. Image (a) was taken at a grazing angle with a scale bar of 2.5 \(\mu\)m and image (b) was taken perpendicular to the surface with a scale bar of 500 nm. Inset is a 2×2 \(\mu\)m AFM height image showing a step height of \(\sim 100\) nm between points indicated by the arrows.

Figure E.1. In 3d, Ga 2p\(_{3/2}\), As 2p\(_{3/2}\) core level XPS spectra with the fitted components for In\(_{0.53}\)Ga\(_{0.47}\)As(100) samples (a) after solvent cleaning (N\(_{ox}\)), (b) after 1 ALD cycle of TMA and water, and (c) after 20 ALD cycles of TMA and water.

Figure E.2. Quantitative XPS analysis for In\(_{0.53}\)Ga\(_{0.47}\)As(100) samples after solvent cleaned and exposed to 1 to 20 cycles of ALD Al\(_2\)O\(_3\) showing (a) XPS peak area ratios between Ga\(_2\)O\(_3\) (□) and In\(_2\)O\(_3\) (▽) to the Ga and In peak of the substrate, (b) XPS peak area ratios between As\(_2\)O\(_3\) (◇) and As\(_2\)O\(_3\) (◇) peaks to As peak of the substrate, (c) the fraction of In in the substrate (△) and the coverage of As terminating the substrate(▲) in monolayer (ML), and (d) interfacial layer thickness (○) and Al\(_2\)O\(_3\) thickness (■) in Å. In (d) a linear regression of Al\(_2\)O\(_3\) thickness versus number of ALD cycles above 10 cycles revealed a slope of 1±0.2 Å/cycle. Other lines in graphs are only to guide eye.
Figure E.3. In 3d/2, Ga 2p3/2, As 2p3/2 core level XPS spectra with the fitted components for an In0.53Ga0.47As(100) sample after (a) solvent cleaning and exposed to 15 cycles of ALD Al2O3 (NoxAox), and for samples processed similarly as in (a) but with a 10 nm thick Al2O3 followed by annealing in (b) forming gas (NoxAoxFGA) and (c) NH3 (NoxAoxNH3). Spectra (b) and (c) were acquired after thinning the ∼10 nm-thick Al2O3 film to 14 and 19 Å using a 1:1000 HF:H2O solution.

Figure E.4. In 3d, Ga 2p3/2, As 2p3/2 core level XPS spectra with the fitted components for In0.53Ga0.47As(100) samples (a) after solvent cleaning and etching in 49% HF (LHF), followed by (b) 15 cycles of ALD Al2O3, (c) sample (b) with additional 85 cycles od ALD to deposit 10 nm-thick Al2O3 (LHFAox), (d) deposition of 10 nm-thick Al2O3 and annealing in forming gas (LHFAoxFGA), (e) deposition of 10 nm-thick Al2O3 and annealing in NH3 (LHFAoxNH3), and (f) deposition of 10 nm-thick Al2O3, 15 nm-thick Ni and 20 nm-thick Au blanket, and annealing in NH3 (LHFAoxMNH3). Spectra (c) thru (e) were acquired after thinning the ∼10 nm Al2O3 film to ∼2.5 nm using a procedure described in the experimental section. Spectra (f) was acquired after etching the Ni/Au blanket film and thinning the Al2O3 film using procedures described in the experimental section. The y-axis scale for the Ga 2p3/2 and As 2p3/2 spectra of liquid phase HF etched sample (a) are 0.4 and 0.2 times the y-axis scale of other samples.

Figure E.5. In 3d/2, Ga 2p3/2. As 2p3/2 core level XPS spectra with the fitted components for an In0.53Ga0.47As(100) sample after (a) solvent cleaning, etched in 49% HF, and exposed to 15 cycles of ALD Al2O3 (LHFAox), and for samples processed similarly as in (a) but with a 10 nm-thick Al2O3 followed by annealing in (b) forming gas (NoxAoxFGA) and (c) NH3 (NoxAoxNH3). Spectra (b) and (c) were acquired after thinning the ∼10 nm Al2O3 film to ∼2.5 nm using a 1:1000 HF:H2O solution.

Figure E.6. XPS composition analysis plotted against surface recombination velocity (SRV in cm·s⁻¹) for solvent cleaned prepared samples, (a) and (b), and liquid phase HF etched samples, (c) and (d), showing interfacial layer coverages of In in In2O3 state (▽), Ga in Ga2O3 state (□), and As in oxide states (●), the fraction of In in the sub surface InGaAs (△), and the coverage of As layer terminating the substrate (▲) in monolayer (ML).
Figure G.1. Schematics of a) the NoxAox stack where an Al$_2$O$_3$ dielectric layer was deposited by ALD on the native oxide of the Ga$_{0.47}$In$_{0.53}$As surface, b) the LHFAox stack where the native oxide was removed with aqueous HF and an Al$_2$O$_3$ layer was deposited by ALD on the As oxide covering the Ga$_{0.47}$In$_{0.53}$As surface, c) the physical location of interface traps including fast states created by dangling bonds at the semiconductor surface and slow states or border traps due to defects in the oxides within approximately 3 nm from the semiconductor surface$^{16}$, and d) the setup to measure C-V curves and large AC signal conductances in which the gate and pad are fabricated on the top surface$^{12}$. . . . . . . . . . . . . . . 161

Figure G.2. C-V curves for standard capacitors with nominal values of 5 pF and 20 pF over the same frequency and DC voltage ranges used to measure MISCAP devices in order to evaluate the background parasitic dispersion. The values differ by less than 2% from 1 kHz to 30 MHz. . . . . . . . . . . . . . . . 162

Figure G.3. Normalized C-V curves for Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices. All C-V curves were normalized to the oxide capacitance, $C_{ox}$, in accumulation of the 30 MHz curves. All C-V curves were recorded by forward scanning (f) from depletion to accumulation followed by backward scanning (b) from accumulation to depletion. Both forward and reverse bias curves are shown at the following frequencies: 1 kHz ($\bigcirc$), 10 kHz ($\square$), 100 kHz ($\triangle$), 1 MHz ($\triangleleft$), 10 MHz ($\triangledown$), 20 MHz ($\triangleright$), 30 MHz ($\leftarrow$). The ideal C-V curves are indicated by the heavy continuous red line. The dielectric constants at 1 kHz and 30 MHz as well as the surface recombination velocity are included with 95% margins of error from Table G.1, where the processing sequences are defined that were used to fabricate the MISCAP devices. . . . . . . . . . . . . . . . . 165

Figure G.4. Large AC signal conductance for Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices: a) NoxAox series where Al$_2$O$_3$ was deposited on top of native oxide and b) LHFAox series where Al$_2$O$_3$ was deposited on an HF-last surface. The process sequences used to label the samples are defined in the text as well as in the note in Table G.1. The curves included in each series are $\otimes$ NoxAoxM and LHFAoxM, $\bigcirc$ NoxAoxMFGA and LHFAoxMFGA, $\square$ NoxAoxMNH$_3$ and LHFAoxMNH$_3$, $\triangle$ NoxAoxFGAM and LHFAoxFGAM, and $\blacklozenge$ NoxAoxNH$_3$M and LHFAoxNH$_3$M. The insets shown for low and high frequency ranges highlight trends in the curves. . 168
Figure G.5. MISCAP equivalent circuit. An ideal MISCAP device with no substrate resistivity contains only an oxide capacitance, $C_{ox}$, and semiconductor capacitance, $C_S$, in series. In accumulation, $C_S$ approaches infinity. The frequency- and voltage-dependent capacitance due to border traps, $C_{bt}$, is in parallel with $C_{ox}$ and causes the frequency dispersion in C-V curves in accumulation, and hence dielectric values at low frequencies. The voltage- and polarity-dependent, but frequency-independent capacitance due to oxide charging, $C_{oc}$, is also in parallel with the oxide capacitance $C_{ox}$. $C_{oc}$ accounts for defects in the Al$_2$O$_3$ that are not in electrical contact with the underlying semiconductor. The polarity reverse (forward) biased $C_{oc}$ due to negative (positive) oxide charges reduces (increases) the capacitance measured in accumulation, and hence the dielectric constant measured at the high frequency Terman condition.

Figure G.6. Bond energies of H, O, and N with Ga, In, As, O, Al, and Si in terms of the equivalent light wavelength and energy.

Figure G.7. Normalized C-V curves (top) and LSC signal (bottom) for MISCAP devices fabricated using LHFAoxMFGAM and LHFAoxMNH$_3$M processes (defined in Table G.1). All C-V curves were normalized to the oxide capacitance in accumulation at 30 MHz. The probe frequencies were 1 kHz (○), 10 kHz (□), 100 kHz (△), 1 MHz kHz (< ), 10 MHz (▽), 20 MHz (>), 30 MHz (-), and the ideal C-V curve is shown by a solid line.

Figure G.8. Compendium of surface recombination velocities for different interfaces, including Si/SiO$_2$, Si/SiO$_2$/Al$_2$O$_3$ and Si/Al$_2$O$_3$, Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ (this work), and Ga$_{0.47}$In$_{0.53}$As/InP. The abbreviations are Tox (thermal SiO$_2$), Cox (chemical SiO$_2$ grown by piranha last), Aox (aluminum oxide Al$_2$O$_3$ deposited by ALD), FGA (forming gas annealing), NH$_3$ (NH$_3$ annealing), VA (vacuum annealing), X (XPS analysis), p (piranha), LHF (liquid HF), and Nox (native oxide).
LIST OF TABLES

**Table 1.1.** Select physical and electrical properties of Si, Ge, GaAs, InP, InAs, InSb, and In$_{0.53}$Ga$_{0.47}$As.$^1$ .......................... 17

**Table 1.2.** List of publication inserted as Appendixes. ......................... 29

**Table 2.1.** Gibbs free energies of overall etching reaction calculated at 298 K (shown for gas phase etching)$^5$. ................................. 31

**Table E.1.** Binding energy (chemical shift with respect to substrate peaks) in eV of InGaAs chemical states present after a processing step. Binding energies for InGaAs substrate in the In 3d$_{5/2}$, Ga 2p$_{3/2}$, and As 2p$_{3/2}$ regions are 445.4, 1118.4, 1323.9 eV, respectively. Sample labels reflect the sequence of processes done prior to surface analysis, which could consist of surface cleaning (Nox for solvent-cleaned or LHF for liquid phase HF etched), Al$_2$O$_3$ deposition using ALD (Aox), post-dielectric deposition annealing in forming gas (FGA) or NH$_3$, and blanket metal deposition (M). Samples with back-etched label denotes that a 10 nm thick Al$_2$O$_3$ film was deposited onto that sample prior to metal deposition and, or annealing, and the Al$_2$O$_3$ film was thinned down using diluted HF prior to XPS analysis. ........................................ 123

**Table G.1.** C-V Device Parameter Values$^a$ ................................. 166

**Table G.2.** Large AC Conductance Results for Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices$^c$ ........................................ 184
Abstract

In-based III-V compound semiconductors have higher electron mobilities than either Si or Ge and direct band gaps. These properties could enable the fabrication of low power, high-speed n-channel metal oxide semiconductor field effect transistors (MOSFETs) and optoelectronics combining MOS technology with photonics. Since thermal and native oxides formed on III-V surfaces exhibit large current leakage and high densities of trap states, a key to incorporating these materials into advanced devices is the development of processing steps that form stable interfaces with dielectric layers. In this thesis, a processing flow consisting of native oxide removal using HF chemistries and deposition of high dielectric permittivity films using atomic layer deposition was investigated. Understanding the reaction mechanisms of these processes could provide the means of controlling composition and structure, yielding a desired electronic behavior. Quantitative X-ray photoelectron spectroscopy analysis of surfaces was coupled with electrical measurements on MOS capacitors of the interface quality in order to understand the nature of high-k/III-V interface defects and their repair.

*Ex situ* liquid phase HF etching removed InSb, InAs, and InGaAs(100) native oxides and produced an Sb- or As-enriched surface, which oxidized when exposed to air. A 5 to 22 Å thick As- and Sb-rich residual oxide was left on the surface after etching and < 5 min of air exposure. The results showed that group V enrichment originated from the reduction of group V oxides by protons in the solution and the preferential reaction of HF with the group III atom of the substrate. A sub-atmospheric *in situ* gas phase HF/H$_2$O process removed native oxide from InSb, InAs, and InGaAs(100) surfaces, producing an In or Ga fluoride-rich sacrificial layer. A 50 to 90% oxide removal was achieved and a 10 to 25 Å-thick overlayer consisting of mainly In and Ga fluorides was produced. The composition and morphology of the sacrificial layer
were controlled by the partial pressure of H$_2$O as well as the ratio of HF to H$_2$O used. Water played a critical role in the process by directly participating in the etching reaction and promoting the desorption of fluoride etching products. Accumulation of thick fluoride layer at high HF to water partial pressure ratios prevented adsorption and diffusion of etchant to the buried residual oxide. When oxide was removed, HF preferentially reacted with In or Ga atoms from the substrate, enriching the surface with group III fluorides and producing approximately one monolayer of elemental group V atoms at the interface.

Interface reactions occurred during atomic layer deposition of Al$_2$O$_3$, in which trimethylaluminum (TMA) removed surface oxides and fluorides. Chemically sharp InSb/Al$_2$O$_3$ and InGaAs/Al$_2$O$_3$ interfaces were achieved for gas phase HF-etched InSb and liquid phase HF-etched InGaAs. A ligand transfer mechanism promotes nucleation of Al$_2$O$_3$ and removal of III-V atoms from the sacrificial oxide and fluoride layers as volatile trimethyl indium, gallium, arsenic, and antimony. These reactions have been explained by the relative bond strength of surface and precursor metal atoms with O and F. Interaction of a InSb(100) surface with TiCl$_4$ as a model for metal halide ALD precursors showed that similar ligand transfer reactions occurred. Adsorbed chlorine from the dissociative adsorption of TiCl$_4$ on the InSb surface at elevated temperature, however, preferentially etched In atoms from the substrate and produced a roughened surface.

The quality of InGaAs/Al$_2$O$_3$ interfaces prepared by solvent cleaning and liquid phase HF were assessed electrically using capacitance-voltage and conductance measurements. Surface recombination velocity (SRV) values were extracted from the measurements to represent the net effect of interface defects, which includes defect density and capture cross section. The InGaAs/Al$_2$O$_3$ interface prepared by solvent cleaning consisted of interfacial native oxides while that etched in liquid phase HF consisted of submonolayer arsenic oxide. The two chemically contrasting interfaces, however, gave similar SRV values of 34.4±3.7 and 28.9±13.4 cm/s for native oxide
and liquid phase HF prepared samples, respectively. This suggests that the presence or absence of oxides was not the only determining factor. Post Al₂O₃ deposition annealing in forming gas and NH₃ ambient significantly improved the electrical quality for both surfaces, as shown by SRV values between 1 to 4 cm/s which is comparable to that of an ideal H-terminated Si surface. XPS analysis showed that the contribution from elemental As and Ga₂O₃ at the interface of both surfaces increased after annealing in forming gas and NH₃, likely due to thermal or hydrogen-induced reaction between interfacial As oxide and Ga atoms in the substrate. There was no correlation between the atomic coverages of interfacial elemental As and oxides to the SRV values. High activity defects at III-V/Al₂O₃ interfaces are associated with interfacial dangling bonds which were passivated thermally and chemically by annealing in forming gas and NH₃.
Chapter 1

Introduction

1.1 Background

III-V compound semiconductors are emerging materials for applications in low power, high speed, logic transistors due to their superior properties compared to Si. These materials consist of group III (Al, Ga, In) and group V (P, As, Sb) atoms combined in binary, ternary, or quaternary compounds. This thesis focuses on In-based III-V materials due to several key properties shown in Table 1.1 and Fig. 1.1 together with that of Si and Ge. InSb, InAs, and InGaAs have significantly lower band gaps than Si. Additionally, the band gap of In$_x$Ga$_{1-x}$As can be tuned by adjusting the proportion of In to Ga. Narrow band gap semiconductors require less energy to promote electrons from the valence to the conduction band and conduct current. These materials also have significantly higher electron mobilities compared to Si, confering higher current velocity and allowing a transistor to be switched from an ON to an OFF state faster. Most of the III-V materials are also direct band gap semiconductors. Interchangeable conversion between photons and current can be achieved without the need for additional energy to overcome the momentum difference between the valence and conduction bands. This property makes III-V materials especially important for optoelectronic applications.

The relatively low abundance and high cost of III-V materials necessitate that they are integrated onto a Si substrate. This requires optimizing material usage and minimizing process costs. The lattice mismatch between III-V’s and Si is from 8 to 19% using the values listed in Table 1.1. This issue was addressed by inserting a thin buffer layer consisting of several III-V materials with graded compositions as
Table 1.1. Select physical and electrical properties of Si, Ge, GaAs, InP, InAs, InSb, and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.  

<table>
<thead>
<tr>
<th>Properties</th>
<th>Si</th>
<th>Ge</th>
<th>GaAs</th>
<th>InP</th>
<th>InAs</th>
<th>InSb</th>
<th>$\text{In}<em>{0.53}\text{Ga}</em>{0.47}\text{As}$</th>
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</thead>
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<td>1.35</td>
<td>1.27</td>
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</table>

Figure 1.1. Plot of electron mobility (cm$^2$V$^{-1}$s$^{-1}$) versus band gap (eV) generated from literature data.$^1$
Figure 1.2. Schematic cross section of InSb quantum well field effect transistor (QWFET) with an Al$_x$In$_{1-x}$Sb barrier layers. A buffer layer consisting of an Al$_y$In$_{1-y}$Sb film with graded composition and GaAs was inserted between the InSb and the Si substrate to enable integration of InSb onto Si. Reproduced with permission from Electronics Letters, Vol 43, Issue no. 14, 2007, Copyright the Institution of Engineering and Technology.

illustrated in Fig. 1.2 for an InSb quantum well field effect transistor (QWFET). In a QWFET device, carriers (electrons or holes) are confined in a low band gap material functioning as a channel for carriers, by sandwiching it between wider band gap materials. The energy structure of the barrier/channel/barrier materials is engineered by doping these material so that the energy band with respect to vacuum level of the channel material are at a lower energy compared to that of the barrier material, mimicking a well structure. Electric field may then be applied to align the barrier/channel/barrier energy so that carriers flow through the channel material in the ON state of the transistor. Significant improvement in supply voltage (Fig. 1.3) and intrinsic gate delay products (Fig. 1.4) over Si metal oxide semiconductor field effect transistors (MOSFETs) has been demonstrated using InSb, InAs, and InGaAs QWFETs fabricated using molecular beam epitaxy. The integration of other materials onto Si alongside a III-V material could potentially circumvent the issue of poor hole mobility, which is much lower than that of Si, and enable implementation of III-V’s in complementary metal oxide semiconductor (CMOS) devices.
Figure 1.3. Supply voltage ($V_{CC}$) versus physical gate length of n-channel field effect transistors (FETs) and Si MOSFETs. The horizontal lines are the $V_{CC}$ values used in the Si industry.\textsuperscript{3}

Figure 1.4. Intrinsic gate delay versus physical gate length of n-channel field effect transistors (FETs) and Si MOSFETs. The dashed line indicates the projected intrinsic gate delay in the absence of source and drain parasitic resistances\textsuperscript{3}.
While QW transistors were successfully fabricated to demonstrate the merits and potential of III-V devices, the formation of low defect interfaces between dielectric layers and III-V materials is key for the wider adoption of III-V compound semiconductors in electronics. Unlike thermally grown SiO$_2$ which forms a superior quality interface with a Si substrate, oxidation of III-V surfaces thermally, anodically, and naturally in air, resulted in a high density of interface states and the device fabricated suffers from high leakage currents. Engineering approaches to eliminate or minimize these defects are done by either preventing surface oxidation in the first place or removing the air grown (native) oxide prior to depositing a dielectric film. Surface oxidation may be prevented by a complete in situ processing, as in the fabrication of QW transistors, or capping the surface with an elemental group V overlayer after crystal growth. Instead of using an oxide or a dielectric film to confine carriers in the III-V channel, InSb QW transistor such as the one shown in Fig. 1.2 utilized a wider bandgap semiconductor as a barrier layer. The Al$_x$In$_{1-x}$Sb barrier layer was deposited by in situ molecular beam epitaxy (MBE), which is time and cost intensive for high volume manufacturing. Deposition of an elemental group V overlayer after crystal growth is also a common practice to prevent oxidation during wafer storage and transport because high quality III-V substrates are typically produced by molecular beam epitaxy (MBE). While elemental As overlayers create mid-gap states, this effect can be reversed upon elemental As removal by in situ cycles of annealing with and without an As atom over-pressure to maintain surface stoichiometry. This approach is convenient for processes involving epitaxial layer growth in an MBE system, but may not be practical for high volume manufacturing.

This project aims to gain fundamental understanding of the native oxide removal from In-based III-V surfaces, namely InSb, InAs, and InGaAs(100), using gas and liquid phase HF etching, the interfacial reactions which occur during the deposition high dielectric constant ($k$) film on these surfaces, and the nature of defects at the III-V/high-$k$ interfaces fabricated. The assessment of a surface preparation method
must account for not only the amount of oxide removed, but also the properties of the surface and residue layers produced and how these are affected by the interfacial reactions during nucleation of high-\textit{k} films. Surface morphology is also an important aspect that needs to be accounted for. A surface with minimal roughness is a prerequisite in thin dielectric film deposition applications because surface roughness induces electron scattering, which could degrade electron mobility. Understanding of \textit{III-V}/high-\textit{k} interface defects is valuable for devising a manufacturing process flow to a desired device quality.

### 1.2 Native oxide removal

Native oxide removal using \textit{ex situ} chemical etching with various acid solutions is generally unsuccessful in obtaining oxide free and stoichiometric \textit{III-V} surfaces due to reoxidation in air and the intrinsic acid/\textit{III-V} chemistry.\textsuperscript{7,9,10} When performed in an inert ambient, etching native oxide-covered InSb(100) and InAs(100) with a 25:1:2 H\textsubscript{2}O:HNO\textsubscript{3}:HCl or HCl/isopropanol solutions removed the oxide and produced indium chloride and excess Sb or As on the surface.\textsuperscript{9–11} Although group V-chlorides were not detected by X-ray photoelectron spectroscopy (XPS) due to the relatively high solubility of SbCl\textsubscript{x} and AsCl\textsubscript{x}, the surfaces were As- and Sb-rich after etching.\textsuperscript{9–11} Annealing in vacuum following HCl/isopropanol etching on InSb resulted in removal of InCl\textsubscript{x} and a change in the surface stoichiometry from Sb/In of \(\sim 1.7\) after etching to \(\sim 1.4\) after annealing at 230\textdegree{}C.\textsuperscript{10} The Sb/In ratio decreased further at higher temperature and saturated at Sb/In \(\sim 1.1\) at 300\textdegree{}C.\textsuperscript{10} The surface reconstruction progress from an Sb-rich asymmetric structure (1\times3) up to the In-rich (4\times1)/c(8\times2) during annealing from 230 to 400\textdegree{}C, is consistent with the desorption of the excess Sb.\textsuperscript{10} Annealing InAs(100) treated in HCl/isopropanol showed qualitatively similar results in which the removal of InCl\textsubscript{x} species occurred at 200 \textdegree{}C and the surface reconstruction progressed from an As-rich to an In-rich surface.\textsuperscript{11} The excess Sb and As produced in
etching using HCl-based solutions is consistent with acid etching of other III-V native oxides. Excess As was produced after acid etching of InGaAs, InAlAs, and InAs(100) native oxides. Qualitatively the elemental As coverage depended on the initial As oxide coverage. The mechanism proposed involves the dissolution of As oxides and reaction of the substrate with the acid solution, leading to the formation of elemental As. This mechanism implies etching of the substrate and possible surface roughening, however, etching rate and surface roughness data were not reported. Other ex situ chemical cleaning techniques have been reported showing incomplete oxide removal due to reoxidation in air. Immersion of InSb(100) in (NH$_4$)$_2$S$_x$ solution for 60 min resulted in removal of native oxide and a 6 to 7 monolayer sulfide overlayer enriched in In. Annealing this surface to 310°C removed the residual oxygen, carbon, and Sb-S moieties and annealing to 400°C removed the In-S moieties, restoring the stoichiometry to bulk InSb. (NH$_4$)$_2$S$_x$ treatment of InAs(100) also resulted in removal of oxide and enrichment of the surface with In sulfide, but no sulfur bonding to As was detected. Residual oxygen and carbon were observed, likely due to air contamination and while etching of the substrate was observed, the etching rate was relatively slow (0.8 nm/min).

The challenges in obtaining oxide-free InSb and InAs surfaces with ex situ methods prompted the development of in situ techniques. Thermal desorption is the most convenient from a process integration perspective. However, this method generally produces group III-enrichment and roughened surfaces. In$_2$O$_3$ has such a high thermal stability that its desorption requires annealing close to or above the noncongruent melting point of the substrate. Thermal treatment of native oxide-covered InSb was divided into two stages which are ultra high vacuum annealing at temperatures below the noncongruent melting point (380°C) and annealing under an Sb$_4$ flux at temperatures above 380°C. Below 380 °C, most of the Sb$_2$O$_5$ desorbed, while a thin layer of In$_2$O$_3$ remained. Thermal oxidation and O transfer from Sb to In resulting in In$_2$O$_3$ and elemental Sb was proposed in this stage of thermal
desorption. Above 380 °C, desorption of In$_2$O$_3$ was evident by XPS analysis while reflection high energy electron diffraction (RHEED) and scanning electron microscopy (SEM) analysis indicated the presence of In droplets on the surface. The formation of In droplets was due to reduction of In$_2$O$_3$ to In which condensed on the surface. Further annealing at 440 °C completely removed the oxide producing a nearly stoichiometric InSb surface. SEM micrographs showed that In droplets were no longer present, indicating that the droplets gained enough energy to combine with the Sb$_4$ flux forming stoichiometric InSb. Heating InAs(100) native oxide to 300°C under an As overpressure of 7.5×10$^{-7}$ to 7.5×10$^{-6}$ Torr removed As oxides but the removal of In$_2$O$_3$ did not start until 480°C. A flash annealing to 580°C completely desorbed the remaining In oxide while gradual annealing resulted in In droplets. Thus, the formation of In droplets depends on the heating rate, the annealing temperature, and the applied As or Sb over pressure. Annealing in a molecular hydrogen pressure of 5×10$^{-6}$ Torr was reported to produce complete removal of InSb(100) native oxide while preserving surface stoichiometry and smoothness at a much lower temperature (250°C) than ultra high vacuum annealing. Similar procedures done on InAs(100) removed native oxide completely at 300-340°C, but surfaces were enriched in indium (In to As atomic ratio of 1.24 to 1.65) and showed nanometer scale aggregates.

In this project, the native oxide removal from InSb, InAs, and InGaAs(100) surfaces was achieved using HF chemistries in gas and liquid phases. Gas phase processing is attractive from a process integration perspective as it is vacuum compatible and the etchants and water consumptions are minimal. Diffusivities of chemical species in gases are typically three orders of magnitude greater than in liquids, providing minimal resistance and rapid transport of reactants or etching products to/from a sample surface. The absence of a bulk liquid water phase may also confer processing advantages in preserving the termination of a surface. Partial pressures of HF and H$_2$O, etching temperature, and etching time were varied systematically to study the oxide removal mechanism as a prerequisite in realizing a controlled oxide removal. The
results were benchmarked with *ex situ* liquid phase HF etching, which is a standard cleaning technology for Si surfaces.

### 1.3 Reaction between atomic layer deposition precursors and III-V surfaces

Recent advances in substituting SiO\(_2\) with high dielectric constant (\(k\)) materials on silicon using atomic layer deposition (ALD) has enabled further scaling of transistors towards smaller feature sizes while maintaining acceptable leakage and breakdown characteristics. Since a deposited oxide could be an alternative to the poor quality native oxide, there has been interests in applying ALD of high-\(k\) film for III-V substrates. An ALD process utilizes the self-terminating characteristics of a gas-solid reaction where the chemisorption of a reactant on the surface can only proceed to saturation (\(\leq\) monolayer coverage).\(^{19,20}\) In contrast to chemical vapor deposition (CVD) where metal and oxygen-bearing precursors are dosed at the same time allowing gas phase reaction between both precursors and deposition of the metal-oxide product on the surface, an ALD process sequence separates precursor pulses with an evacuation/purge step, allowing the reaction between a particular precursor and surface functional groups to occur one at a time. Precise thickness control, lower deposition temperatures compared to CVD, and excellent conformality of high-\(k\) materials grown by ALD have been demonstrated.\(^{20,21}\)

Since an ALD process is dominated by reactions occurring on a surface, both the starting surface and ALD processing parameters, such as precursor chemistry and temperature, combine to determine the composition and thickness of the interfacial layer formed and eventually the quality of the gate stack built on III-V surfaces.\(^{22–25}\) Deposition of Al\(_2\)O\(_3\) with trimethylaluminum (TMA) and HfO\(_2\) with tetrakis(ethylmethylamino) (TEMA-Hf) removed Ga and As atoms from the native oxide and oxide layers formed after a NH\(_4\)OH treatment on GaAs surfaces.\(^{22}\) A lig-
and transfer mechanism, where As–O and Ga–O in the oxide and Al–CH$_3$ bonds in TMA were replaced by As–CH$_3$, Ga–CH$_3$, and Al–O bonds, leads to the deposition of Al$_2$O$_3$ and the desorption of volatile trimethyl arsenic and trimethyl gallium.\textsuperscript{22} The preferential removal of As$_2$O$_3$ over As$_2$O$_5$ in the TMA process was attributed to the ligand transfer mechanism favoring similar oxidation states, a +3 oxidation state for both As$_2$O$_3$ and Al$_2$O$_3$.\textsuperscript{22} In the case of HfO$_2$, the +4 oxidation state of Hf did not warrant a direct ligand exchange mechanism, but the ionicity and high coordination number of Hf in HfO$_2$ favors the removal of an oxide with a high coordination number, in this case As$_2$O$_5$ over As$_2$O$_3$.\textsuperscript{22} An irreversible HfO$_2$ initial growth rate with HfCl$_4$/H$_2$O precursors measured using time of flight secondary ion mass spectroscopy (TOFF SIMS) was attributed to the variability of residual oxide produced from reoxidation of GaAs surfaces in air after HCl etching.\textsuperscript{4} Surface oxides act as Hf nucleation sites, thus the partial removal of oxide and uncontrolled reoxidation in air from the ex situ HCl treatment resulted in an island growth mode and a less homogeneous HfO$_2$ film compared to that grown on the native oxide surface.\textsuperscript{4}

In this project, the interaction between surfaces prepared by solvent cleaning, liquid phase HF etching, and gas phase HF etching with a metalorganic (TMA) and a Cl-based (TiCl$_4$) ALD precursors were investigated. TMA is the smallest ligand among Al-based metalorganic precursors, thus steric hindrance is minimized. A relatively high Al$_2$O$_3$ growth rate was reported, 0.9 Å and 1.1 Å of Al$_2$O$_3$ at 573 K and 450 K, respectively.\textsuperscript{19,20} Impurity incorporation into the Al$_2$O$_3$ film was reported to be minimal, amounting to 0.2 atomic % C and 0.7 atomic % hydrogen at 573 K.\textsuperscript{19} TiCl$_4$ is both a model precursor for the more technologically important HfCl$_4$ and is commonly used to deposit TiO$_2$ and TiN by ALD. Understanding the reactions of chlorine-based metal precursors with III-V surfaces is also of importance because Cl$_2$ is a common dry etchant for these materials.\textsuperscript{26} On GaAs(100) prepared by aqueous HF etching and air exposure, a single TiCl$_4$ pulse at 135 to 300°C removed the residual oxide.\textsuperscript{27}
1.4 Nature of III-V surface defects

Modulation of the interface composition as well as the atomic and electronic structure during oxidation or deposition of materials onto clean III-V surfaces introduces energy states within the band gap (mid-gap states).\(^4,8,28,29\) This is illustrated for GaAs, which is the most widely studied III-V material, by the density functional theory calculation shown in Fig. 1.5.\(^4\) Mid-gap states are detrimental to device performance since they act as centers for nonradiative recombination of electron-hole pairs, leading to thermal dissipation of energy. Mid-gap states also act to capture or give away carriers, causing the Fermi level (\(E_F\)) position to deviate from that of an ideal device of which the \(E_F\) is mainly controlled by the extrinsic doping level of the semiconductor. When Fermi level pinning occurs, more energy is required to drive the device from conducting to insulating character. Theoretical studies suggest that the lattice strain induced by oxide formation leads to the ejection of Ga atoms from the GaAs lattice to the oxide film, creating unsatisfied dangling bonds which are responsible for mid-gap states.\(^4\) Arsenic oxides and gallium oxides contribute to energy states close to the valence and conduction bands, respectively.\(^4\) Doubly O-coordinated Ga formed upon oxygen chemisorption on GaAs(100) surfaces was proposed to generate mid-gap states.\(^28\) Interface states could also be generated by antisites, for example, excess As atoms occupying Ga vacancy sites in GaAs(100).\(^29\) The deposition of an elemental As overlayer on GaAs(110) also induces mid-gap state, which is an effect that can be reversed upon heating to desorb the As.\(^8\)

Studies on the effect of surface treatment and deposition of high-\(k\) films on III-V have also shed some light on the nature of III-V/high-\(k\) interface defects. Sulfur passivation of GaAs using \((\text{NH}_4)_2\text{S}\) improved the frequency dispersion behavior compared to hydroxylation using \(\text{NH}_3\text{OH}\).\(^24\) Although both interfaces contained Ga–O, better performance of the S-passivated GaAs was associated with thinner interfacial layers formed between ALD Al\(_2\)O\(_3\) on a \((\text{NH}_4)_2\text{S}\)-treated surface.\(^24\) \(\text{NH}_3\) plasma treatment,
which resulted in an interfacial layer consisting of As–N and Ga–N, produced higher capacitance values attributed to fewer interface traps compared to aqueous HF treatment, which resulted in an interfacial layer of As–O, As–As, and Ga–O. A map of the electronic states within the bandgap obtained using admittance spectroscopy revealed that S-passivation as well as forming gas anneals only suppressed states close to the conduction and valence bands. Mid-gap states, however, were insensitive to these treatments, leading to the conclusion that they arise from dangling bonds, Ga-Ga and As-As bonds due to structural defects.

In this project, the electrical quality of InGaAs(100)/Al₂O₃ interfaces was investigated by capacitance-voltage (C-V) and a large AC conductance technique (LSC) in order to correlate the chemical information to the device performance. In a C-V measurement, the position of the Fermi level is scanned across the bandgap to probe defects distributed within the band gap. In C-V method, a small AC signal is submitted.
perimposed on the DC biasing to fill and empty traps. Under Terman condition, the presence of defect states leads to stretch-out of a C-V curve compared to an ideal curve, the presence of interface traps with various activity (capture cross-section) leads to the dispersion of C-V curves in frequency, and defects in dielectric leads to the deviation of the dielectric constant ($k$) from the bulk value. In addition to characterization using C-V techniques, a new method based on conductance was developed to identify activity and correlation of defects at semiconductor-dielectric interfaces. A large AC signal is applied to a semiconductor-dielectric interface at different frequencies in order to modulate the Fermi energy from the conduction to the valence band. The modulation causes simultaneous filling and emptying of traps across the band gap. Deconvolution of conductance data in frequency space yields peaks that correspond to correlated trap states and a value of the surface recombination velocity (SRV) for that group of correlated states could be extracted from it. The SRV representative of a semiconductor-dielectric interface is obtained by summation of the individual SRV values. The total SRV obtained in this way is independent of band bending, fixed oxide charges, external potential, metal work function, doping density, and material thickness. This makes large ac signal conductance a practical method for investigating a wide range of interfaces in various types of devices. Characterization of the III-V/high-$k$ interface chemically and electrically permit inferences about the effect of interface chemistry on the electrical response.

1.5 Explanation of dissertation format

This dissertation adopts the published paper format whereby manuscripts of papers that are published, submitted, or to be submitted are included as appendices shown in Table 1.2. Summaries of the most important results and findings for each manuscript are given in the chapter entitled “Present Study.”
Table 1.2. List of publication inserted as Appendixes.

<table>
<thead>
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<th>Appendix</th>
<th>Title, Authors, Status</th>
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<tbody>
<tr>
<td>A</td>
<td>InGaAs(100) native oxide removal by liquid and gas phase HF/H$_2$O chemistries, F. L. Lie, W. Rachmady, and A. J. Muscat, published in Microelectronic Engineering.</td>
</tr>
<tr>
<td>B</td>
<td>Controlled oxide removal and surface morphology of InSb(100) native oxide using gas phase HF etching, F. L. Lie and A. J. Muscat, in press at the Journal of Physical Chemistry C.</td>
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<tr>
<td>D</td>
<td>Oxide removal and selective etching of In from InSb(100) with TiCl$_4$, F. L. Lie and A. J. Muscat, in preparation for submission to a peer-reviewed journal.</td>
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<tr>
<td>E</td>
<td>Passivation of InGaAs interface by atomic layer deposition of Al$_2$O$_3$ and post deposition annealing, F. L. Lie, B. Imangholi, A. J. Muscat, in preparation for submission to a peer-reviewed journal.</td>
</tr>
<tr>
<td>G</td>
<td>Characterization of defect states at n-type Ga$<em>{0.47}$In$</em>{0.53}$As and Al$_2$O$_3$ interfaces using surface recombination velocity, B. Imangholi, F. L. Lie, and A. J. Muscat, submitted to the IEEE Transaction on Electron Devices.</td>
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Chapter 2

Present Study

The detailed methods, results, and conclusions of these studies are presented in papers appended to this dissertation. The following are summaries of the most important findings.

2.1 In$_{0.53}$Ga$_{0.47}$As(100) native oxide removal by liquid and gas phase HF/H$_2$O chemistries

Liquid phase HF etching removed InGaAs native oxide but surfaces reoxidized after samples were removed from solution and transferred to the vacuum chamber. The InGaAs native oxide was 12.7±0.2 Å thick and consisted of In$_2$O$_3$, Ga$_2$O$_3$, As$_2$O$_5$, and As$_2$O$_3$. XPS confirmed the complete removal In$_2$O$_3$ and As$_2$O$_5$ while a 4.8 Å thick residual oxide containing mostly As$_2$O$_3$ was still present. The presence of water soluble As$_2$O$_3$ after aqueous etching and ultra pure water rinsing confirms that it was a result of reoxidation in air. The air oxidation was also likely the cause of the residual Ga$_2$O$_3$ observed. Removing the native oxide by liquid phase HF etching produced an arsenic-rich surface. The sub-surface InGaAs was composed of 17% In, 16% Ga, and 66% As, indicating that the oxide removal process terminated at the As layer producing either As-As or As-H bonds; these are difficult to distinguish by binding energy peak shifts in XPS because As and H have similar electronegativities.

A gas phase HF/H$_2$O process (100 Torr, 29 °C, 0.5 min) completely removed As$_2$O$_3$ and produced mainly In and Ga fluorides, since As fluoride is volatile at these experimental conditions. The overall reactions are thermodynamically favorable as shown in Table 2.1. The results suggest that HF and H$_2$O are both required for etching. The accumulation of fluorides still allows HF to react with the semiconductor,
Table 2.1. Gibbs free energies of overall etching reaction calculated at 298 K (shown for gas phase etching)⁵.

<table>
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<th>Reaction</th>
<th>∆G° [kJ/mole]</th>
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<tr>
<td>(1) In₂O₃(s)+6 HF(g)→2 InF₃(s)+3 H₂O(g)</td>
<td>-437</td>
</tr>
<tr>
<td>(2) Ga₂O₃(s)+6 HF(g)→2 GaF₃(s)+3 H₂O(g)</td>
<td>-224</td>
</tr>
<tr>
<td>(3) As₂O₃(s)+6 HF(g)→2 AsF₃(g)+3 H₂O(g)</td>
<td>-3</td>
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but inhibits the adsorption of water. This resulted in a much lower etching rate once a critical F coverage was reached. The highest oxide removal (4.2 Å residual oxide) was achieved after 5 min of etching. As₂O₃ and As₂O₅ were completely removed and considerably more InF₃ and GaF₃ were produced. The surface contained a group III-fluoride rich overlayer (34% In, 36% Ga) on a slightly As-rich bulk (21% In, 21% Ga, and 58% As). The As produced with both liquid and the prolonged gas phase HF treatments indicates that this substrate termination is intrinsic to HF-InGaAs chemistry.

2.2 Controlled oxide removal and surface morphology of InSb(100) native oxide using gas phase HF etching

Ex situ liquid phase HF etching performed as a baseline for the gas phase counterpart did not effectively remove InSb(100) native oxide. The In-rich native oxide was removed, but the surface contained more Sb oxide than that present initially in the native oxide due to air oxidation of excess Sb produced by the etching process. The Sb enrichment of surfaces after aqueous HF etching is consistent with acid etching of other III-V native oxides⁹–¹². The best oxide removal, corresponding to 56%, was obtained by etching with a concentrated 49% HF solution. Ultra pure water rinsing after an etch removed fluorides, allowing elemental Sb to oxidize, suggesting that fluoride is a poor barrier. The overall oxide removal mechanism in liquid phase HF is expected to be similar to that in gas phase HF. The polarity of In–O and Sb–O bonds
drives nucleophilic attack by HF, resulting in the breaking of M–O bonds and fluorination of In and Sb. When oxide was removed, HF reacted with the substrate and produced excess Sb. A prolonged liquid phase HF experiment showed that immersion in 49% HF for 5 h resulted in the consumption of approximately 200 nm of the InSb substrate and roughened the surface, which is not desirable when building a device. The 0.67 nm/min etching rate is evidence of the kinetically inhibited etching of the substrate. This is consistent with the bond polarity being the driving force for the oxide removal reaction. A correlation between elemental Sb coverage and the activity of protons in solution suggests elemental Sb may also be generated by proton-driven reduction of Sb$_2$O$_5$.

Gas phase HF etching at high water partial pressures (HF to H$_2$O ratios of 0.3, 0.8, and 1.2) resulted in at least 90% oxide removal, producing an Sb-terminated substrate covered by a monolayer of excess Sb and an indium fluoride rich overlayer. The results suggest that water participated directly in the etching reaction as part of the active etchant and indirectly by enhancing the desorption of fluoride etching products, rendering the partial pressure of water as one of the key etching parameters. Since bulk-like InF$_3$ films are impervious to water, its accumulation on a surface increased the barrier for active etchant adsorption and diffusion to the oxide/fluoride interface. A bulk-like InF$_3$ film formed connecting InF$_x$ moieties via bridging F. At high water partial pressure conditions, hydrogen bonding between water and In–F inhibited the formation of bridging F, rendering InF$_x$ volatile at 29°C, effectively promoting oxide removal. Despite the similar F coverages obtained after etching at the highest water partial pressure, increasing the HF to H$_2$O ratio diminished the hydrogen bonding effect, resulting in agglomeration of fluorides (HF:H$_2$O ratios of 0.8 and 1.2). The presence of an underlying Sb layer aided this agglomeration process by providing a high energy surface and increasing the mobility of InF$_x$ moieties. Excess Sb was produced by the reaction between HF and the InSb substrate when oxide was removed, which is intrinsic to HF/III-V chemistry. Its formation can be avoided
by having a fluoride/oxide barrier layer between HF and the substrate, which was demonstrated by etching at an HF to water partial pressure ratio of 2.3. This is not plausible with liquid phase HF etching because of the excess Sb produced by proton reduction of Sb$_2$O$_5$.

2.3 ALD of Al$_2$O$_3$ films on gas phase HF etched InSb and InAs(100)

The native oxides composition of InSb and InAs were different. In$_2$O$_3$ is known to be the prevalent In oxide state of In-based III-V materials and this was evident for InAs(100), but not directly resolved for InSb(100), although the XPS spectrum is consistent with this oxide composition. The group V oxidation state was +5 on InSb(100) forming Sb$_2$O$_5$, whereas even though the +5 state was dominant on InAs(100) forming As$_2$O$_5$, the +3 state also was present forming As$_2$O$_3$. The InSb native oxide was In$_2$O$_3$-rich, but that of InAs was As$_2$O$_5$-rich.

Aqueous HF etching more effectively removed the native oxides on InAs, as shown by the complete removal of As$_2$O$_5$ and In$_2$O$_3$. The residual As$_2$O$_3$ was due to reoxidation, likely partial oxidation during air exposure of the elemental arsenic formed by the aqueous HF etch. The strength of the As–F bond and the lack of fluorides on the surface after etching suggest that As fluorides are water soluble. Liquid phase etching of InSb did not completely remove Sb$_2$O$_5$ and In$_2$O$_3$, as a result of terminating the surface with F and reoxidation during air exposure. Aqueous HF etching consequently was less effective in removing oxide species and preventing reoxidation of InSb compared to InAs. Both materials showed an enrichment of the group V atom on the surface after etching, although elemental group V state was observed only on InAs.

Gas phase HF etching of InSb completely removed Sb$_2$O$_5$, but not In$_2$O$_3$, leaving SbF$_3$ and InF$_3$ on the surface. The presence of SbF$_3$ and InF$_3$ was expected since these compounds are stable at room temperature, and the complete removal of Sb$_2$O$_5$
promoted F termination on the available surface sites, producing stoichiometric fluorides. Gas phase HF completely removed As$_2$O$_3$, which could not regrow because the samples were kept in vacuum. Gas phase HF did not completely remove As$_2$O$_3$ nor In$_2$O$_3$ on InAs, and the surface was fluorinated after processing. Stoichiometric AsF$_3$ was not expected, since it has a melting point of -6°C and would be volatile in vacuum. Based on the chemical shift, the In–F bonding did not appear to be stoichiometric InF$_3$ and this may be attributed to having an As and In oxide matrix acting as a diffusion barrier for F species. The bulk InSb metal was stoichiometric after etching and the overlayer was In-rich arising from preferential F-termination on In surface sites. Two surface stoichiometries were obtained on InAs: a stoichiometric bulk metal and an As-rich overlayer for most HF to water molar ratios studied and an As-rich bulk metal and In-rich overlayer for an HF to water molar ratio of 0.3.

ALD Al$_2$O$_3$ growth on InSb and InAs after gas phase HF etching produced interfacial reactions between surface species and gas phase precursors. Based on the bond dissociation energies, Al–F bonds are considerably stronger than metal–F bonds of In, As, and Sb, which explains the driving force for removal of these fluorides from the interface. Similarly Al–O bonds are stronger than In–O and Sb–O, but similar in strength to As–O bonds, leading to removal of the In and Sb oxides during ALD film growth, but leaving As–O bonding at the interface. This study demonstrated that F-termination enabled deposition of Al$_2$O$_3$ directly onto InSb. Deposition of Al$_2$O$_3$ on an In-rich overlayer with an As-rich bulk metal on InAs(100) resulted in an interfacial layer containing As-oxide. The range of surface stoichiometries and the F-termination obtained after gas phase HF etching could be a mean to tailoring subsequent interfacial reactions for engineering surfaces prior to high-κ film deposition.
2.4 Interaction of TiCl$_4$ with native oxide-covered InSb(100)

A cut-off temperature of 600 K was established for processing native oxide covered InSb(100) surface in vacuum. Annealing at 600 K completely desorbed Sb$_2$O$_5$, but residual In$_2$O$_3$ were stable on the surface up to 650 K at which preferential desorption of Sb ensued, bulk etching occurred, and In droplets formed. Exposing native oxide surface to TiCl$_4$ at room temperature followed by annealing to 500 K partially removed both In and Sb oxide. 27% of the native oxide was etched and a sub monolayer TiO$_2$ was detected, suggesting that TiCl$_4$ reacted with InSb oxide via a ligand transfer mechanism which either deposited TiO$_2$ or produced and desorbed TiOCl$_2$. Etching reaction prevailed when TiCl$_4$ was dosed with the substrate temperature maintained between 470-560 K, resulting in complete removal of native oxide. When oxide was removed, TiCl$_4$ preferentially chlorinated In of the InSb substrate, leading to desorption of In as chlorides and accumulation of at least 72 Å elemental Sb layer on the surface. While Sb chlorides has higher volatility than In chlorides, the accumulation of relatively thick elemental Sb layer suggested a higher kinetic barrier for chlorination of Sb compared to In. The lone pair electrons of tricoordinated Sb atoms on a surface could result in a repulsive interaction with Cl ligands. Group V-enrichment was also obtained by etching III-V surfaces using HF and HCl, suggesting that this is intrinsic to III-V/halogen interaction. A Ti to Sb atomic ratio of $\sim$0.43 to 0.46 indicates that Sb could also be passivated against chlorination by the formation of TiSb$_2$. Out-diffusion of In assisted in making In available on the surface for chlorination despite a buried InSb/interface when an elemental Sb layer formed. Grain boundaries and surface height modulation in the order of $\sim$100 nm, which was observed using SEM and AFM, could contribute in enhancing the diffusivity of In to surface.
2.5 Passivation of InGaAs interface by atomic layer deposition of Al$_2$O$_3$ and post deposition annealing

Identification of the source of interfacial defects between high-k films and III-V substrates is crucial for developing methods to remove or passivate them. The modification of InGaAs(100) surfaces due to surface cleaning, Al$_2$O$_3$ deposition, and post deposition annealing (PDA) was investigated systematically using capacitance-voltage (CV), large AC signal conductance (LSC), and x-ray photoelectron spectroscopy (XPS). Al$_2$O$_3$ films were deposited by atomic layer deposition (ALD) on native oxide covered InGaAs(100) surfaces prepared by solvent cleaning, as well as on As rich InGaAs(100) surfaces prepared by aqueous HF etching. Quantitative XPS analysis on a solvent cleaned sample revealed surfaces consisting of $\sim$8 Å native oxide (52% As, 29% Ga, and 21% In) and a monolayer excess As on As-terminated substrate. Reactions between surface moieties and TMA during ALD Al$_2$O$_3$ resulted in thinning of native oxide to $\sim$4.2 Å (45% As, 29% Ga, and 27% In). Similar characterization performed on aqueous HF prepared sample showed surfaces consisting of $\sim$4.2 Å oxide (91% As) and 1.5 monolayer excess As on As-terminated surface. ALD Al$_2$O$_3$ on this surface resulted in the complete removal of In and Ga oxides, but approximately a monolayer of As oxide remained. CV and LSC measurements were performed on metal-insulator-semiconductor stacks containing Au/Ni/10 nm Al$_2$O$_3$/InGaAs(100). A surface recombination velocity (SRV) value is extracted from the measurement to represent the net effect of interface defect, which includes defect density and capture cross section. SRV values of 34 and 29 cm/s were obtained for solvent cleaned and HF prepared surfaces, respectively. The similar SRV values obtained by both surface preparation methods suggest that the presence or absence of oxides was not the only determining factor. PDA in forming gas and NH$_3$ ambient significantly improved the electrical quality, which is reflected on SRV values of 1 to 5 cm/s for both surfaces. XPS analysis showed increased contribution from elemental As and Ga$_2$O$_3$ at the in-
terface of both surfaces, likely due to thermally or hydrogen induced reaction between interfacial As oxide and Ga atom of the substrate. These results suggest that high activity defects could be associated with interfacial dangling bonds and H-passivation method which has been an integrated part of Si technology may be applicable to III-V.

2.6 Effect of Deep-Level Defects on Surface Recombination Velocity at the Interface Between Silicon and Dielectric Films

A modified conductance technique, namely the large AC signal conductance (LSC), was developed to probe the density and activity of deep-level defects across the band gap, yielding a surface recombination velocity (SRV) value. The development of this characterization method enables a direct and straightforward assessment and comparison of interfaces because the SRV measurement by this method is not affected by the choice of semiconductor and dielectric materials, the semiconductor doping density, and the band bending due to fixed oxide charges, mobile ion charges, charged interface defects, and work function differences between the gate metal and the semiconductor substrate. As a proof of concept, the SRV values obtained by LSC was compared to that obtained by other methods. The interface studied were Si in contact with thermal SiO$_2$ (Tox), chemical SiO$_2$, and atomic layer deposition Al$_2$O$_3$, which were annealed and exposed to a low flux of X-rays. The SRV values based on LSC at Si interfaces with SiO$_2$ and Al$_2$O$_3$ film stacks were found to be in good agreement with literature values obtained by other methods. The total SRV was $112 \pm 19$ cm/s for Si/Tox, $1045 \pm 150$ cm/s for Si/chemical SiO$_2$/Al$_2$O$_3$, and $578 \pm 96$ cm/s for Si/Al$_2$O$_3$ interfaces. After forming gas annealing at 400 °C, high frequency defect states were eliminated. This was reflected in the decreased SRV, $\sim 1$ cm/s for both Si/Tox and Si/chemical SiO$_2$/Al$_2$O$_3$. The improvement was attributed to restructuring of the interface and H-passivation of either lone Si or O dangling bonds.
Annealing in vacuum only reduced the defect activity since SRV was decreased to 150 cm/s for Si/chemical SiO$_2$/Al$_2$O$_3$. Although the chemical composition of defects and the detailed mechanism for defect elimination cannot be extracted from the LSC measurements, the SRV provides a quantitative measure of the electrical activity at the interface. For example, exposing a vacuum annealed surface to X-rays and high-energy electrons during XPS was sufficient to degrade the interface since the activity of defects increased, which resulted in SRV increasing from 408±47 cm/s on vacuum annealed Si/chemical SiO$_2$/Al$_2$O$_3$ to 855±62 cm/s. The approximately factor of two change in activity is entirely due to XPS analysis since the clustered apparatus used for this portion of the processing prevented air exposure.

2.7 Characterization of defect states at n-type In$_{0.53}$Ga$_{0.47}$As and Al$_2$O$_3$ interfaces using surface recombination velocity

The electrical behavior of the interfaces formed between In$_{0.53}$Ga$_{0.47}$As and an Al$_2$O$_3$ film deposited by ALD depended on the native or residual oxide present, the reactive annealing step, and light exposure. With native oxide present, dangling bonds localized predominately on the semiconductor surface were the primary defects and were passivated by hydrogen supplied by the FGA, resulting in an SRV of 1±0.3 cm/s. In the absence of native oxide after aqueous HF etching, atom vacancies localized in the Al$_2$O$_3$ layer were the primary defects in the interfacial region and were passivated by nitrogen atoms supplied by the ammonia anneal, resulting in an SRV of 1.5±0.3 cm/s. Reactive annealing with or without native oxide present produced interfaces comparable to thermally-prepared and reactive annealed Si/SiO$_2$ with SRV values in the vicinity of ~1 cm/s. Fabrication of InGaAs/Al$_2$O$_3$ with native oxide interface eliminates oxide removal step, yet the thinner As oxide starting surface after HF treatment may be more advantageous than one containing a buffer native oxide in scaling down devices, similar to Si/SiO$_x$/Al$_2$O$_3$ due to the low dielectric constant of SiO$_x$.31.
After FGA, values of the dielectric permittivity for Al$_2$O$_3$ without native oxide were smaller than expected for a bulk film. The low value of the dielectric permittivity extracted from C-V curves at the high frequency Terman condition is due to trapped and fixed oxide charges in the Al$_2$O$_3$ film. This effect was explained by proposing a frequency independent, but polarity-dependent capacitance in parallel with the oxide capacitance that can increase or decrease the capacitance in accumulation, and hence the value of the dielectric constant. Exposing III-V interfaces to ambient light had a deleterious effect even with annealing in reactive gases.

2.8 Future work

There are at least two extensions of this project that could benefit the advancement of In-based III-V devices. Systematic study of the surface reaction mechanisms in real time and at a molecular level between TMA and several InGaAs starting surfaces, namely native oxide covered, gas phase HF etched, and liquid phase HF etched, during the first few ALD cycles could aid in further understanding the formation of defects at Al$_2$O$_3$/III-V interfaces. Preliminary studies showed that precursor-surface reactions occurred in the first few ALD cycles (1 to 5 cycles) as shown in Fig. 2.1 for an InGaAs(100) surface prepared by gas phase HF. Oxidized In, Ga, and As states due to bonding with fluorine were drastically reduced after the first ALD cycle. Residual indium and arsenic fluorides were completely removed after exposure to five ALD cycles. Further exposure to TMA and H$_2$O pulses deposited Al$_2$O$_3$ film, causing the attenuation of photoelectron signals from InGaAs substrate. A closer look at the first five ALD cycles was done by acquiring XPS scans after each TMA and H$_2$O pulse. As shown by the F 1s core level spectra in Fig. 2.2, fluorides were drastically reduced by the first TMA pulse. The F 1s peak shifted $\sim$2.2 eV to higher binding energy (BE). This indicates bonding to Al, which has a lower electronegativity than In, Ga, and As, as a result of the ligand exchange mechanism. Residual oxide which was on
the gas phase HF etched sample remained after the TMA pulse, but the peak shifted \( \sim 1 \) eV to higher BE. This also supports the ligand exchange mechanism, resulting in the deposition of Al\(_2\)O\(_3\). Removal of In, Ga, and As atoms in the fluoride layer, likely as trimethyl indium, trimethyl gallium, and trimethyl arsenic, were evident in the In 3d, Ga 2p\(_{3/2}\), and As 2p\(_{3/2}\) spectra in Fig. 2.3. Subsequent H\(_2\)O and TMA pulses up to 3 cycles of TMA/H\(_2\)O revealed a systematic peak shift of the overlayer signals. F 1s, O 1s, and Al 2p peaks shifted towards lower BE after a H\(_2\)O pulse and shifted back to their original positions after a TMA pulse. The BE differences between peaks after a TMA and a H\(_2\)O pulse were 0.9 ev (F 1s), 0.4 eV (O 1s), and 0.2 eV (Al 2p). This could be direct evidence of different charge distributions when surfaces were terminated by F bonded to Al (after a TMA pulse) or OH bonded to Al (after a H\(_2\)O pulse). Further quantitative XPS analysis may be done to obtain surface coverages and further elucidate this interpretation. Similar studies on other starting surfaces such as native oxide and liquid phase HF etched InGaAs could allow construction of an Al\(_2\)O\(_3\) nucleation mechanism at a molecular level. Potential limitations of this approach are the obstruction of chemical effects by charging and the need for the surface to be terminated by largely electronegative atoms. As shown in Fig. 2.3(g), In 3d, Ga 2p, and As 2p peaks were asymmetric suggesting additional surface species at higher BE. An XPS scan after the samples was left overnight in the analysis chamber, however, revealed symmetric peaks. The discrepancy could either be due to surface charging effect or the possibility of having intermediate surface species that desorbed after some time in ultra high vacuum. The BE differences between peaks after a TMA and a H\(_2\)O pulse on a native oxide and liquid phase HF etched surface may not be as large as on the F-terminated surface due to smaller electronegativity difference between an oxide and a hydroxide surface termination, making it more difficult to detect.

While annealing in forming gas and NH\(_3\) was shown to be beneficial for passivation of III-V dangling bonds and vacancies in the Al\(_2\)O\(_3\) film directly adjacent to the
Figure 2.1. Core-level XPS spectra with the fitted components for an InGaAs(100) sample after gas phase HF etching at $P_{HF}:P_{H_2O}$ 1.23, 29°C, 100 Torr and subsequent 1 to 20 ALD cycles of $Al_2O_3$. 
Figure 2.2. F 1s, O 1s, and Al 2p core-level XPS spectra for an InGaAs(100) sample after gas phase HF etching at $P_{\text{HF}}:P_{\text{H}_2\text{O}}$ 1.23, 29°C, 100 Torr and subsequent TMA and H$_2$O pulses.
Figure 2.3. Core-level XPS spectra for an InGaAs(100) sample after gas phase HF etching at $P_{HF}:P_{H_2O}$ 1.23, 29°C, 100 Torr and subsequent TMA and H$_2$O pulses.
interface, detection of hydrogen is beyond the capability of XPS. An *in situ* ultra high vacuum H\textsubscript{2} dosing capability paired with thermal desorption spectroscopy (TDS) was established in an attempt to mimic the forming gas annealing process to some extent and provide direct evidence of H passivation as well as the bonding configuration that leads to passivation of defects. The setup is capable of delivering high vacuum ($10^{-8}$ to $10^{-7}$ Torr) pure hydrogen metered by a high precision leak valve. A doser assembly attached to a linear motion arm directs the hydrogen gas onto the sample surface with at least a 60 times flux enhancement. Thermal desorption spectroscopy increases the sample temperature at a controlled rate and monitors the desorbed species using a mass spectrometer. Since desorption of surface moieties involves breaking surface chemical bonds, the temperature at which a desorption peak of a species is detected is related to the bond strength, and in turn can be used to deduce the chemical bonding configuration and structure of the interface. A plot of pressure versus temperature may be used to derive kinetic parameters such as the activation energy of desorption of the various phases and the order of the desorption reaction. Since TDS is typically used for adsorption-desorption studies of monolayer species, applying this method for a buried Al\textsubscript{2}O\textsubscript{3}/InGaAs interface would require a more careful interpretation of desorption spectra. Recombination, decomposition, and reaction of interface species as they diffuse through the Al\textsubscript{2}O\textsubscript{3} film could contribute to the results. From a processing perspective, since the forming gas anneal was done at slightly above atmospheric pressure and a 4 to 10% hydrogen concentration for several hours, achieving an analogous process with a high vacuum H\textsubscript{2} ambient necessitates initial probing of working parameters such as time, temperature, and thickness of the Al\textsubscript{2}O\textsubscript{3} film. An optimum Al\textsubscript{2}O\textsubscript{3} thickness must be chosen such that precursor surface reactions are completed and a homogeneous conformal Al\textsubscript{2}O\textsubscript{3} film is deposited while allowing reasonable time for hydrogen to diffuse into the interface and passivate defects states. A 1.5 to 2 nm thick Al\textsubscript{2}O\textsubscript{3} film is typically sufficient for this purpose. Understanding of how hydrogen passivates interface defect could
provide directions in establishing a universal passivation method for III-V surfaces.
REFERENCES


APPENDIX A

**InGaAs(100) native oxide removal by liquid and gas phase HF/H$_2$O chemistries**

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In_{0.53}Ga_{0.47}As(100) native oxide removal by liquid and gas phase HF/H$_2$O chemistries

F.L. Lie$^a$, W. Rachmady$^b$, A.J. Muscat$^{a,**}$

$^a$ Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ 85721, USA
$^b$ Components Research, Intel Corporation, Hillsboro, OR 97124, USA

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A B S T R A C T
The native oxide removal, surface termination, and stoichiometry of In$_x$Ga$_{1-x}$As(100) surfaces using liquid and gas phase HF/H$_2$O etching were studied using X-ray photoelectron spectroscopy. Oxide removal in liquid phase HF stopped at the As$_x$ layer, producing either elemental or H-terminated As. The surface oxidized upon air exposure, forming a 4.8 Å As$_x$O$_y$ layer on an As-rich In$_x$Ga$_{1-x}$As sub-surface (175 Å, 165 Ga, 665 As). A sub-atmospheric gas phase HF/H$_2$O process (100 Torr, 29 °C, 0.5 min) completely removed As$_x$O$_y$ and produced mainly In and Ga fluorides, since As fluoride is volatile at these experimental conditions. Once enough F accumulated on the surface, the water sticking probability decreased and the etching reaction proceeded at a much lower rate. The highest oxide removal (4.2 Å residual oxide) was achieved after 5 min of etching. As$_x$O$_y$ and As$_2$O$_3$ were completely removed and considerably more InF$_x$ and GaF$_x$ were produced. The surface contained a group III-fluoride rich overlayer (345 Å, 365 Ga, 365 Ga) on a slightly As rich bulk (213 In, 213 Ga, and 585 As). The As rich In$_x$Ga$_{1-x}$As sub-surface produced with both liquid and the longer gas phase HF treatments is intrinsic to HF-In$_x$Ga$_{1-x}$As chemistry, although the oxide removal mechanism is likely different.

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1. Introduction

Surface preparation prior to gate dielectric deposition plays an essential role in the formation of a good quality insulator/III-V semiconductor interface for high performance field effect transistor devices. Several techniques to remove III-V native oxides, such as thermal annealing, ex situ chemical etching, in situ chemical etching, and plasma treatment, have been explored [1–7]. Thermal annealing alone was not successful in removing the III-V native oxide due to the relatively high thermal stability of group II-V oxides compared to group V-oxides [1,2]. Ex situ chemical etching is attractive due to the installed technology base. Aqueous HF, HCl, and H$_2$SO$_4$, etching of As-bearing III-V materials generally produced an As-rich surface [3–5]. The residual As oxide observed is thought to be the result of air oxidation when the sample is removed from solution [5]. In$_x$O$_y$, and elemental As were observed when In$_x$As$_y$(001) oxide was treated with HCl/isopropanol solutions [6]. NH$_3$ plasma treatment of GaAs(100) removed the native oxide and produced Ga-N and As-N on the surface [7]. This study reports the native oxide removal, surface termination, and stoichiometry of In$_x$Ga$_{1-x}$As(100) surfaces using gas phase HF/H$_2$O etching. Gas phase surface preparation is attractive from a process integration perspective. The greater control of surface termination could facilitate engineering of surfaces for subsequent processing such as high-k layer deposition. Partial pressures of HF and H$_2$O etching temperature, and etching time were varied systematically to study the oxide removal mechanism. In situ X-ray photoelectron spectroscopy (XPS) was used to characterize surface termination and composition after reaction without exposing the sample to air. Ex situ aqueous phase HF was performed to benchmark the gas phase counterpart.

2. Experimental

Samples were composed of 1 μm films of In$_{0.53}$Ga$_{0.47}$As(100) (n-type, Si doped to 5 x $10^{17}$ cm$^{-3}$, Intelligent Epitaxy) grown epitaxially on an InP(100) substrate and were cleaved into 1 x 1 cm pieces. Prior to oxide removal, samples were degraded by sonication in acetone and methanol for 5 min each followed by drying in ultrapure N$_2$. Native oxide removal was performed either in liquid phase or gas phase mixtures of hydrofluoric acid (HF) and water. The liquid phase HF etching procedure consisted of immersing a sample in an aqueous solution of HF (40%, Ashland Chemical, Cleanroom Electronic Grade) and ultrapure water (UPW, 18 MΩ-cm resistivity) at an HF to water volumetric ratio of 1:50 for 5 min at room temperature, rinsing with UPW, and drying with
ultra pure N₂. Samples were loaded into a vacuum chamber for XPS analysis within 5 min of being removed from solution. Gas phase HF etching was performed by exposing a sample to a gaseous mixture of anhydrous HF (Air Products, 99.999%) and ultra pure water vapor. The partial pressures of HF and water were varied from 3.6 to 14.2 Torr and from 6.2 to 11.5 Torr, respectively. The etching temperature was varied between 29 and 45 °C, and the etching time between 0.5 and 5 min. Ultra pure N₂ was fed to the reactor to make up a constant total pressure of 100 Torr in the reactor during etching. Sample transfer to the XPS chamber was carried out under ultra high vacuum (10⁻⁷ Torr base pressure), enabling studies without air exposure.

Surface analysis was performed by XPS equipped with a non-monochromatic Al Kα X-ray (1486.6 eV) source and a double-pass cylindrical mirror analyzer (Physical Electronics 540). Spectra were acquired at a constant pass energy of 50 eV. Surface charging was compensated for by assigning the As 3d edge peak of InGaAs to a binding-energy (BE) of 42 eV. The details of the XPS spectrum analysis are included in the Supplementary Material (Appendix A). The native oxide thickness was measured by ellipsometry (J.A. Woollam Co. M-2000S) and modeled using a Cauchy dispersion relation for the refractive index. Surface roughness measurements were done in tapping mode using a Digital Instruments Multimode atomic force microscope (AFM) with a Nanoscope III controller. Root mean square (RMS) values are reported with margins of error computed at 95% confidence.

3. Results and discussion

High resolution XPS of an oxide layer on an In₀.₇₅Ga₀.₂₅As(100) surface prior to etching is shown in Fig. 1a. The In 3d, Ga 2pₓᵧ, As 2pₓᵧ, and As 3d regions show peaks at binding energies (BE) of 445.4 eV (In 3d₁ₓ₂), 1118.4 eV (Ga 2pₓᵧ), 1223.9 eV (As 2pₓᵧ), and 42 eV (As 3d₃₂) due to the sub-surface InGaAs. Peaks due to the oxides were at higher binding energies relative to these peaks. Oxide species were not identified based on the absolute BE, but rather on the BE shift (ΔBE) relative to the substrate peaks, which is independent of the charge reference choice. Based on shifts reported in the literature [8–12], the oxide constituents were assigned as In₂O₃ (ΔBE = +1.3 eV), Ga₂O₃(+1.3 eV), As₂O₅(+4.3 eV), and As₂O₅(+3.1 eV). As₂O₅ and As₂O₅ could not be resolved in the less surface sensitive As 3d region and were lumped into a single peak shifted by +3.4 eV from the bulk. The presence of non-stoichiometric oxides, In₉As₉O₃(+7), As₂O₅ and Ga₂O₃ (Ga=3, As=5), are possible and were previously identified in thermal and UV-ozone grown oxides of InAs and GaAs analyzed using valence band photoemission [10]. However, the chemical oxidation states would not allow discrimination of either In₂O₃ from In₉As₉O₃ and As₂O₅ or Ga₂O₃ from Ga₂O₃ using XPS. The native oxide thickness measured by ellipsometry was 12.7 ± 0.2 Å.

Based on XPS peak area analysis, the oxide was composed of 8% In, 21% Ga, and 70% As distributed nonuniformly in the overlayer. The photoelectron inelastic mean free paths (IMFP) of the In 3d(1−22 Å), Ga 2pₓᵧ(1−11 Å), and As 2pₓᵧ(−7 Å) states [13] imply that the In 3d signal originated primarily from sub-surface InGaAs, while the Ga 2pₓᵧ and As 2pₓᵧ signals were from the oxide. The 21:70 proportion of Ga:As oxide means that the topmost surface was As oxide rich. A nonuniform distribution of oxides was predicted thermodynamically with In₂O₃ and Ga₂O₃ located mainly at the oxide/InGaAs interface and arsenic oxide present in increasing oxidation state from As=1 near the oxide/InGaAs interface to As=5 approaching the O-rich airoxide interface [14]. After 5 months of storage, the oxide was 13% In, 31% Ga, and 56% As with a larger As₂O₅ to As₂O₅ ratio, indicating that the surface region of the InGaAs film had not yet reached thermodynamic equilibrium. Liquid phase HF etching removed InGaAs native oxide with no residual fluoride detected. Fig. 1b shows that the peaks due to In₂O₃ and As₂O₅ were completely removed. A small peak due to Ga₂O₃ and a peak due to As₂O₅ were still present. In the As 3d region, two oxidized As peaks were needed to obtain a reasonable full width at half maximum (FWHM) in the peak fit. The two peaks were assigned as As₂O₅ (ΔBE = 3.2 eV) and As₂O₅ (ΔBE = 1.7 eV). The AsO₃ peak was not resolved in the As 2pₓᵧ region and resulted in a +0.3 eV shift of the sub-surface As peak. The presence of water soluble As₂O₅ after aqueous etching and UPW rinsing suggests that it grew during air oxidation after samples were removed from solution and transferred to the vacuum chamber. The air oxidation was also likely the cause of the residual Ga₂O₃ observed. Based on the O 1s peak area analysis described in the Supplementary Material (Appendix A), the residual oxide was 4.8 Å thick.

Removing the native oxide by liquid phase HF etching produced an arsenic rich surface. The InGaAs was composed of 17% In, 16% Ga, and 66% As, indicating that the oxide removal process terminated at the As layer producing either As₂As or As−H bonds; these are difficult to distinguish by XPS because As and H have similar electronegativities. Group V atom enrichment after native oxide removal by various acid solutions has also been reported for both

![Fig. 1. Core-level XPS spectra with the fitted components for InGaAs(100) samples after (a) degreased, (b) liquid phase HF etching at 1:50 HF:H₂O, and (c) gas phase HF etching at P₉ = 14.2 Torr, P₉ = 11.6 Torr, and 29 °C for 0.5 min.](image-url)
binary and ternary III–V materials [3,15]. Etching GaAs(100) with HCl resulted in a GaCl(4) overlayer on Cl-terminated Ga and H-terminated As [15]. Deionized water rinsing of this surface removed the chlorinated overlayer, leaving a H-terminated As layer on top of bulk GaAs. Native oxide removal of InAs and InSb(100) studied by XPS showed that As and Sb-rich surfaces, respectively, were obtained after aqueous HF etching [5]. Synchrotron XPS and XRR [5] and InAs/Au(n+1) cleaning by acidic solutions containing HCl, H$_2$SO$_4$, and HF reported elemental As buildup after etching [3].

In contrast to its liquid phase counterpart, gas phase HF etching completely removed As$_2$O$_3$ and produced a non volatile overlayer of fluorinated etching products. Fig. 1c shows a representative spectrum from a sample etched at $P_{HF}$ of 14.2 Torr, $P_{NH}_3$ of 11.6 Torr, and 29 °C for 0.5 min. The presence of fluorine-containing In and Ga is indicated by the larger full width at half maxima of the oxidized In (1.9–2.1 eV) and Ga (2.4–2.5 eV) peaks compared to In$_2$O$_3$ (1.9 eV) and Ga$_2$O$_3$ (2.2 eV) on the native oxide covered surface. The binding energy shifts are between that of As and a trivalent fluoride, InF$_3$, and GaF$_3$. In the As$_2$F$_6$(n+1) region, the As$_2$O$_3$ ($ΔE_B$ = 3.1 eV) was completely removed, while a small peak with a characteristic $ΔE_B$ of As$_2$O$_3$ was still present. Residual oxide was not observed in the less surface sensitive As 3d region. However, for samples with high fluorine coverage, a peak with a $ΔE_B$ of 4.6–5 eV was observed (not shown). This BE shift is larger than the 4.1–4.5 eV shift reported for As$_2$O$_3$ [9–11], suggesting that As–F bonding was formed.

The presence of fluoride-bearing In and Ga is consistent with the high fluorine coverage obtained after gas phase HF processes, which is summarized in Fig. 2. The F 1s peak area correlates with the oxidized In and Ga chemical shifts, especially when $P_{NH}_3$ was varied (Fig. 2b). Based on the chemical shift, mono to trivalent In and Ga fluorides were present. There was no significant correlation between the F 1s peak area and the oxidized As chemical shift. Although As–F bonds may be present, the oxidized As peak was mainly due to As$_2$O$_3$.

![Diagram](image.png)

Fig. 2. O 1s (a) and F 1s (b) XPS peak areas (ln$A_p$) and the corresponding oxidized In 3d ($I_n$), Ga 2p ($I_g$), As 2p$_{3/2}$ ($I_{As}$) chemical shifts (bottom) of InGaAs(100) after gas phase HF etching at (a) $P_{NH}_3$ of 11.6 Torr and increasing $P_{HF}$ (b) $P_{NH}_3$ = 14.2 Torr and increasing $P_{HF}$. As a comparison, the 0 1s peak areas of the native oxide covered sample and after liquid phase HF:HF$_3$H$_2$O 1:50 etching are shown as solid and dashed lines, respectively. Error bars show 95% confidence intervals.

The reaction of InGaAs oxides using liquid and gas phase HF is thermodynamically favorable based on Gibbs free energies (Table 1). Fluorides were not observed after liquid phase HF etching, indicating that there is a removal mechanism. InF$_3$ and GaF$_3$ are insoluble and impervious to water [17,18]; however, InF$_3$ and GaF$_3$ in HF solutions yield soluble hydrates, GaF$_3$·3H$_2$O and InF$_3$·3H$_2$O [18]. In contrast, gas phase HF etching depends on the fluorides being volatile. Clearly in the case of As–O bonds were broken and replaced by As–F bonds, producing trivalent AsF$_3$. AsF$_3$ is a liquid at room temperature with a vapor pressure of 140 Torr at 292 K [19]. Desorption of AsF$_3$ is plausible at the operating pressure of 100 Torr. Indium and Gallium fluorides were also produced but are not volatile. Although vapor pressure data are not available, the instability of InF$_3$ and GaF$_3$, may be inferred from the high melting points, which are ~1200 and 1000 °C, respectively [17]. The Gibbs free energy of reactions (1) and (2) are also positive when the etching products are gaseous InF$_3$ and GaF$_3$, meaning that this desorption is not energetically favorable.

The accumulation of fluoride etching products after gas phase HF processes is consistent with an increase in the surface roughness. Representative AFM topography images from InGaAs(100) surfaces after different treatments are shown in Fig. 3. The RMS value, which is a statistical measure of height variations on a surface, was based on a 2 × 2 μm AFM image. After solvent cleaning and after liquid phase HF etching, the RMS values were 0.18 ± 0.02 nm and 0.19 ± 0.02 nm, respectively (Fig. 3a and b). After gas phase HF etching at a $P_{HF}$ of 14.2 Torr, a $P_{NH}_3$ of 11.6 Torr, and 29 °C for 0.5 min, the RMS value increased slightly to 0.25 ± 0.03 nm due to nonvolatile etching products (InF$_3$ and GaF$_3$) left on the surface (Fig. 3c). When etching was done at 45 °C for 5 min, the increase in fluorine coverage was accompanied by a higher RMS value of 1.34 ± 0.28 nm (Fig. 3d). This surface exhibits irregular island-like features with heights of about 2 nm from the averaged center line which is consistent with an approximately 2 nm fluoride overlayer thickness estimated from XPS peak area analysis (Table 1 in the Supplementary Material, Appendix A). The accumulation of InF$_3$ and GaF$_3$ moieties on the surface may induce segregation and the formation of bulk-like InF$_3$ and GaF$_3$.

Statistically at a 95% margin of error, the native oxide removal and fluorination of InGaAs(100) surface was a weak function of $P_{NH}_3$ and $P_{NH}_3$. Increasing $P_{NH}_3$ at a fixed $P_{HF}$ removed slightly more oxide in the 0.5 min etches (Fig. 2a). Doubling $P_{NH}_3$, however, did not change the amount of oxide removed (Fig. 2b). This suggests that etching does not proceed in a liquid phase-like regime at about one-third of the saturation pressure of water or that the underlying mechanism is more complicated. Fig. 2 also shows that the etching rate is not correlated with oxide removal. The fluorine coverage followed a parabolic dependence (Fig. 3b). The parabolic dependence indicates that the relative ratio of PMF to $P_{HF}$ could be a metric for describing the reaction. One possibility is that a strong HF self-association and HF/H$_2$O cross-association causes cluster formation [20] and affects the HF adsorption rate. It was reported that the thermodynamic stability of these clusters depends on the number...
of HF and H2O molecules involved, as well as the relative concentrations [20].

F coverages also increased with both temperature and time as shown in Fig. 4. The increased F-termination, however, had only a weak association with the oxide removal. Although fluorination is required for etching, this suggests that the active etching species is not HF alone. Many studies conducted on the HF etching of SiO2 show that the presence of H2O enhances oxide removal rates [21,22]. An adsorbed water layer, which can be formed due to high water partial pressures and the hydrophilic nature of a surface, was found to assist oxide removal by increasing the concentration of adsorbed HF and promoting liquid phase-like etching [21]. A theoretical study showed that the etching reaction energy barrier is lower when HF and H2O attack cooperatively [22]. Since a gas phase HF/H2O mixture behaves non-ideally due to strong hydrogen bonds, polymerized species as well as molecular HF and H2O may be present in the gas phase [20].

Water vapor was fed to the reactor for 5 min before HF was introduced. Since III-V native oxide surfaces are hydrophilic [23,24], water likely adsorbed, which facilitated the initial reaction. As gas phase HF etching proceeded, InF3 and GaF3 accumulated on the surface, which caused etching to slow down, since both fluorides are impervious to water [18]. The residual oxide layer after etching for 0.5 min was ~4.7 to 5.7 Å (~2 monolayers) regardless of PH2O, P02, and etching temperature (Table 1 in the Supplementary Material, Appendix A). When the etching time was increased to 5 min (~10 Å), only slightly more oxide was removed (0.5 Å). The removal of the last 2 monolayers of oxide progressed at a much slower rate than the initial 3 monolayers. In a sense, the etching reaction was self-inhibiting once a critical coverage of F was reached.

The high resolution XPS spectra from a sample etched at 45 °C for 0.5 and 5 min are shown in Fig. 5. The In 3d, Ga 2p1/2, As 2p1/2, and As 3d peaks due to the sub-surface InGaAs and residual oxides and fluorides after etching at 45 °C are similar to those after etching at 29 °C (Fig. 1c). However, the relative intensity of the oxidized In, Ga, and As peaks to the sub-surface peaks is higher in Fig. 5 due to fluorides. This is consistent with the higher F coverage obtained. Contributions from two oxidized states with ΔBE of +2.6 and +1.5 eV, which are in the range of shifts expected for GaF3 and Ga2O3, were resolved in the Ga 2p1/2 region. Prolonged etching completely removed As2O3 and As2O5 with considerably more InF3 and GaF3 produced (Fig. 5b). In both the As 2p1/2 and As 3d regions, peaks shifted by +1.7 eV (As 2p1/2) and +1.5 eV (As 3d) from the sub-surface As peak were observed. These peaks could be due to As–As, As–H, AsOx, AsF, or a mixed compound. A small peak shifted by +6.1 eV in the As 2p1/2 region is likely due to higher valent As–F bonds.

The sub-surface InGaAs was enriched in As after gas phase HF processes. At the best oxide removal conditions (PH2O/P02 = 14.2/11.6 Torr, at 45° for 5 min), the surface was composed of a group III-fluoride rich overlayer (54% In, 30% Ga) on a slightly As rich InGaAs sub-surface (21% In, 21% Ga, and 58% As). The increased arsenic at the interface is consistent with oxide removal stopping at the arsenic layer of the (100) substrate, which was also observed in liquid phase HF etching. This suggests that although the oxide removal mechanism is different for liquid and gas phase HF, the substrate termination is intrinsic to HF-InGaAs (100) chemistry. The (100) surface of a zinc-blende crystal structure consists of alternating planes of all group III and group V atoms [25]. The electronic configuration of both planes differs when a bulk semiconductor is terminated at either As or In and Ga, since arsenic dangling bonds are occupied and that of indium and gallium are empty [25]. When an etching process reaches the bulk semiconductor and a group III plane is exposed to HF, nucleophilic attack of In or Ga could still be facilitated by the empty dangling bonds of In and Ga and the localized negative charge present on fluorine. However, when an arsenic plane is exposed, the filled dangling bonds of arsenic prevent further fluorination of arsenic atoms. Hydrogen termination or formation of As–H dimers are more plausible reaction routes.

In an overall fabrication process flow, native oxide removal can be thought of not only as an isolated etching step, but also as a conditioning step for subsequent processes. Comparing the 0.5 and 5 min gas phase HF etching results illustrates this point. Etching for a longer time removed another 0.5 Å of oxide, but also significantly increased the surface roughness due to the fluoride etching products. Since surface roughness induced electron scattering degrades electron mobility [26], the choice of the shorter or longer etching time depends on the roughness at the interface after deposition, which is typically the subsequent step. Processes such as
atomic layer deposition of high-k films are known to react with surface species modifying the interface [4,5]. In this view, the versatility of gas phase HF etching could allow optimization. Modulating the HF and H₂O partial pressures, total pressure, temperature, and time could provide control of the rate of fluorination and oxide removal as well as the thickness and composition of nonvolatile products that are used as sacrificial layers in subsequent processes.

4. Conclusions

Native oxide removal from InGaAs(100) using liquid phase HF stopped at the As layer, producing either elemental As or H-terminated As, which oxidized upon exposure air. The surface was highly As-rich and consisted of an overlayer of AS₂O₃ on an As-rich InGaAs sub-surface (17% In, 40% Ga, and 46% As). For the gas phase etching counterpart, As₂O₃ was completely removed and F-termination of InGaAs was observed. The results suggest that HF and H₂O are both required for etching. The accumulation of etching products still allows fluorination of the semiconductor atoms, but inhibits the adsorption of water. This resulted in a much lower etching rate once a critical F coverage was reached. The highest oxide removal was achieved at prolonged etching times, which produced a group III-fluoride rich overlayer (34% In, 36% Ga) on a slightly As rich sub-surface region (21% In, 21% Ga, and 58% As). The As produced with both liquid and the prolonged gas phase HF treatments indicates that this substrate termination is intrinsic to HF-InGaAs chemistry.

Appendix A. Supplementary Material


References

SUPPLEMENTARY MATERIAL:

**In_{0.53}Ga_{0.47}As(100) native oxide removal by liquid and gas phase HF/H_2O chemistries**

F. L. Lie \textsuperscript{a}, W. Rachmady \textsuperscript{b}, and Anthony J. Muscat \textsuperscript{a} \textsuperscript{*}

\textsuperscript{a}Department of Chemical and Environmental Engineering
University of Arizona, Tucson AZ 85721

\textsuperscript{b}Components Research, Intel Corporation, Hillsboro, OR 97124, USA

**XPS data analysis procedure**

Surface analysis was performed by XPS using a nonmonochromatic Al K\alpha x-ray (1486.6 eV) source and a double-pass cylindrical mirror analyzer (Physical Electronics 549). Spectra were acquired at a constant pass energy of 50 eV. Data analysis was performed as follows: (1) raw spectra were corrected for surface charging by assigning the As 3d\textsubscript{5/2} peak of InGaAs to a binding energy (BE) of 42 eV; (2) the intensity and binding energy shift (\Delta BE) of the satellite peaks due to the K\alpha\textsubscript{2,3} x-ray were modeled based on literature [1] and were subtracted from a measured spectrum; (3) contributions from the elastic and inelastic backgrounds were modeled using a Shirley algorithm [2]; (4) peak fitting was performed using the multipeak fit packages included with IGOR PRO (WaveMetrics, Inc., v.6); (5) the composition of the surface species and the sub-surface was computed by scaling the XPS peak areas of the In 3d\textsubscript{5/2}, Ga 2p\textsubscript{3/2}, As 2p\textsubscript{3/2} states using relative sensitivity factors from

S1
the literature [3, 4].

The amounts of oxygen and fluorine remaining on a surface after etching were estimated from the O 1s and F 1s peak areas. The peaks were height normalized based on the number of counts on the low binding energy side at 528 eV for O and 681 eV for F. Normalization was necessary to account for variations in photoelectron counts arising from different sample alignments. Overlayer thickness information was computed with the areas using the following equation [5]:

\[ d = -\lambda \cos \theta \ln(1 - \frac{I_{f,d}}{I_{f,\infty}}) \] (1)

where \( d \) is the overlayer thickness, \( I_{f,d} \) is the intensity of photoelectrons measured from an overlayer with thickness \( d \), \( I_{f,\infty} \) is the intensity of photoelectrons originating from an infinitely thick overlayer, \( \lambda \) is the electron inelastic mean free path (IMFP) for the overlayer, and \( \theta \) is the detection angle from the surface normal. Since IMFP data for InGaAs native oxide or fluoride matrices are not available, IMFP values were approximated using the values reported for an Al\(_2\)O\(_3\) matrix. The IMFP of O 1s and F 1s electrons in bulk Al\(_2\)O\(_3\) is 20.4 \( \pm \) 2 \( \AA \) and 17.9 \( \pm \) 1 \( \AA \), respectively [6]. The detection angle was 25\(^\circ\) off from the surface normal. \( I_{f,\infty} \) was obtained from a native oxide covered sample, in which the thickness was determined by ellipsometry to be 12.7 \( \pm \) 0.2 \( \AA \). The coverage calculation did not take into account structure and composition. Table 1 shows the coverage calculation results.
Table 1: Overlayer thickness calculated using equation 1.

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References


APPENDIX B

CONTROLLED OXIDE REMOVAL AND SURFACE MORPHOLOGY OF INSB(100) NATIVE OXIDE USING GAS PHASE HF ETCHING

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Controlled Oxide Removal and Surface Morphology on InSb(100) Using Gas Phase HF/H₂O

Fee Li Lie and Anthony J. Muscat

Department of Chemical and Environmental Engineering, University of Arizona, Tucson, Arizona 85721, United States

ABSTRACT: The native oxide removal, surface termination, composition, and morphology of InSb(100) surfaces etched in gas phase HF/H₂O mixtures at a total pressure of 100 Torr and 29 °C were investigated using quantitative X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning electron microscopy (SEM) as a function of the HF to water partial pressure ratio. Gas phase HF/H₂O etching preferentially removed antimony oxide and left a residue that was indium fluoride rich. Water played a critical role in the process by directly participating in the etching reaction and promoting the desorption of fluoride etching products. The lowest HF to H₂O ratio studied was 0.3, and this mixture removed over 90% of the native oxide, producing a smooth surface that consisted of an Sb-terminated substrate, an elemental Sb layer (2 Å), and an indium fluoride-rich overlayer (<10 Å). Excess elemental Sb was only observed at low oxygen coverages, suggesting that its formation was a byproduct of HF preferentially reacting with In atoms from the substrate. Moderate HF to H₂O ratios of 0.8–1.2 removed the oxide and yielded the same surface composition as the lowest ratio; yet, oblate spheroid islands were produced on the surface with heights of 4–60 nm and composed of indium fluoride that had aggregated due to the surface energy of the underlying elemental Sb layer. These islands covered over 10% of the surface area and were imaged using AFM and SEM. The highest HF to H₂O ratio studied was 2.3, and this mixture removed about 70% of the native oxide. The surface was smooth and terminated with Sb covered by a ~7 Å thick indium fluoride-rich overlayer. The accumulation of indium fluoride on the surface at high HF to H₂O ratios must have created a barrier for transport of the etchants to the surface. Control of both the composition and the morphology of the InSb(100) surface was possible with gas phase HF, providing more process latitude than observed with liquid phase HF etching, which was used as a baseline.

INTRODUCTION

InSb has the narrowest band gap, highest electron mobility, smallest electron effective mass, and largest electron magnetic moment among III–V compound semiconductors, making it a suitable material for infrared detectors and a promising candidate for high speed, low power field effect transistors and spintronics. Whether device fabrication involves growth of an epilayer, a thin dielectric film, or a nanostructure, the preparation of a clean InSb surface with low surface defects is often a first step. Studies conducted mostly on GaAs reveal that oxidation of clean III–V surfaces introduces fast interface states. Energy levels within the band gap could arise during an oxidation process due to the displacement of substrate atoms into the oxide film, leading to dangling bonds, the formation of As and Ga oxides with a particular oxidation state or structure, and the formation of antisites. An engineering approach to eliminate or minimize these defects is generally done by either preventing surface oxidation in the first place or removing the air grown (native) oxide prior to a subsequent device fabrication step. Because high quality III–V substrates are typically produced by molecular beam epitaxy (MBE), deposition of an elemental group V overlayer after crystal growth is a common practice to prevent oxidation during wafer storage and transport. While elemental As overlayers create midgap states, this effect can be reversed upon elemental As removal by in situ cycles of annealing with and without a group V atom overpressure to maintain surface stoichiometry. This approach is convenient for processes involving epitaxial layer growth in an MBE system but may not be practical for high volume manufacturing.

Native oxide removal using ex situ chemical etching with various acid solutions is generally unsuccessful in obtaining oxide free and stoichiometric III–V surfaces. Because reoxidation occurs instantly when clean III–V surfaces are exposed to air, oxide free InSb has only been demonstrated when etching was performed in an inert ambient using HCl dissolved in water or isopropanol. Compositional analysis by X-ray photoelectron spectroscopy (XPS) showed that HCl/isopropanol etching resulted in a thin indium chloride overlayer and an Sb-rich underlayer, both of which could be desorbed in vacuum at 230 °C. It was noted that indium chloride is easily hydrolyzed, making it prone to carbon contamination. The excess Sb produced is consistent with acid etching of other III–V native oxides. Excess As was produced after acid etching of InGaAs, InAlAs, and InAs(100).
native oxides. Qualitatively, the elemental As coverage depends on the initial As oxide coverage. The mechanism proposed involves the dissolution of As oxides and reaction of the substrate with the acid solution, leading to the formation of elemental As. This mechanism implies etching of the substrate and possible surface roughening; however, the etching rate and surface roughness data were not reported.

The challenges in obtaining an oxide free InSb surface with ex situ methods prompted the development of in situ techniques. Thermal desorption is the most convenient from a process integration perspective; however, it faces major challenges due to the low noncongruent melting point of InSb (380 °C) and the high thermal stability of In₃O₅. InSb oxides can be completely removed by annealing at 440 °C at the expense of producing indium droplets and a nonstoichiometric surface, unless an Sn flux is applied. In situ molecular hydrogen annealing was reported to produce complete removal of InSb native oxide and stoichiometric InSb at a much lower temperature (250 °C) than using thermal desorption alone.

An alternative in situ oxide removal method using subatmospheric gas phase HF/H₂O was demonstrated for InSb(100) surfaces in a previous study. Gas phase processing is attractive from a process integration perspective, as it is vacuum compatible and the etchants and water consumption are minimal. In contrast to liquid phase HF etching, which produces surfaces highly enriched in antimony oxide, gas phase HF produces surfaces rich in indium fluoride. Excess elemental Sn was also produced, but the coverage was lower than in liquid phase etching. These results reveal the potential of gas phase HF processes in controlling InSb surface composition after oxide removal. The current work aims to investigate the mechanism and key parameters in gas phase HF etching of InSb(100) native oxide, baselined with its liquid phase counterpart. Quantitative XPS analysis was used to determine the fate of surface species and surface composition after etching. These data are relevant for the study of mechanisms and valuable for the design of subsequent processes to build an electronic device.

### EXPERIMENTAL SECTION

InSb(100) wafers (Wafer World, 50.8 mm, n-type, Te doped 2 × 10¹⁷ cm⁻³) were cleaved into 1 cm² samples and cleaned by sonication in acetone (99.99%, Pharmco-Aaper) for 5 min and blown dry with nitrogen followed by the same procedure using methanol (100%, Mallinckrodt AR). The thickness of the native oxide layer was 34.7 ± 1.5 Å (95% confidence interval), measured using ellipsometry (J.A. Woollam Co. M-2000S) and modeled using a Cauchy dispersion relation for the refractive index. Surface analysis was performed using XPS at a 65° take-off angle. Photoelectronics were excited using a twin anode X-ray source (Al/Kα) and energy analyzed using a double pass cylindrical mirror analyzer system (Physical Electronics 549) at 50 eV pass energy. Nonmonochromatic Al Ka X-rays (1486.6 eV) were used throughout this study. Neglecting elastic scattering effects, the Sn and In 3d photoelectron signals were estimated to originate from a maximum depth of ~65-70 Å using an average escape depth of ~22 Å. The surface topography was imaged with both atomic force microscopy (AFM) using a Digital Instruments Multimode AFM with a Nanoscope III controller in tapping mode and scanning electron microscopy (SEM) using a Hitachi S-4500 field-emission SEM operated at 15 keV accelerating voltage.

![Figure 1](image.png)

**Figure 1.** (a) Partial pressures of HF and water vapor used to etch native oxides on InSb (100), shown above the points are the ratio of HF to H₂O. (b) A schematic of the model used for quantitative XPS analysis described in the Supporting Information. The analysis volume was modeled as a stack consisting of an InSb substrate, an elemental Sn layer (thickness d₁), and an overlay (thickness d₂). InSb substrates in the [100] direction consist of alternating group III and group V atomic planes, which were accounted for in the model as planes of A and B atoms. The substrate was terminated by A atoms with coverage β₁, which could be In or Sn depending on the atom in excess. The overlay consisted of In and Sn in oxidation states +0.

Samples were etched using either aqueous HF solutions or gas phase mixtures of HF and water vapor to remove native oxide layers. Aqueous HF solutions were made by diluting hydrofluoric acid (49%, Ashland Chemical, Clearroom Electronic grade) with ultra pure water (UPW, 18 MΩ cm resistivity from in house UPW facility) at ratios of 1:100 to 1:0 volume. Samples were dipped into these solutions at room temperature for 5 min with no stirring, blown dry with ultra pure nitrogen (no UPW rinsing), and loaded into the vacuum chamber for XPS analysis within 5 min of being taken out of the etching solution. For select samples, an UPW rinsing step was done between an HF/H₂O 1:0 dip and nitrogen dry.

Gas phase HF experiments were done in a clustered reactor system to prevent exposure of samples to air. Pure streams of anhydrous HF gas (Air Products, 99.999%) and water vapor were fed separately to a manifold and mixed with nitrogen before flowing to the reactor. The flow rates of each reactant were controlled to produce HF partial pressures (pHF) between 3 and 14 Torr and H₂O partial pressures (pH₂O) between 6 and 12 Torr. Independent control of each reactant over these ranges permitted variations in the partial pressure ratios of HF to water vapor between 0.3 and 2.3. The partial pressure ratios are shown in Figure 1a as a function of the absolute pHF and pH₂O. Water vapor was fed to the reactor for 5 min prior to introducing HF to achieve a stable partial pressure. The start of etching was defined when HF entered the reactor. The etching time was 30 s in all experiments. Samples were heated convectively, and the temperature was measured indirectly using a thermocouple spot-welded to a showerhead positioned 1 cm away from the sample. Sample temperatures were held at 29 ± 0.5 °C. The total pressure in the reactor was maintained at 100 ± 0.5 Torr. XPS spectra were analyzed using the following procedure: (1) the binding energy (BE) scale was referenced to the Sn 3d₄/₅ metal peak assigned to 537 eV, (2) satellite peaks produced by Kα₂,₃ X-ray radiation were modeled and subtracted from a measured spectrum, (3) contributions from elastic and inelastic electron scattering were removed using a Shirley algorithm, and peak deconvolution was performed using multiplet fitting packages included with Igor Pro (WaveMetrics, Inc., v6) and custom procedures. Specifically for the Sn 3d spectrum, the Sn 3d₄/₅ peak was treated as a single peak.
plasmon loss peak was modeled and subtracted from a spectrum before peak fitting because of its proximity to the Sb 3d_{3/2} oxidized state. Peak assignments are based on the chemical shift (ΔE) referenced to the In and Sb peak of the InSb substrate. A more detailed description of the analysis procedure is provided in the Supporting Information.

The relative amounts of oxygen and fluorine remaining on a surface after etching were obtained by integrating the O 1s, KLL, and F 1s peaks. The O 1s XPS peak overlapped with the oxidized Sb 3d_{3/2} peak and was not resolved. Extraction of the O 1s peak from the Sb 3d_{3/2} peak envelope is plausible but has a large variability. An oxidized Sb 3d_{3/2} peak may be approximated and generated from that of the Sb 3d_{3/2} peak based on the 9.4 eV spin-orbit splitting characteristic of Sb 3d photoelectrons\(^{19}\) and the 3.2 spin-orbit branching ratio of 3d_{3/2} to 3d_{5/2} photoelectrons. The generated oxidized Sb 3d_{3/2} peak could then be subtracted from a spectrum to resolve the O 1s peak. The extraction process, however, resulted in O 1s peaks that were asymmetric and in some cases had negative intensities on the lower BE side. This is due to the propagation of errors from all of the steps used in the extraction, which is discussed in the Supporting Information. The O KLL, KLL, Auger peak consequently had a lower variability than the O 1s peak for quantitative analysis.

A physical description of the composition of a surface after etching was obtained by modeling using a stack consisting of an In- or Sb-terminated substrate, an elemental Sb layer, and an overlayer as shown in Figure 1b. The bulk substrate was terminated by either an In or a Sb layer since InSb in the [100] direction consists of alternating planes of In and Sb. The elemental Sb layer was necessary to account for excess Sb in a +0 oxidation state, that is, In to Sb ratio <1, observed in most etching results. The overlayer consisted of In and Sb in oxidation states >0. Attenuation of the photoelectron intensity due to the elemental Sb layer and overlayer was taken into account. Because quantification using the O 1s peak was not reliable, the analysis only made use of Sb and In 3d_{3/2} spectra. A set of nonlinear equations were generated for each surface based on the model and solved for composition, thickness, and coverage. The detailed procedure is described in the Supporting Information.

**RESULTS**

Native Oxide. The Sb 3d and In 3d XPS spectra each contain two peak envelopes due to spin-orbit coupled states as shown in Figure 2a for a native oxide-covered sample after solvent cleaning. Within the Sb 3d_{3/2} peak envelope, two states were resolved and assigned to Sb_{2}O_{5} at 539.7 eV (ΔE = +2.7 eV) and to Sb of the InSb substrate at 537 eV. The Sb 3d_{5/2} peak envelope contained two states assigned to Sb_{2}O_{5} overlapped by the O 1s peak at 530.5 eV (ΔE = +2.9 eV) and Sb of the InSb substrate at 527.6 eV. The peak area ratio of Sb_{3d_{5/2}} to Sb_{3d_{3/2}} in the InSb states is 1.6, within the peak fitting error from the known spin-orbit branching ratio of 1.5 for 3d orbitals.\(^{20}\) The peak area ratio of the Sb_{3d_{5/2}} to Sb_{3d_{3/2}} oxide states is 2.1, deviating from 1.5 due to a contribution from the O 1s state. The spin-orbit split peaks in the In 3d X-ray spectrum were broadened (FWHM 2.6 eV) by contributions from In_{2}O_{3} which has a chemical shift of 0.4–1.4 eV,\(^{21,22,23,24}\) and but not resolved in the native oxide. The list of binding energies and chemical shifts tabulated in Table 1. Quantitative analysis of the surface composition is shown in Table 2. The native oxide layer consisted of 69% In oxide and was estimated to be 33.8 ± 3.2 Å with 95% confidence.

![Figure 2. Sb 3d and In 3d core-level XPS spectra with the fitted components for InSb(100) samples (a) solvent cleaned and after liquid phase HF etching at HF to water volume ratios of (b) 1:100, (c) 1:10, (d) 1:1, (e) 1:0, and (f) 1:0 with an UPW rinse. Data are shown by open circles, and the peak fits are shown as solid lines.](image-url)

**Liquid Phase Etching.** The Sb 3d and In 3d XPS spectra after liquid phase HF etching of solvent-cleaned InSb(100) are shown for increasing HF concentrations in Figure 2b—e. The effect of UPW rinsing is shown in Figure 2f. The Sb 3d_{3/2} peak envelope was deconvoluted into peaks assigned to Sb_{2}O_{5} at 539.6–539.8 eV (ΔE = +2.6–2.9 eV) and Sb of the InSb substrate at 537 eV. The Sb 3d_{5/2} peak envelope consisted of overlapping Sb_{2}O_{5} and O 1s states at 530.2–530.5 eV (ΔE = +2.6–3.0 eV) and Sb of the InSb substrate at 527.6 eV. Two states in the In 3d_{3/2} and 3d_{5/2} peak envelopes were resolved, belonging to In_{2}O_{3} at 452.3–452.7 eV (ΔE = +1.0–1.3 eV) and In of the InSb substrate at 453.1–453.4 eV. Oxide removal and fluorination of the InSb surface are evident in the O KLL, O KLL, and F 1s peaks shown in Figure 3. Trends in liquid phase HF etching are summarized in Figure 4. Increasing the HF concentration resulted in more F in the overlayer and less O. The increase in F was accompanied by a shift in the F 1s peak from 683.6 to 684.4 eV (Table 1). The overlayer/bulk ratios of In and Sb shown in Figure 4 and the oxidized In and Sb BE shifts shown in Table 1 increased with HF concentration. It is evident that both In and Sb were fluorinated although oxide and fluoride states were not resolved in the spectra. The BE shifts of 2.6–2.9 eV for Sb and 1.0–1.3 eV for In suggest that only low valent fluorides were present (InF_{x} and SbF_{x} with x ≤ 2). UPW rinsing after etching resulted in the removal of F and increased O. Although data are not shown, it is also worth noting that the
Table 1. Binding Energy (Chemical Shift) in eV of InSb Chemical States Present after Solvent Cleaning and Etching with Liquid and Gas Phase HF Mixtures

<table>
<thead>
<tr>
<th>process</th>
<th>Sb 3d_{5/2}</th>
<th>O 1s +</th>
<th>In 3d_{5/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ShF₃</td>
<td>Sb₂O₃</td>
<td>InSb</td>
</tr>
<tr>
<td>native oxide</td>
<td>530.7 (2.7)</td>
<td>537</td>
<td>520.5 (2.9)</td>
</tr>
<tr>
<td>liquid V₁₀⁶/V₁₃₆₀</td>
<td>1:100</td>
<td>530.6 (2.6)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>1:10</td>
<td>530.7 (2.7)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>530.8 (2.8)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>1:0</td>
<td>530.9 (2.9)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>1:0 + UPW</td>
<td>530.5 (2.5)</td>
<td>537</td>
</tr>
<tr>
<td>gas Pw/P₁₀⁶/O</td>
<td>0.3</td>
<td>540.2 (3.3)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>540.2 (3.5)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>540.3 (3.3)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>540.7 (3.7)</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>540.7 (3.7)</td>
<td>537</td>
</tr>
</tbody>
</table>

² The HF:H₂O volume ratios are listed for liquid phase etching, and the HF:H₂O partial pressure ratios are listed for gas phase etching processes.
³ Unresolved metal and oxide peak.

Table 2. Coverages and Thicknesses of the Terminating Atom and Overlayers on InSb(100) Surfaces after Solvent Cleaning and Etching with Liquid and Gas Phase HF Mixtures

<table>
<thead>
<tr>
<th>process</th>
<th>substrate</th>
<th>elemental Sb</th>
<th>overlayer</th>
<th>α (ML)</th>
<th>dₓ (Å)</th>
<th>αₓ₋ₓ (ML)</th>
<th>dₓ₋ₓ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>native oxide</td>
<td>Sb</td>
<td>1</td>
<td></td>
<td>0.69</td>
<td>33.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid V₁₀⁶/V₁₃₆₀</td>
<td>1:100</td>
<td>Sb</td>
<td>1</td>
<td>3.1</td>
<td>0.11</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:10</td>
<td>Sb</td>
<td>1</td>
<td>1.6</td>
<td>0.19</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>Sb</td>
<td>1</td>
<td>3.7</td>
<td>0.13</td>
<td>30.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:0</td>
<td>Sb</td>
<td>1</td>
<td>4.4</td>
<td>0.18</td>
<td>36.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:0 + UPW</td>
<td>In</td>
<td>0.7</td>
<td>0</td>
<td>0.10</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>gas Pw/P₁₀⁶/O</td>
<td>0.3</td>
<td>Sb</td>
<td>1</td>
<td>2.0</td>
<td>0.84</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>Sb</td>
<td>1</td>
<td>2.8</td>
<td>0.83</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>Sb</td>
<td>1</td>
<td>2.8</td>
<td>0.79</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>Sb</td>
<td>1</td>
<td>2.8</td>
<td>0.80</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>Sb</td>
<td>0.7</td>
<td>0</td>
<td>0.88</td>
<td>26.8</td>
<td></td>
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</tbody>
</table>

⁴ The XPS analysis volume is modeled as a stack of an In- or Sb-terminated substrate, an elemental Sb layer, and an overlayer as depicted in Figure 1b. The substrate is characterized by α, the element that terminates the bulk, and its coverage, β, in monolayers (ML). The elemental Sb layer is characterized by the film thickness, dₓ, in Å. The overlayer film is characterized by the atomic fraction of In in the film (αₓ₋ₓ) and the film thickness, dₓ₋ₓ, in Å.

- The XPS analysis volume is modeled as a stack of an In- or Sb-terminated substrate, an elemental Sb layer, and an overlayer as depicted in Figure 1b. The substrate is characterized by α, the element that terminates the bulk, and its coverage, β, in monolayers (ML). The elemental Sb layer is characterized by the film thickness, dₓ, in Å. The overlayer film is characterized by the atomic fraction of In in the film (αₓ₋ₓ) and the film thickness, dₓ₋ₓ, in Å.

- Carbon coverage was reduced by 46–86% after liquid phase HF etching with no trend in concentration. This indicates C
either reacted with the solution producing a soluble compound or lifted off of the topmost surface layer when the oxide was etched.

- Quantitative XPS analysis (Table 2) shows that liquid phase HF etching produced an Sb-rich surface consisting of an Sb-terminated substrate, an elemental Sb layer, and Sb₂O₃-rich overlayer. UPW rinsing resulted in the complete removal of both InF₃ and ShF₃ and thinning of the overlayer (Figure 4). The removal of fluoride exposed the underlying elemental Sb layer to air, resulting in its oxidation. This explains the absence of an elemental Sb layer after etching and water rinsing. The InSb surface after liquid phase HF etching and UPW rinsing consisted of an In-terminated substrate and Sb₂O₃-rich overlayer.

Figure 3. O KLL Auger transition and F 1s core level XPS spectra for InSb(100) samples (a) solvent cleaned and after liquid phase HF etching at HF to water volume ratios of (b) 1:100, (c) 1:10, (d) 1:1, (e) 1:0, and (f) 1:0 with an UPW rinse.
Gas Phase Etching. XPS spectra after gas phase HF etching at selected HF$_2$H$_2$O ratios are presented together with the spectrum for a native oxide after solvent cleaning in Figure 5. The HF$_2$H$_2$O ratios chosen represent systematic variation of HF and H$_2$O partial pressures yielding two series at fixed water and HF partial pressures. The HF$_2$H$_2$O ratios from 0.3 to 1.2 (Figure 5b–d) were obtained by keeping the p$_{HF}$ constant at 1.15 Torr and increasing the p$_{H_2O}$ from 3.6 to 14.2 Torr (last column in Figure 1a). The HF$_2$H$_2$O ratios from 1.2 to 2.3 (Figure 5d–f) were obtained by fixing p$_{HF}$ at 14.2 Torr and decreasing p$_{H_2O}$ from 11.5 to 6.2 Torr (top row in Figure 1a).

The Sb 3d$_{3/2}$ peak envelope was deconvoluted into two peaks assigned to SbF$_3$ at 540.2–540.7 eV (ΔE = +3.2–3.7 eV) and Sb of the InSb substrate at 537 eV. The SbF$_3$ peak on the starting surface was no longer present after etching at these HF$_2$H$_2$O ratios. While the observed shifts are within the range of the 3.4 and 3.7 eV shifts reported for SbF$_3$,$^{2,7}$ there is a trend of increasing BE shift with increased HF$_2$H$_2$O ratio. This indicates that low valent Sb fluorides coexist with SbF$_3$ at low HF$_2$H$_2$O ratios, and as the ratio was increased, a greater proportion of stoichiometric SbF$_3$ was produced. The Sb 3d$_{3/2}$ peak envelopes consisted of overlapping SbF$_3$ and O 1s states at 531.5–531.8 eV (ΔE = +3.9–4.2 eV) and Sb of the InSb substrate at 527.6 eV. The In 3d$_{5/2}$ and 3d$_{3/2}$ peak envelopes were fit using two or more states due to In$^{3+}$, in either a fluoride or an oxide, and In of the InSb substrate. At an HF$_2$H$_2$O ratio of 1.2 (Figure 5d), three distinct states were obtained from the peak fitting analysis and assigned to InF$_5$, at 454.6 eV (ΔE = +2.6 eV), In$_2$O$_5$, and InF$_{x}$ (x ≤ 2) at 452.9 eV (ΔE = +1.5 eV), and In of the InSb substrate at 451.4 eV. A chemical shift of 1.5 eV for In$_2$O$_5$, larger than the 0.4–1.3 eV cited in the literature,$^{2,7,12,23,24}$ indicating that low valent fluorides were likely present but were not resolved. At the other HF$_2$H$_2$O ratios, the In$^{3+}$ state was broad (FWHM 2.4 eV) and had an intermediate chemical shift (ΔE = +1.8–2.0 eV), suggesting that In$_2$O$_5$, InF$_{x}$, and low valent In fluorides contributed.

As shown by the O 1s peaks in Figure 6, oxide was completely removed, and surfaces were fluorinated after gas phase HF etching. The O 1s peak at 530.5 eV was no longer observed after etching at HF$_2$H$_2$O ratios of 0.3 to 1.2. However, the BE shifts of the oxidized Sb 3d$_{3/2}$ peaks were greater than the 3.4–3.7 eV expected for SbF$_3$. This indicates that the O 1s peak was present. The F 1s peak was observed at a binding energy of 685–685.2 eV, which is higher than that observed after liquid phase etching. This is consistent with gas phase HF producing higher valent fluorides, while its liquid phase counterpart produced lower valent fluorides. As shown in Figure 7, increasing p$_{HF}$ at a constant p$_{H_2O}$ (HF$_2$H$_2$O ratios of 0.3 to 1.2) produced...
the same O KLL, L2,3, and F L2,3 peak areas. However, decreasing $P_{O_2}$ at a constant $P_{H_2}$ (HF:H$_2$O ratios of 1.2 to 2.3) increased both the O KLL and L2,3 and the F L2,3 peak areas. Quantitative XPS analysis (Table 2) shows that gas phase HF etching produced a surface consisting of an Sb-terminated substrate, an elemental Sb layer, and an InSb-rich overlayer for most of the HF:H$_2$O ratios. An elemental Sb layer was absent after etching at an HF:H$_2$O ratio of 2.3. The carbon coverage after gas phase HF was similar to that on the native oxide (within a 95% margin of error) regardless of HF concentration (data not shown). This indicates that C did not react with vapor phase mixtures of HF and water, that the product of the reaction was not volatile at the etching temperature, or that the lift off mechanism proposed to explain the liquid phase results did not occur in the gas phase. Despite the presence of C, oxide removal was not inhibited.

**Surface Topography.** Figure 8 shows 2 $\mu$m $\times$ 2 $\mu$m topographical images of InSb surfaces recorded with an AFM after solvent cleaning and gas phase HF etching at selected HF:H$_2$O ratios. A solvent-cleaned InSb(100) surface was relatively flat with a root-mean-square (RMS) roughness value of 0.45 $\pm$ 0.09 nm. After liquid phase HF etching, the RMS value increased slightly to 0.68 $\pm$ 0.08 nm with no appreciable change in the surface topography (not shown). Variations in surface topography were only observed after gas phase HF etching. Etching at HF:H$_2$O ratios of 0.31 and 2.3 resulted in surfaces similar to solvent-cleaned InSb with RMS values of 0.46 $\pm$ 0.2 and 0.4 $\pm$ 0.07 nm, respectively. Etching at HF:H$_2$O ratios of 0.8 and 1.2 (Figure 8c,d), however, produced surfaces with oblate spheroid islands. For the HF:H$_2$O ratio of 0.8, islands were 4–60 nm tall and covered approximately 9% of a 10 $\mu$m $\times$ 10 $\mu$m area. For the HF:H$_2$O ratio of 1.2, islands were 10–36 nm tall and covered approximately 12% of a 10 $\mu$m $\times$ 10 $\mu$m area. An SEM image of a sample etched at an HF to H$_2$O ratio of 1.2 is shown in Figure 9, confirming the presence of the islands. At the center of the left image, two smaller islands appear to be in the process of coalescing or separating.

To gauge the consistency between XPS and AFM observations, a different XPS model from the one shown in Figure 1b was used to estimate the height of the islands that consisted of a homogeneous Sb-terminated substrate, a homogeneous elemental Sb layer, and an inhomogeneous indium fluoride-rich overlayer. The model overlayer contained pillars or islands covering a minimum of 20% of the surface area. A lower coverage was not plausible as the model approached an asymptotic solution. This model yielded a height of 50 nm for the fluoride pillars at HF to H$_2$O ratios of 0.8 and 1.2. This height agrees roughly with the AFM measurements, considering the limitations of the model and the likely oxidation and contamination of the surface during air exposure to do AFM. The ~10 Å overlayer thickness computed for these two surfaces (Figure 7 and Table 2) is thus not an accurate physical description but rather provides a means of comparing absolute coverages between samples.

**Discussion**

Oxide removal was demonstrated using gas phase HF at HF: H$_2$O $\leq$ 1.2, as evident by the reduction of the O KLL, L2,3 peak to within the noise level (Figure 6b–d). The BE shifts of the oxidized Sb 3d$_{5/2}$ state, however, were 0.2–0.5 eV greater than that expected for SbF$_5$ (Table 1), which indicates that O is photoelectrons contributed to the peak. The larger BE shifts of the oxidized Sb 3d$_{5/2}$ state as compared to the 3d$_{5/2}$ state also supports this argument. The inconsistency observed between the O KLL, L2,3 Auger and the O 1s XPS peaks is likely due to our XPS system, which was not optimized for Auger peak detection, making it insensitive to low O coverages. Although the O 1s peak extraction process has a large variability as mentioned in the Experimental Section, the residual oxide coverage can be approximated. Assuming a homogeneous oxide layer, the residual oxide was 3–4 Å thick for samples etched with HF:H$_2$O ratios $\leq$ 1.2. These coverages correspond to removal of more than 90% of the native oxide. The residual oxide must be due to In oxide, since Sb$_2$O$_3$ was completely removed.

![Figure 7: Quantitative XPS analysis for samples after gas phase HF etching at increasing HF to water partial pressure ratios. Left axis: scatter plots of F 1s XPS peak areas (Δ), O KLL, L2,3 Auger peak areas (Δ), and overlayer to bulk In (O) and Sb (S) XPS peak area ratios. Right axis: bar plot of the total overlayer thickness in Å. The overlayer thickness was calculated assuming a homogeneous layer for comparisons among gas phase HF processes. The first category (Nox) represents corresponding values for the solvent-cleaned sample. The error bar is one standard deviation.](image)

![Figure 8: AFM height image of InSb(100) samples (a) solvent cleaned and after gas phase HF etching at 29 °C, a total pressure of 100 Torr, and HF to water partial pressure ratios of (b) 0.3, (c) 0.8, (d) 1.2, and (e) 2.3. The color scale corresponds to the vertical range of the image. Each image is 2 $\mu$m $\times$ 2 $\mu$m.](image)
Liquid phase HF removed the In-rich native oxide, but surfaces reoxidized when samples were exposed to air. A mixed oxide and fluoride layer that was 25–37 Å thick and contained about 80–90% Sb was left on the surface after aqueous etching (Table 2). The atomic concentration of Sb on the surface was higher than what was present initially in the native oxide, which was 34 Å thick and contained about 70% In$_2$O$_3$ and 30% Sb$_2$O$_3$. Additionally, the In$_2$O$_3$ surfaces were terminated by 1.6–4.4 Å of elemental Sb. The best oxide removal using liquid phase HF$_2$ corresponding to a 56% reduction in the native oxide, was achieved when the P coverage was highest (HF:HF$_2$ 1:0, Figure 3e). This suggests that low valent fluorides (SF$_6$ and InF$_x$, with $x \leq 2$), which coexist with residual Sb$_2$O$_3$ and In$_2$O$_3$ in the overlayer, act as a poor oxidation barrier. Surfaces were reoxidized to a greater extent when fluorides were rinsed with water, resulting in only a 33% reduction in the native oxide (HF:HF$_2$ 1:0 + UPW rinse, Figure 3f and Figure 4).

In addition to the amount of oxide removed, the assessment of a surface preparation method must account for the properties of the surface and residue layers produced and how these interact with subsequent processing. For example, a surface with minimal roughness is a prerequisite in thin dielectric film deposition applications. Surface roughness induces electron scattering, which could degrade electron mobility. In atomic layer deposition of high dielectric constant materials, such as Al$_2$O$_3$ and HfO$_2$, surface compositions are often altered due to reactions with the precursors. In this view, the drawback of aqueous acid cleaning is the inherent tendency to produce an excess of the group V atom, which will oxidize unless performed under a controlled environment.

When a group V$_{3+}$ oxide is in contact with a III–V substrate and subjected to thermal treatment, the thermodynamic driving force is reaction with the substrate atoms, producing elemental group V atoms and group III oxide.

The surface composition and morphology obtained using gas phase HF etching depend on the reactant partial pressures and the relative amounts of HF to H$_2$O, affording control of the process. Gas phase HF removed the In-rich native oxide and produced a relatively thin In fluoride-rich sacrificial layer (9.5–26.8 Å, 79–89% In, Table 2) for all HF to H$_2$O ratios studied. The best oxide removal result without surface roughening was achieved by etching at the lowest ratio of 0.3. In contrast to liquid phase HF etching with gas phase HF did not produce excess elemental Sb at all HF to H$_2$O ratios studied. Elemental Sb was produced when the oxygen coverage was low (HF to H$_2$O ratios of 0.3–1.6, Figure 7 and Table 2). The elemental Sb coverage was generally lower than that observed in liquid phase-treated samples (Table 2). Etching at the highest HF to H$_2$O ratio of 2.3 resulted in the least effective oxide removal (69% oxide removal, Figure 7), highest fluorine coverage, and no excess Sb (Figures 6f and 7 and Table 2). Insights into the key parameters and mechanism of gas phase HF/H$_2$O etching could enable a greater control of surface termination and composition.

The partial pressure of water is one of the key etching parameters. The best oxide removal result was achieved at the highest $P_{H_2O}$ (12 Torr), regardless of $P_{HF}$ (HF:H$_2$O 0.3–1.2, Figures 6b–d and 7). Increased residual oxide was observed when $P_{H_2O}$ was decreased at a constant $P_{HF}$ (HF:H$_2$O 1.2–2.3, Figures 6d–1 and 7). This suggests that the active etching species is not HF alone. A theoretical study conducted on the HF etching of SiO$_2$ could shed some light on other HF/oxide systems. The study revealed that the energy barrier for etching was lowered when HF and H$_2$O attack cooperatively, suggesting a catalytic role for water. In gas phase HF etching of InSb oxide, the accumulation of a relatively thick fluoride overlayer at HF:H$_2$O > 1.2 created a barrier for the H$_2$O-containing active etchant from accessing the oxide layer. A bulklike InF$_x$ film is known to be impervious to water. In bulk InF$_3$ indium is octahedrally coordinated to fluorine forming InF$_6$ moieties, and each InF$_6$ moiety is connected by bridging F. The negative charge residing on fluorine could cause steric shielding, increasing the resistance to diffusion of active etchant into the oxide layer. As a result, the etching rate decreased, and the overall oxide removal was limited. The thickest InF$_6$ film was formed consistently on the surface with the most oxide (HF to H$_2$O ratio of 2.3). H$_2$O could also play an indirect role in etching by increasing the concentration of adsorbed HF when a condensed layer is formed as proposed for HF/vapor etching of SiO$_2$. In this model governed by thermodynamics, HF and H$_2$O condense only when the combination of $P_{H_2O}$ and $P_{HF}$ is high enough. The threshold vapor pressures depend on temperature and surface hydrophobicity. Yet, this argument may not apply to III–V materials. Learning from the gas phase HF etching of InGaAs native oxide, prolonged HF/H$_2$O etching further fluorinated the surface but did not continue to etch oxide. Although the formation of a condensed water layer may be inhibited by the presence of fluorides, the adsorption of HF was not, indicating that H$_2$O has a more direct role in the etching kinetics, consistent with H$_2$O being part of the active etchant.

Water vapor also plays a role in the removal of etching products, as is evident by the relatively low fluorine coverages obtained at the highest $P_{H_2O}$. With melting points of 87 °C for bulk SnF$_2$ and 1772 °C for InF$_3$, desorption is energetically unfavorable at the etching temperature of 29 °C. The low fluorine coverages (~10 Å, Table 2) left on surfaces after etching at HF:H$_2$O ratios of 0.3–1.2, however, indicate that fluorides were removed efficiently. Analogous to the formation of hydrated InF$_2$ in aqueous HF solutions, hydration of fluoride moieties likely occurs in excess H$_2$O conditions (HF:H$_2$O $\leq$ 1.2). This could increase the fluoride volatility and promote its desorption. Hydrogen bonding between H–O–H $\cdots$ F–In moieties suppresses the probability of having bridging F between InF$_6$ moieties, which would otherwise lead to the formation of bulklike InF$_6$ occurring fluorides on the surface. From this perspective, water indirectly affected the etching kinetics by enhancing fluoride removal. In addition to the water partial pressure, the HF to H$_2$O ratio is a key parameter. This is illustrated by the contrasting surface morphology between samples etched at HF:H$_2$O ratios 0.3–1.2 (Figure 8b–d). Despite the similar fluorine coverages obtained after etching at these three ratios (Figure 7), a smooth InSb
surface with an RMS 0.46 ± 0.2 nm was only obtained at the lowest HF:H₂O ratio of 0.3. This could be a further consequence of H−O−H−F−In bond formation in suppressing the agglomeration of InF₅ and island formation. Because the probability of forming H−O−H−F−In depends on the relative amount of HF to H₂O present, the H−O−H−F−In stabilizing effect is expected to diminish at an increasing HF:H₂O ratio.

Surfaces with oblate spheroid islands, with diameters on the order of a few hundred nm, were observed for samples etched at HF:H₂O ratios of 0.8 and 1.2, supporting these conclusions. In contrast, etching at the highest HF:H₂O ratio produced the highest flouride coverage and a smooth surface (HF:H₂O ratio of 2.3, RMS 0.4 ± 0.07 nm, Figure 8e). The absence of InF₅ islands on this surface shows that the gas phase composition is not the only determining factor.

The interaction between the fluoride moieties and the underlayer atoms, whether it is an elemental Sb layer or the InSb substrate, must have an effect on the process of etching products agglomerating on the surface. Sb has been utilized as a surfactant to promote two-dimensional growth in homo- and heteroepitaxial systems, for example, of Ag on Ag(111) and Ge on Si(001). Sb was proposed to decrease the surface energy, promoting monolayer formation and a larger critical thickness for the transition from two- to three-dimensional growth. A contrasting theory suggested that Sb dispersed randomly acts as repulsive centers, leading to a decreased surface mobility of the deposited atoms. Although a fundamental understanding has not been established, the presence of submonolayer Sb coverages could obviously affect the energetics and kinetics of film growth. For gas phase HF/H₂O etched surfaces, we speculate that the presence of a monolayer of elemental Sb underlying the InF₅ increases the surface energy and the mobility of InF₅ clusters. Elemental Sb consists of tricoordinated Sb atoms with a doubly occupied lone pair state. Repulsive interactions between the filled dangling bond of Sb and the localized negative charge on F−In increase the surface energy and cluster mobility. As a consequence, the thin fluoride film coarsened and formed large islands. Agglomeration of indium fluoride proceeds through coalescence of detached and mobilized fluoride moieties and clusters, analogous to Ostwald ripening. Figure 9 shows evidence for two islands that are in the midst of coalescing. When a residual oxide layer was present in lieu of an elemental Sb layer (HF:H₂O ratio of 2.3, Figure 8e), there was no thermodynamic or kinetic driving force for the agglomeration of fluorides, and islands were not observed.

The details of surface composition and overlayer thickness obtained from quantitative XPS analysis provide insights on the mechanisms of InSb native oxide etching using HF chemistries. The large electronegativity difference between In on the Pauling scale (1.78) or Sb (2.05) and O (3.44) means that In−O and Sb−O bonds are polar. The M−O and H−F bond polarities provide a kinetic driving force for nucleophilic substitution reactions, resulting in the breaking of M−O bonds and fluorination of In and Sb. The overall reactions are thermodynamically favorable, as shown by reactions 1 and 2 in Table 3. Overall reactions are shown for SbO₂ instead of Sb₂O₃ to balance the reaction without the need to generate O₂, which is unlikely. The higher accumulation of In fluorides as compared to Sb fluorides in the overlayer after etching is expected based on its relatively higher thermodynamic stability (larger ΔG) and melting point. When oxide was removed and substrate atoms were exposed, HF reacted with InSb to produce either elemental Sb or SbF₅ and InF₅. These reactions are thermodynamically favorable and shown

<table>
<thead>
<tr>
<th>reaction</th>
<th>ΔG (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) InO₂(s) + 4HF(g) → 2InF₄(s) + 3H₂O(g)</td>
<td>-437</td>
</tr>
<tr>
<td>(2) SbO₂(s) + 6HF(g) → 2SbF₅(g) + 3H₂O(g)</td>
<td>-101</td>
</tr>
<tr>
<td>(3) InSb + 3HF(g) → InF₅(s) + Sb + 1.5H₂O(g)</td>
<td>-266</td>
</tr>
<tr>
<td>(4) InSb + 6HF(g) → InF₅(s) + SbF₅(g) + 3H₂O(g)</td>
<td>-340</td>
</tr>
<tr>
<td>(5) Sb₂O₃(s) + 6HF(g) → 2SbF₅(g) + 6H₂O(l)</td>
<td>-279</td>
</tr>
<tr>
<td>(6) SbO₂(s) + 4HF(g) + 6e− → 2Sb + 3H₂O(l)</td>
<td>-77</td>
</tr>
</tbody>
</table>

Table 3. Gibbs Free Energies (kJ/mol) for Possible Etching Reactions of In and Sb Oxides with Gas and Liquid Phase HF Calculated at 298 K.

The etching mechanism in liquid phase HF is expected to be similar to that in gas phase HF. Reactions 1–4 in Table 3 are also thermodynamically favorable in the liquid phase (not shown). Only low valent fluorides remained at the end of liquid phase etching due to the solubility of SbF₅ and InF₅ in water. Because SbF₅ is soluble in water, the Sb-rich surfaces observed after aqueous etching suggest that there is a competing reaction for Sb₂O₃ removal in liquid phase HF as will be proposed in the next paragraph. Yet, the proposed reaction cannot fully account for the higher atomic concentration of Sb on surfaces after liquid phase etching compared to that in the native oxide. A portion of the elemental Sb must be produced at the expense of the InSb substrate according to reaction 3. A prolonged immersion of a sample in 49% HF for 5 h resulted in the consumption of approximately 200 nm of the InSb substrate and roughened the surface (not shown). The RMS value increased from 0.68 ± 0.08 nm after 5 min to 1.3 nm after 5 h of etching. The 0.67 nm/min etching rate is evidence of the kinetically inhibited etching of the substrate. This is consistent with the bond polarity being the driving force for the oxide removal reaction.

The coverage of elemental Sb generated in liquid phase HF etching was correlated with the activity of H⁺ (aq) in solution obtained from pH measurements as shown in Figure 10. The correlation suggests an additional reaction involving protons. Sb₂O₃ could be reduced by protons in solution as depicted by reactions 5 and 6 in Table 3. The elemental Sb coverage increased sharply in a narrow window of relatively low aH⁺ values and saturated at ~4 Å with increasing aH⁺ (Figure 10). This suggests that the proton activity in HF, which is a weak acid, was sufficient for this mechanism to proceed. Thus, acid etching of InSb oxide should be insensitive to the type of acid and the concentration and generally should produce elemental Sb. This was reported qualitatively in the acid etching of InGaAs in InAlAs(100) native oxides, although the mechanism proposed there is slightly different.

The chemical species present and their concentrations must also have an effect on the gas phase etching mechanism. HF/H₂O mixtures are known to behave nonideally even at relatively low HF
concentrations. Theoretical calculations indicate that hydrogen bonding between HF and H$_2$O molecules is strongest, and large (HF)$_m$(H$_2$O)$_n$, clusters, (m + n > 3) are thermodynamically favorable. While there is no direct evidence that clustering of HF and H$_2$O affects the etching mechanism, the results suggest that H$_2$O participated directly in etching and a dilute to equimolar HF/H$_2$O gaseous mixture removed the native oxide from InSb and minimized the fluoride etching products left on the surface. Experimental determination of the gas phase HF/H$_2$O etching species at different HF to H$_2$O ratios and real-time monitoring of surface species would aid in better understanding of the reaction mechanism at the molecular level.

The results show that >90% oxide removal can be achieved using gas phase HF; however, the characteristics of HF/III–V chemistry may provide a constraint for choosing an optimum etching condition. For applications in thin film deposition, maintaining a stoichiometric InSb interface and flat curvature are critical. Group V enrichment, typically produced on III–V surfaces treated in acid, is perceived to create midgap states, which are detrimental to metal–insulator–semiconductor function. This study suggests that complete oxide removal should be avoided as it leads to the generation of excess Sb. Low HF:H$_2$O ratios of ~0.3 are recommended for processes that require a smooth surface, low oxygen and fluorine coverages, and can tolerate a small excess of Sb. In cases where excess Sb is intolerable, an HF:H$_2$O ratio between 1.2 and 2.3 could produce a flat surface with controlled O and F coverages as needed. While elemental Sb becomes a limitation in thin film deposition, the agglomeration of InF$_5$ provides an opportunity for applications in selective growth processes. Depending on the deposited material and electronic properties, either InF$_5$ islands or an elemental Sb layer formed by self-assembly could serve to n-dope the deposition or growth of another material. Modulating the HF:H$_2$O ratio, temperature, and pressure could provide control of island properties.

CONCLUSION

Ex situ liquid phase HF etching did not effectively remove InSb(100) native oxide. The In-rich native oxide was removed, but the surface contained more Sb oxide than that present initially in the native oxide due to air oxidation of excess Sb produced by the etching process. The best oxide removal, corresponding to 56%, was obtained by etching with a concentrated 49% HF solution. UPW rinsing after an etch removed fluorides and allowed elemental Sb to oxidize, suggesting that fluoride is a poor barrier. The overall oxide removal mechanism in liquid phase HF is expected to be similar to that in gas phase HF. The polarity of In–O and Sb–O bonds drives nucleophilic attack by HF, resulting in the breaking of M–O bonds and fluorination of In and Sb. When oxide was removed, HF reacted with the substrate and produced excess Sb. A correlation between the elemental Sb coverage and the activity of protons in solution suggests that elemental Sb may also be generated by proton-driven reduction of Sb$_2$O$_3$.

Gas phase HF etching at high p$_{HF}$ conditions (HF:H$_2$O ratios of 0.3, 0.8, and 1.2) resulted in at least 90% oxide removal, producing an Sb-terminated substrate covered by a monolayer of excess Sb and an indium fluoride-rich overlayer. The results suggest that water participated directly in the etching reaction as part of the active etchant and indirectly by enhancing the desorption of fluoride etching products. Because bulklike InF$_5$ films are impervious to water, its accumulation on a surface increased the barrier for active etchant adsorption and diffusion to the oxide/fluoride interface. A bulklike InF$_5$ film formed connecting InF$_5$ moieties via bridging F. At high p$_{HF}$O$_3$ conditions, hydrogen bonding between H–O–H····F–In inhibited the formation of bridging F, rendering InF$_5$ volatile at 29 °C, effectively promoting oxide removal. Despite the similar F coverages obtained after etching at the highest p$_{HF}$O$_3$ increasing the HF to H$_2$O ratio diminished the hydrogen bonding effect, resulting in agglomeration of fluorides (HF:H$_2$O ratios of 0.8 and 1.2). The presence of an underlying Sb layer aided this agglomeration process by providing a high energy surface and increasing the mobility of InF$_5$ moieties. Excess Sb was produced by the reaction between the HF and the InSb substrate when oxide was removed, which is intrinsic to the chemistry of HF with III–V materials. Its formation can be avoided by having a fluoride/oxide barrier layer between the HF and the substrate, which was demonstrated by etching at an HF to H$_2$O equal to 2.3. This is not plausible with liquid phase HF etching because of the excess Sb produced by proton reduction of Sb$_2$O$_3$.

ASSOCIATED CONTENT

Supporting Information. XPS spectrum processing and quantitative analysis procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: muscat@erc.arizona.edu.

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REFERENCES


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Supporting information for: Controlled oxide removal and surface morphology on InSb(100) using gas phase HF/H₂O

Fee Li Lie and Anthony J. Muscat*

Department of Chemical and Environmental Engineering, University of Arizona, Tucson, Arizona
85721, USA

E-mail: muscat@erc.arizona.edu

*To whom correspondence should be addressed
The supporting information provides detailed XPS spectral processing and quantitative analysis procedures. This information was used to determine the sources of error and variability and to interpret the analysis results. Due to the considerable contribution from plasmon loss features, a plasmon subtraction step was introduced into the spectral processing of the Sb 3d state. The assumptions made and the implications for the spectra are discussed at the end of section I. The XPS peak intensities obtained by deconvolution of states present in a spectrum were further processed to generate a quantitative, and in most cases, physical descriptions of the different surfaces in section II. The analysis takes into account the crystal structure of InSb in the [100] direction as well as the attenuation of photoelectron intensities due to overlayers. Error and variability of the results arises mainly due to the assumption that surfaces consist of discrete homogeneous layers and that the electron inelastic mean free path (IMFP) is a weak function of the matrix it travels in.

**XPS spectral processing**

1. Each raw XPS spectrum was aligned in energy using the Sb 3d peak to account for surface charging due to the insulating overlayer. In lieu of the C 1s peak, which had an intensity that was too small to assign with confidence in every experiment, the Sb 3d$_{3/2}$ metal peak (Sb of the InSb substrate) was chosen to correct for surface charging. This peak was largely unaffected by other states, since the closest contributions were from Sb oxides more than 1.5 eV away. Alignment was made by assigning it to a binding energy of 537.0 eV.\(^1\)

2. The Al Kα$_2$ and Kα$_3$ X-ray satellite peaks for the In and the Sb 3d$_{3/2}$ and 3d$_{5/2}$ states were generated and subtracted from a measured spectrum. For the Al anode, satellite peaks generated by Kα$_2$ and Kα$_3$ radiation can be modeled by two states, which are shifted by 9.8 and 11.8 eV to lower binding energy with intensities of 6.4% and 3.2%, respectively, relative to the primary peak.\(^1\)

3. A constant background based on the featureless region on the low binding energy side of the 3d peaks was subtracted from each spectrum, and the elastic and inelastic electron scattering
backgrounds were removed using a Shirley algorithm.\textsuperscript{2}

4. Specifically for the Sb 3d spectrum, the Sb 3d\textsubscript{5/2} plasmon loss peak was modeled and subtracted from a spectrum before peak fitting because of its proximity to the Sb 3d\textsubscript{3/2} oxidized state. The bulk semiconductor is dominating the loss mechanism for photoelectrons emitted at angles below 80°.\textsuperscript{3} Thus, the plasmon peak from the cleanest InSb surface was used as a basis and the ratio between the bulk Sb 3d\textsubscript{5/2} peak to the basis plasmon peak was used as a reference. For all other samples with an overlayer of oxide or fluoride, the basis plasmon peak was scaled so that the peak area ratio of the plasmon to bulk Sb 3d\textsubscript{5/2} state of that sample resembled that of the cleanest InSb spectrum. This was done to account for the attenuation of both the bulk substrate and bulk plasmon peaks due to the presence of an overlayer. The plasmon loss shift, which dictates the binding energy scale of the generated plasmon peak, was obtained from the plasmon loss shift of the In 3d spectrum. The plasmon loss shift ranged from 13.7 to 14.3 for solvent-cleaned samples covered with native oxide, 13.7 to 14.6 eV for liquid phase etched samples, and 13.2 to 13.9 eV for gas phase etched samples. These values are consistent with the 13.5 to 14 eV range observed previously for InSb.\textsuperscript{4}

5. Deconvolution of states present in a spectrum was done using a multipeak fit packages included with \textsc{igor pro} (WaveMetrics, Inc., v.6) and custom procedures. Indium 3d spectra were fit with pairs of peaks corresponding to the 3d\textsubscript{3/2} and 3d\textsubscript{5/2} spin-orbit coupled states using the Voigt-pair fit package v.1.01. The peak width, chemical shift due to oxidation state, plasmon loss shift, and spin-orbit separation and branching ratio were allowed to vary to achieve the best fit. The full width at half maximum (FWHM) of the In 3d metal peak fits ranged from 1.8 to 2 eV. The spin-orbit splitting of 7.54-7.6 eV and spin-orbit branching ratio of 1.4-1.45 are comparable to literature values.\textsuperscript{5} Since the O 1s peak overlapped with the oxidized Sb 3d\textsubscript{5/2} peak, Sb 3d spectra were not fit with pairs of peaks. The Sb 3d spectra were fit using a Voigt line shape, letting peak width, intensity, and position vary. The FWHM of the Sb metal peak ranged from 2 to 2.1 eV. The spin-orbit separation was 9.35-9.4 eV and
the spin-orbit branching ratio was 1.3-1.5, which are comparable to literature values.\(^1\)

The procedure used in generating a Sb 3d\(_{5/2}\) plasmon peak for each sample spectrum is straightforward. However, the plasmon peak intensity is expected to deviate slightly from the real value due to the reference sample used. The sample used as a basis has to be a clean InSb(100) surface, free from oxide and fluoride overlayers, to best represent the plasmon originating from bulk InSb. Variability is also minimized by using spectra from the same instrument and geometrical configuration. The basis plasmon peak was obtained from a sample etched in gas phase HF:H\(_2\)O at a ratio of 1.2 for 30 s followed by annealing at 550 K for 20 min to remove all oxidized species. This process produced an InSb surface free from oxide and fluoride. However, annealing also preferentially desorbed Sb, resulting in indium droplets. The governing mechanism and cross-section for the generation of a surface plasmon in the presence of metallic In droplets likely departs slightly from that of a clean InSb surface. The subtraction of a generated plasmon peak from the Sb 3d\(_{3/2}\) peak envelope, thus, introduces variability, mainly for the oxidized Sb 3d\(_{3/2}\) peak.

The relative amounts of oxygen and fluorine remaining on a surface after etching were obtained by integrating the O KL\(_{23}\)L\(_{23}\) Auger and F 1s XPS peaks. The O 1s XPS peak overlapped with the oxidized Sb 3d\(_{5/2}\) peak and was not resolved. Extraction of the O 1s peak from the Sb 3d\(_{5/2}\) peak envelope is plausible but had a large variability. An oxidized Sb 3d\(_{5/2}\) peak may be approximated and generated from that of the Sb 3d\(_{3/2}\) peak based on the 9.4 eV characteristic spin-orbit split of Sb 3d photoelectrons\(^1\) and the 3:2 spin-orbit branching ratio of 3d\(_{5/2}\) to 3d\(_{3/2}\) photoelectrons. The generated oxidized Sb 3d\(_{5/2}\) peak could then be subtracted from the spectra to obtain an O 1s peak. The extraction process, however, resulted in O 1s peaks that were asymmetric and in some cases had negative intensities on the lower BE side. The variability of the oxidized Sb 3d\(_{3/2}\) peak, which depends on the plasmon subtraction process, as well as the spin orbit branching ratio assumption, and deconvolution of peaks through peak fitting contribute to the error.
Figure S1: A schematic of the analysis volume modeled as a stack of In- or Sb- terminated substrate, elemental Sb layer, and overlayer. Notation used to represent XPS intensities from each layer are shown.

Quantitative analysis

Each surface was modeled as a stack consisting of the following layers: In- or Sb-terminated substrate, elemental Sb layer, and overlayer as depicted in Figure S1. Since the structure of the InSb crystal in the [100] direction consists of alternating In and Sb planes, the substrate can either be In- or Sb-terminated. The intensity of core level photoelectrons originating from In and Sb atoms in the bulk can be expressed as the summation of signals from each In and Sb plane. The signals from each plane are attenuated by the planes above. XPS intensities or integrated peak areas, $I_i$, from the In and Sb layers may be expressed mathematically as:

\[
I_{\text{In}} = I_0 \left[ \beta \sum_{n=0}^{m} e^{2\omega n} + (1 - \beta) \sum_{n=0}^{m} e^{-2\omega n} \right] \\
I_{\text{Sb}} = I_0 \left[ \beta \sum_{n=0}^{m} e^{-2\omega n} + (1 - \beta) \sum_{n=0}^{m} e^{2\omega n} \right]
\]  

(1)

(2)

where $I_{\text{In}}$ (i=In or Sb) in equation (Eq. (1)) represents the XPS intensity of the element that comprises the topmost plane (the terminating layer) of the InSb substrate, $I_{\text{Sb}}$ in equation (Eq. (2)) represents the intensity of the other element, $I_0$ is the photoelectron intensity from a single layer of $i$ atoms, $\beta$ is the coverage of atom $i$ terminating the substrate in monolayers, $a$ is the atomic spacing between planes in the [100] direction, which is 1.623 Å for InSb(100), $\lambda_i$ is the IMFP of
factors. The intensity ratios were defined as

\[ R_1 = \frac{I_{\text{In}-(\text{elemSb+ov})}}{I_{\text{Sb}-(\text{elemSb+ov})} + I_{\text{elemSb},\text{ov}}} \]  

(7)

\[ R_2 = \frac{I_{\text{In},\text{ov}}}{I_{\text{Sb},\text{ov}}} \]  

(8)

\[ R_3 = \frac{I_{\text{Sb},\text{ov}}}{I_{\text{Sb}-(\text{elemSb+ov})} + I_{\text{elemSb},\text{ov}}} \]  

(9)

The Sb XPS intensities from the elemental Sb attenuated by the overlayer \( I_{\text{elemSb},\text{ov}} \) and the In and Sb XPS intensities from the overlayer \( I_{\text{In},\text{ov}} \) and \( I_{\text{Sb},\text{ov}} \), were expressed mathematically according to equation \( (\text{Eq. (5)}) \). Values for \( R_1 \) through \( R_3 \) were obtained from experimental data.

**Table 1: Atomic density of In and Sb in several compounds used for XPS quantitative analysis.**

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<tr>
<th>i-matrix</th>
<th>( N_i )-matrix ( \times 10^{22} ) atoms cm(^{-2})</th>
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<tr>
<td>In-In(_2)O(_3)</td>
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<tr>
<td>In-In(_3)F(_3)</td>
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<tr>
<td>In-elemental In</td>
<td>3.83</td>
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<tr>
<td>Sb-Sb(_2)O(_3)</td>
<td>1.41</td>
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<tr>
<td>Sb-Sb(_3)F(_3)</td>
<td>1.48</td>
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<tr>
<td>Sb-elemental Sb</td>
<td>3.3</td>
</tr>
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The `fsolve` algorithm in Matlab (version 7.8.0.347) was used to solve equations \( (\text{Eq. (7)}) \) through \( (\text{Eq. (9)}) \) simultaneously to obtain \( \beta \), \( d_2 \), and \( x_{\text{In},\text{ov}} \). As a first approximation in determining whether an elemental Sb layer was present, the \( R_1 \) value from a sample was compared to calculated values for a clean InSb substrate. When the InSb substrate was terminated by a plane of Sb atoms, \( R_1 \) was equal to 0.93, and when the substrate was terminated by a plane of In atoms, \( R_1 \) was equal to 1.07. When \( 0.93 < R_1 < 1.07 \), the substrate was stoichiometric although it was not terminated by a complete monolayer of either Sb or In and thus, \( I_{\text{elem Sb},\text{ov}} = 0 \). When the value of \( R_1 \) was outside of this range, there was more than one plane of like atoms terminating the substrate,
i.e. multiple Sb planes gives $R_1<0.93$. For these cases, the substrate was assumed to be terminated on an Sb plane ($\beta=1$), $I_{\text{elem Sb,ov}} \neq 0$, and the signal attenuation due to elemental Sb was accounted for. Equations (Eq. (7)) through (Eq. (9)) were solved simultaneously to obtain $d_1$, $d_2$, and $x_{\text{In-ov}}$. The excess Sb manifested itself in the parameter $d_2$. Since the assumption of a homogeneous film was invoked in the derivation of equations (Eq. (4)) and (Eq. (5)), film thicknesses provide an accurate physical description of a surface only when the surface morphology was flat. This was true for all samples except those treated with gas phase HF:H$_2$O ratios of 0.8 and 1.2.

References


APPENDIX C

A COMPARISON OF LIQUID AND GAS PHASE SURFACE PREPARATION OF III-V COMPOUND SEMICONDUCTORS FOR ATOMIC LAYER DEPOSITION

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A comparison of liquid and gas phase surface preparation of III–V compound semiconductors for atomic layer deposition

F.L. Lie\textsuperscript{a}, W. Rachmady\textsuperscript{b}, A.J. Muscat\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ 85721, USA
\textsuperscript{b} Composites Research, Intel Corporation, Hillsboro, OR 97124, USA

1. Introduction

Significantly higher electron mobilities compared to silicon make III–V compound semiconductors the materials of choice for high speed, low power devices [1]. The poor quality of thermal oxide layers grown on these surfaces, however, has limited the use of III–V materials in microelectronics. Recent advances in depositing high-k films on silicon using atomic layer deposition (ALD) could expand the use of III–V materials in high volume manufacturing. ALD offers precise control of film thickness, low processing temperatures, and excellent conformality on high aspect ratio structures [2–4]. ALD relies on self-terminating chemisorption of a reactant on a surface producing up to a monolayer coverage [5]. Techniques must be developed to form low defect interfaces by chemically saturating the atoms on a III–V surface with covalent bonds to a high-k film deposited by ALD.

Surface preparation prior to ALD to remove native oxides and to passivate or activate III–V atoms ensures that the best possible interfaces will be made and improves reliability. Surface treatment affected the composition and the thickness of interfacial layers and the ultimate quality of gate stacks on III–V surfaces, such as GaAs [6,7]. There are several reported etching techniques to remove native oxides from InAs and InSb [8–12]. Chemical etching using liquid mixtures of HCl and isopropanol removed oxides from InAs and InSb, generating elemental group V atoms and InCl\n species on these surfaces, which were subsequently thermally desorbed in ultrahigh vacuum [8,9]. Due to the relatively high thermal stability of In\n\textsubscript{2}O\n\textsubscript{3}, thermal treatment of In-based III–V substrates faces preferential loss of the group V species causing In droplets to form on the surface [10,11]. The formation of In droplets depends on the heating rate, the annealing temperature, and the applied As over pressure [11]. Recently the removal of native oxides from a InSb(100) surface was demonstrated without surface roughening by annealing at 250 °C under a molecular hydrogen flux [12]. The aim of this study was to investigate and compare native oxide removal and termination of InSb and InAs(100) surfaces using gas phase HF etching prior to ALD. Gas phase surface prepa-
deposition of subsequent layers. In this paper, gas phase HF etching is benchmarked with its liquid phase counterpart, which has played an invaluable role in silicon technology. Films of AlO₃ were successfully deposited by ALD on InAs and InSb surfaces prepared using a gas phase process. Comparative studies of binary substrates to explore the interaction of group III and group V atoms as elements and oxides in a compound and the fate of these atoms during etching of subsequent films may grow may improve the understanding of ternary and quaternary substrates.

2. Experimental

InSb(100) wafers (n-type, Te doped 2 × 10¹⁵ cm⁻³, Wafer World) and InAs(100) wafers (n-type, undoped, Wafer Technology) were cleaved into 15 × 15 mm pieces and solvent-cleaned in acetone followed by methanol with sonication for 5 min each to remove organics. Native oxide removal was performed either in liquid phase or gas phase mixtures of HF and water. The liquid phase HF etching was performed by immersing samples in an aqueous solution of hydrofluoric acid (49%, Ashland Chemical, Cleanroom Electronic Grade) diluted with ultra pure water (UPW, 18 MΩ cm resistivity) using HF to water ratios of 1:100 to 1:1 by volume for 5 min at room temperature. Samples were dried with ultra pure nitrogen and loaded into a vacuum chamber for X-ray photoelectron spectroscopy (XPS) analysis within 5 min of being removed from the etching solution. The gas phase experiments were conducted in a clustered reactor apparatus, which permitted sequential etching, deposition, and surface analysis steps without exposing a sample to atmosphere [13]. A gaseous mixture of anhydrous HF (Air Products, 99.5%+, and ultra pure water vapor at molar (partial pressure) ratios between 0.3 and 2.3 as shown in Fig. 1 were generated in the reactor by metering the gas flows. Experiments were performed at a total pressure of 100 Torr and 29°C for 30 s. ALD of Al₂O₃ films was carried out at 170°C. Trimethylaluminum (TMA), Al(CH₃)₃ (Hi-k grade, Rohm and Haas) and ultra pure water vapor were pulsed into a deposition reactor in a carrier gas of ultra pure nitrogen, which was also used to purge the reactor between reactant pulses. One ALD cycle consisted of a 1 s TMA pulse, 30 s purge, 0.1 s H₂O pulse, and 30 s purge. A growth rate of 1 Å/cycle was determined ex situ by ellipsometry of Al₂O₃ films deposited on Si(100).

XPS spectra were recorded at a pass energy of 50 eV in a surface analysis chamber equipped with an Al Kα radiation source (1486.6 eV) and a double-pass cylindrical mirror analyzer (Physical Electronics 540). Spectra were corrected for surface charging by referencing to the Sn 3d₃/₂ metal peak assigned to a binding energy of 537 eV on InSb and to the As 3d₅/₂ metal peak assigned to 42 eV on InAs. Contributions from the elastic and inelastic backgrounds were modeled using a Shirley algorithm [14], and peak fitting was performed using the multi peak fit packages included with IGOR PRO (WaveMetrics, Inc., v.6). An overlapping plasmon loss peak was subtracted from the oxidized Sb peak in the 3d₃/₂ region. The stoichiometry ratio of the group III to the group V atom was calculated based on XPS peak areas corrected by sensitivity factors from the literature [15-17]. The thickness of InSb and InAs native oxide layers measured using ellipsometry (A-L-Y Materials, Co. M-2000S) was 3.5 ± 0.15 nm and 3.1 ± 0.04 nm, respectively, where the margins of error were computed with 95% confidence.

3. Results and discussion

3.1. InSb

High resolution XPS of a native oxide layer on InSb(100) showed spin-orbit split 3d₃/₂ and 3d₅/₂ states of Sb and In (Fig. 2a). Each state contained a contribution from the oxide layer and one from the substrate. The Sn 3d₅/₂ state consisted of one peak at 539.7 eV due to Sn oxide and another at 537 eV due to Sn metal (bulk InSn semiconductor). The peak at 530.5 eV in the Sb 3d₅/₂ region contained contributions from both Sn oxide and from the Sn 1s XPS state, which typically occurs in the range of 530–532 eV and was difficult to separate. For this reason, the Sb 3d₅/₂ region was used to monitor chemical shifts caused by changes in the oxide state of Sn, since there were no overlapping peaks with other atoms. Oxygen removal from the surface was followed using the K₁L₂₃ oxygen Auger peak at a kinetic energy of 508.6 eV (not shown). The Sn oxide states were not resolved from the Sn metal states.

The native oxide of InSb(100) was composed of InO₂ and Sb₂O₅, but showed enrichment in InO₃. The Sb₂O₅ component obtained from desorption of the Sn 3d₃/₂ envelope was found at a binding energy of 530.7 eV, which is shifted by +1.7 eV from bulk metal InSb as shown in Fig. 2a, which agrees with previously reported chemical shifts for SnO₂ [18,19]. In the Sb 3d₅/₂ region, the peak at 530.5 eV (ΔE = +2.9 eV) was a combination of both SnO₂ and any oxide species present due to overlap with the Sn 1s state. The In oxide could not be resolved from the metal states in the single broad peaks (FWHM = 2.6 eV) observed in the In 3d₃/₂ and 3d₅/₂ regions. In oxide as InO₃ has a chemical shift between 0.4 and 1.4 eV [18,20,21]. The In to Sn ratio computed from

![Fig. 1. Partial pressures of HF and H₂O vapor used in gas phase HF etching, and the molar ratios of HF to H₂O vapor, which are shown above the points.](image1)

![Fig. 2. Sn 3d and In 3d core-level XPS spectra with the fitted components for InSb(100) samples (a) solvent-cleaned native oxide and (b) after liquid phase HF etching at an HF to water volume ratio of 1:1.](image2)
the 3d$_{z^2}$ states containing both the oxidized and metal peaks was 1.71, which indicates that the near surface region was In rich. Assuming that the bulk metal was stoichiometric InSb, this result suggests that the native oxide was In$_2$O$_3$ rich. Analysis of an In-Sb-O phase diagram predicted a multilayer and multiphase oxide where In$_2$O$_3$ prevailed in all layers and Sb oxide was present at increasing oxidation state from Sb$^+$ near the interface with the bulk metal to Sb$^+$ near the interface with air [22]. Ambient oxidation of a InSb(110) film deposited by molecular beam epitaxy (MBE) showed that the native oxide consisted predominantly of In$_2$O$_3$ with Sb$_2$O$_3$ enrichment only at the air interface [18]. At non-equilibrium oxidation conditions, kinetic factors may play a role in the composition of native oxides.

Representative high resolution XPS spectra for an InSb(100) sample after liquid phase HF etching are shown in Fig. 2b for an HF-to-water ratio of 1:1 by volume. The oxidized Sb peak grew relative to the metal peak, and the chemical shift of +1.8 to +2.0 eV depending on HF concentration was slightly larger than on the native oxide surface. The In 3d states were asymmetric, allowing the oxidized In peak to be resolved after peak fitting at a chemical shift of +1.0 to +1.3 eV from the bulk metal state, which is characteristic of In$_2$O$_3$ [18,20,21]. Increasing the HF concentration decreased the O Auger K$_{LL}$O$_{LM}$ peak area, but increased the F 1s peak area, the oxidized Sb to bulk Sb ratio, and the oxidized In to bulk In ratio. The lower residual oxygen on the surface resulting from the increased HF concentration in the fluid yielded a higher fluorine termination, creating Sb-F and In-F bonds contained in the oxidized In and Sb peaks. A range of Sb and In oxidation states could have been produced depending on the number of F atoms up to the trivalent species, which are discrete molecules. Based on the measured chemical shifts, both Sb and In were bonded to one or two F atoms. This is consistent with the chemical shifts of +3.4 eV previously reported for SbF$_3$ [19] and +1.9 to +2.3 for InF$_3$ [15,23] and with HF etching stopping at the bulk semiconductor producing a surface terminated by F atoms. Reoxidation in air may have contributed to the observed residual oxygen on the surface. The In to Sb oxidized peak area ratio was 0.12 but that of the metal peaks was 0.05, which suggests a model of an Sb-rich layer over an approximately stoichiometric bulk metal after aqueous HF etching.

In contrast to the aqueous process, gas phase HF etching completely removed Sb$_2$O$_3$ from InSb(100). For all HF to water vapor ratios studied, the Sb oxidized 3d$_{z^2}$ peak shifted to higher binding energy as shown in Fig. 3b–c. Peak fitting showed that the Sb$_2$O$_3$ state was absent, but a state at 540.5 eV appeared, which is within the range expected for SbF$_3$ at 540.2–540.7 eV (ΔE = +3.2–3.7 eV) [19]. The In oxidized state contained contributions from both InF$_3$ and In$_2$O$_3$, which were manifested in a broad peak (FWHM ~ 2.4 eV) shifted by +1.8 to +2.0 eV from the bulk. These chemical shifts are between values reported for InF$_3$ and In$_2$O$_3$ [15,18,20,21,23]. The peak due to InF$_3$ at 454 eV (ΔE = +2.6 eV) was resolved by peak fitting from the peak of In$_2$O$_3$ at 452.9 eV (ΔE = +1.5 eV) for an HF to water vapor ratio of 1:1 (Fig. 3c). Gas phase HF etching consequently produced a lower F coverage on the compound semiconductor surface than aqueous etching but left a higher F coverage.

The bulk semiconductor after gas phase HF etching was stoichiometric as shown by an In to Sb metal XPS peak area ratio of 0.73 to 1.05, but the termination layer was In rich, since the In to Sb oxidized peak area ratio was 3.6–7.8. Based on bond dissociation energies, an In–F bond is significantly stronger than an Sb–F bond (Table 1). The results indicate that etching stopped on the In atoms of the crystalline semiconductor surface leaving them terminated by two or three F atoms.

The lowest oxygen and fluorine coverages on the InSb(100) surface were obtained at an HF to water vapor molar ratio of 1.2, so this surface was chosen for atomic layer deposition of Al$_2$O$_3$.

![Figure 3. Sb 3d and In 3d core-level XPS spectra with fitted components for InSb(100) samples: (a) solvent-cleaned native oxide, and after gas phase HF etching at HF to water molar ratios of (b) 1.2, (c) 2.3, (d) 1.2 and (d) 1.2 followed by 20 ALD cycles of Al$_2$O$_3$ at 170°C.](image)

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>In</th>
<th>As</th>
<th>Sb</th>
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<tr>
<td>F</td>
<td>502</td>
<td>346</td>
<td>484</td>
<td>434</td>
</tr>
<tr>
<td>O</td>
<td>675</td>
<td>516</td>
<td>418</td>
<td>459</td>
</tr>
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Exposing an HF-cleaned sample to 20 ALD cycles of Al$_2$O$_3$ produced the XPS spectra shown in Fig. 3d. A thin Al$_2$O$_3$ layer allowed the interface between the dielectric and the semiconductor to be probed using XPS. The SbF$_3$, InF$_3$, and In$_2$O$_3$ left after HF etching were reacted and removed from the surface. Based on the bond dissociation energies listed in Table 1, Al–F and Al–O bonds are considerably stronger than metal–F and metal–O bonds in InSb so there is a driving force for Al in the film to scavenge the F and O at the interface. It is not yet clear whether the TMA precursor reacted with F and O on the surface producing a volatile species or whether Al atoms in the dielectric layer scavenge F and O from the interface. Based on the XPS, the Sb and In are bonded only to one another in the bulk semiconductor, which makes a chemically sharp interface with the Al$_2$O$_3$ layer.

3.2. InAs

In contrast to antimony in indium antimonide, arsenic in the native oxide on indium arsenide exists in a nominally +3 oxidation state as As$_2$O$_3$ in addition to a +5 state as As$_2$O$_5$. The As $2p_{3/2}$, As $3p$, and In $3d$ XPS spectra for native oxide-covered InAs(100) are shown in Fig. 4a. The oxidized As peak at a binding energy of 1327.8 eV is larger than the metal peak at 1324 eV in the $2p_{3/2}$ spectrum, whereas the relative peak heights are inverted in the 3d state, since the As $3p_{3/2}$ state is more surface sensitive than the 3d. Electrons with moderate kinetic energies (photon energy – binding energy) in the range of 10–1000 eV have the lowest escape depth and are the most surface sensitive. Deconvolution
of the As 2p$_{3/2}$ state revealed peaks belonging to As$_2$O$_3$ at 1338.4 eV ($\Delta E = +6.4$ eV [25–27]) and As$_2$O$_5$ at 1327.1 eV ($\Delta E = +3.1$ eV [25–28]) with an As$_2$O$_5$ to As$_2$O$_3$ peak area ratio of 2.2, which is representative of the oxide/air interface. In the As 3d region, the oxidized As peak was broad (FWHM = 3 eV) and shifted by +3.9 eV from the bulk InAs peak, suggesting that As$_2$O$_5$ co-existed with As$_2$O$_3$, although these states were not resolved. By comparing the measured chemical shift to reported shifts for As$_2$O$_5$ ($\Delta E = +3.0$ to 3.1 eV) and As$_2$O$_3$ ($\Delta E = +4.2$ eV) in the 3d region [25–28], As$_2$O$_5$ was the dominant oxidized As species near the oxide/substrate interface. An oxidized In state with a chemical shift characteristic of In$_2$O$_3$ at 447.1 eV ($\Delta E = +1.3$ eV) was resolved in the In 3d spectrum after peak fitting. Formation of the nonstoichiometric oxide In$_x$As$_{3-x}$O$_y$, which is comprised of As$_2$O$_5$ or As$_2$O$_3$ (As$^{5+}$) and In$_2$O$_3$ (In$^{3+}$) moieties, is also possible and was previously identified in thermal and UV-ozone grown oxides of InAs using valence band photoemission [26]. Since the oxidation states of As and In are similar, the chemical shift of In$_x$As$_{3-x}$O$_y$ should be close to As$_2$O$_5$ and In$_2$O$_3$ [26], and analysis using only XPS chemical shifts is insufficient to determine whether In$_x$As$_{3-x}$O$_y$ was present. The native oxide was As-rich, since the oxidized In to As ratio was 0.41, but the bulk semiconductor was In-rich, since the metal In to As ratio was 2.79 based on peak areas of the In 3d$_{5/2}$ and As 2p$_{3/2}$ states corrected by sensitivity factors. Inelastic mean free paths for several semiconductor materials monotonically increase with electron energy above 50 eV [29]. This implies that In 3d photoelectrons originate from deeper within the semiconductor than As 2p$_{3/2}$ photoelectrons. Trends in composition ratios are consequently more meaningful than absolute values.

Liquid phase HF etching completely removed both As$_2$O$_3$ and In$_2$O$_3$. Representative XPS spectra after etching in aqueous 49% HF are shown in Fig. 4b. Removal of As$_2$O$_3$ and the presence of an oxidized As peak attributed to As$_2$O$_5$ were evident in both the As 2p$_{3/2}$ and As 3d regions. Since As$_2$O$_5$ is water soluble [30], the presence of this oxide after etching in aqueous HF suggests that As was reoxidized either in the etching solution or during transfer of the sample to the vacuum chamber for analysis. A peak due to As–As bonding ($\Delta E = +1.2$ eV) was observed at a binding energy of 43.2 eV in the As 3d$_{5/2}$ region, suggesting that elemental As segregated near the overlayer/substrate interface. This is supported by the metal In to As peak ratio of 0.2 to 0.34. When the last layer of In oxide was removed exposing the bulk semiconductor surface, neighboring As atoms once bonded to the same In atom could bond to one another forming a dimer. The formation of As–As dimers could be problematic for device manufacturing, since states within the bandgap may be formed and pin the Fermi level as modeled in GaAs [31]. In contrast to InSb where bonds to F were formed terminating the surface, HF or the active etching species in solution either did not add F to these As dimer atoms or the As fluoride that was formed was water soluble and dissolved. Since the As–F bond strength is comparable to that for Sb–F (Table 1), the latter mechanism appears to be the most probable. The kinetics of removing the last oxide layer and terminating the surface appear to be different for InAs and InSb. Once the HF-etched surface was exposed to air, oxygen likely diffused into the As overlayer forming As$_2$O$_3$.

Gas phase HF etching completely removed As$_2$O$_5$ for all HF to water vapor ratios studied. Representative XPS spectra after etching are shown in Fig. 5. An oxidized As peak with a characteristic shift of As$_2$O$_5$ was still present at 1328.3 eV in the As 2p$_{3/2}$ spectrum. However, the oxidized As peak shifted to higher binding energy in the 3d spectrum compared to the native oxide, which shows that this state is not only As$_2$O$_5$, but rather the result of As–F bond formation. Without a bulk fluid to dissolve these fluorides as with liquid phase etching, they are stable on the surface even in ultrahigh vacuum. In the In 3d region, the XPS spectrum indicates that the oxidized state increased after gas phase etching relative to the metal peak. This also must be due to forming In fluorides, which is corroborated by a chemical shift of +1.3 to +1.6 eV. The O to peak areas were approximately equal for all HF to water vapor ratios studied. Quantitatively the bulk semiconductor was stoichiometric after gas phase HF etching with metal In to As peak area ratios of 0.96 to 1.23, and the terminating layer was As-rich, since the oxidized In to As peak area ratio was 0.40 to 0.57 for most of the HF to water vapor ratios used in this study. Elemental As ($\Delta E = +0.8$ eV) was produced by etching samples with low HF and high water concentrations, such as HF/H$_2$O = 0.3, as shown by a peak at a binding energy of 42.8 eV for As 3d$_{3/2}$ state in the
As 3D region in Fig. 5c, this surface contained an As-rich bulk metal (In/As \( \geq 0.62 \)) with an In-rich overlay (oxidized In/As \( \geq 1.35 \)). After exposing a sample terminated by F atoms and containing elemental As to 20 ALD cycles of As₂O₃ at 170 °C, the XPS spectra showed oxidized peaks shifted to lower binding energies indicating that F atoms were removed from the substrate surface and As–As bonds were broken leaving a small coverage of As oxide at the interface (Fig. 5d). These results are consistent with the bond dissociation energies listed in Table 1, which show that a metal–F bond in InAs is considerably weaker than an Al–F bond, while an In–In bond is weaker than an Al–O bond, but an As–O bond is comparable in strength to an Al–O bond.

4. Comparison and conclusions

The dominant oxidation states of the group V atoms in the native oxides of InSb and InAs were different, which affected the composition, but the group III In oxidation state was the same. InO₃ is known to be the prevalent oxide of In-based III–V materials and this was evident for InAlO₃, but not directly resolved for InSbO₃, although the XPS spectrum is consistent with this oxide composition. The group V oxidation state was +5 on InSbO₃/100 forming Sb₂O₅ whereas even though the +5 state was dominant on InAlO₃ forming Al₂O₃, the +3 state also was present forming Al₂O₃. The InSb native oxide was InO₂ rich, but that of InAs was Al₂O₃ rich. Based on Gobis free energies [24,26,30], formation of group V +5 oxidation states are favored over +3 states, which explains the predominance of Sb₂O₅ and Al₂O₃. However, the availability of O source, the solubility and diffusion rate of O in the oxides, and the mechanism of oxidation of metal atoms play a role in ambient oxidation processes [32,33].

Aqueous HF etching more effectively removed the native oxides on InAlAs, as shown by the complete removal of InSbO₃ and InO₃. The residual In₂O₃ was due to reoxidation, likely partial oxidation during air exposure of the elemental arsenic formed by the aqueous HF etch. The strength of the As–F bond and the lack of fluorides on the surface after etching suggest that As fluorides are water soluble. Liquid phase etching of InSb did not completely remove Sb₂O₅ and InO₂, as a result of terminating the surface with F and reoxidation during air exposure. InSb has a higher oxidation rate than InAs [32]. Aqueous HF etching consequently was less effective in removing oxide species and preventing reoxidation of InSb compared to InAlAs. Both materials showed an enrichment of the group V atom in the semiconductor and overlayer, although elemental group V bonding was observed only on InSb. Elemental Sb is possible thermodynamically [22], but may not have been resolved using the XPS apparatus in this study.

Gas phase HF etching of InSb completely removed Sb₂O₅ but not InO₃, leaving Sb₂O₃ and InF₃ on the surface. The presence of Sb₂O₃ and InF₃ was expected since these compounds are stable at room temperature [23,19], and the complete removal of Sb₂O₅ promoted F termination on the available surface sites, producing stoichiometric fluorides. Gas phase HF completely removed Al₂O₃, which could not regrow because the samples were kept in vacuum. Gas phase HF did not completely remove As₂O₃, nor InO₃, and InAs was fluorinated after processing. Stoichiometric Al₂O₃ was not expected, since it has a melting point of ~6 °C [34] and would be volatile in vacuum. Based on the chemical shift, the In–F bonding did not appear to be stoichiometric InF₃ and this may be attributed to having an As and In oxide matrix acting as a diffusion barrier for F species. Further study of the distribution of the phases as a function of depth could aid in explaining these results. The bulk InSb metal was stoichiometric after etching and the overlayer was In-rich arising from preferential F-termination on In surface sites. Two surface stoichiometries were obtained on InAs: a stoichiometric bulk metal and an As-rich overlayer for most HF to water molar ratios studied and an As-rich bulk metal and In-rich overlayer for an HF to water molar ratio of 0.3.

Al₂O₃ growth on InSb and InAs after gas phase HF etching produced interfacial reactions between surface species and gas phase precursors. Thinning of interfacial layers has been reported for ALD processes and attributed to the high reactivity of the trimethylaluminum precursor [7]. Based on the bond dissociation energy listed in Table 1, Al–F bonds are considerably stronger than metal–F bonds of In, As, and Sb, which explains the driving force for removal of these fluorides from the interface. Similarly Al–O bonds are stronger than In–O and Sb–O, but similar in strength to As–O bonds, leading to removal of the In and Sb oxides during ALD film growth, but leaving As–O bonding at the interface. This study demonstrated that F-termination enabled deposition of Al₂O₃ directly onto InSb. Deposition of Al₂O₃ on an In-rich overlayer with an As-rich bulk metal of InAs(100) resulted in an interfacial layer containing As-oxide. The range of surface stoichiometries and the F-termination obtained after gas phase HF etching could be a potential route in engineering surfaces prior to high-k film deposition.

Acknowledgements

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References


APPENDIX D

OXIDE REMOVAL AND SELECTIVE ETCHING OF IN FROM InSb(100) WITH TiCl₄
Oxide removal and selective etching of In from InSb(100) with TiCl$_4$

D.1 Introduction

Indium antimonide is a III-V compound semiconductor with a direct and narrow band gap (0.17 eV at 300 K), a very high electron mobility ($7.8 \times 10^4$ cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K), and a small effective electron mass of 0.14. These properties make InSb promising for high-speed electronic devices operating at very low supply voltages$^{2,3}$ as well as for long-wavelength optoelectronic devices (operating range of 3-5 $\mu$m)$^4$. In addition, the large Landé $g$ factor offers the potential to combine logic operations with spin states in spintronic devices.$^5$ Yet the lack of surface passivation techniques has limited the wider adoption of InSb and III-V compound semiconductors in general. Implementation of atomic layer deposition (ALD) to deposit high dielectric constant (k) materials, including Al$_2$O$_3$, HfO$_2$, and TiO$_2$,$^6$–$^8$ as both a functional and a passivation layer for III-V surfaces could spur the development of high performance devices.

In order to gain control of the III-V/high-k interface and the resulting device performance, it is important to understand the surface chemistry between the ALD precursor and the III-V surface. The reactions during the first few ALD cycles modify the surface composition by depositing the high-k metal atom and by removing semiconductor atoms from the oxide layer. Interfacial oxide cleaning is strongly influenced by the starting surface composition, the ligand on the metal precursor, and the temperature.$^6$–$^{12}$ Most III-V/high-k interface studies to date have focused on metalorganics and alkylamide metal precursors.$^6$–$^{11}$ Compared to the similarly technologically relevant metal chloride precursors, metalorganics and alkylamide precursors generally have higher growth rates, and the high-k film nucleation stage is relatively invariant
to the surface preparation method.\textsuperscript{7,9} In contrast, the few studies of metal chloride precursors done primarily on GaAs(100) show that the starting surface is important in determining the extent of interfacial oxide removal and film nucleation.\textsuperscript{6,7,9,12} A study by Caymax and coworkers showed that deposition of HfO\textsubscript{2} using HfCl\textsubscript{4} and H\textsubscript{2}O ALD precursors completely removed the oxide at 300\textdegree{}C from a GaAs(100) surface prepared by immersion in an aqueous mixture of H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2}.\textsuperscript{7} Time-of-flight secondary ion mass spectroscopy (TOFSIMS) depth profile analysis showed that the growth of HfO\textsubscript{2} in the first ALD cycle was enhanced due to ligand exchange between HfCl\textsubscript{4} and surface hydroxyl groups as well as to the formation of HfCl\textsubscript{3}OH, which could desorb resulting in removal of oxygen from the surface or could partly readsort onto HfCl\textsubscript{x} sites forming multilayer HfO\textsubscript{2} islands.\textsuperscript{9} Yet Frank et al. found that air-grown oxide on an epi-ready GaAs(100) surface was intact upon exposure to HfCl\textsubscript{4} and H\textsubscript{2}O ALD at 300\textdegree{}C.\textsuperscript{6} On aqueous HF-etched GaAs(100), Granados and Muscat showed that a single TiCl\textsubscript{4} pulse at 135 to 300\textdegree{}C removed the As-rich residual oxide without growth of TiO\textsubscript{2}.\textsuperscript{12} An elemental As layer terminated by Cl atoms was left that chemically passivated the surface to complete ALD cycles of TiCl\textsubscript{4} and water.

Understanding the reactions of metal chloride precursors with III-V surfaces is also of importance because the chlorides of III-V materials have relatively high volatilities making Cl\textsubscript{2} a common dry etchant. A review of halogen/III-V surface reactions by Simpson and Yarmoff reported that chlorine etched GaAs(100) at temperatures as low as 320 K depending on the Cl\textsubscript{2} dose, the surface stoichiometry, and the crystallinity.\textsuperscript{13} The studies were all conducted on clean GaAs(100) surfaces prepared by high temperature annealing in vacuum to remove the native oxide. The etching kinetics were temperature dependent, and three etching regimes were identified, characterized by the different etching products: below 400 K, AsCl and GaCl\textsubscript{2} were produced and were stable on the surface; between 400 and 650 K, GaCl desorbed and an elemental As
layer formed and accumulated; and above 650 K, Cl$_2$ etched Ga and As stoichiometrically. Murrell and co-workers showed that above a Cl$_2$ exposure of 10 Langmuir, bulk chlorination of InP(100)(4×2) produced In-rich chlorides and a phosphorus-enriched InP/In chloride interface.\textsuperscript{14} Vasquez \textit{et al.} demonstrated native oxide removal and bulk chlorination of InSb(100) using a Cl$_2$ plasma.\textsuperscript{15} An InCl$_3$ film that was 60-80 Å thick accumulated on the surface and desorbed when the samples were heated to 623 K. Prolonged Cl$_2$ plasma treatment (>5 min) resulted in a thicker InCl$_3$ overlayer and discoloration of the InSb surface. The lateral inhomogeneity on the surface was thought to be due to the presence of excess elemental Sb, and it was irreversible even after desorbing the InCl$_3$ overlayer by annealing.

Generation and segregation of excess elemental group V atoms at III-V/oxide and III-V/halide interfaces is a well-known phenomenon. In a review paper by Wilmsen, Sb pile-up at the InSb/thermal oxide interface was attributed to the instability of Sb$_2$O$_3$ in contact with an InSb substrate, causing a solid-state reaction that produced elemental Sb and In$_2$O$_3$.\textsuperscript{16} While thermodynamic considerations account for the accumulation of elemental Sb at the interface, kinetic contributions were also deemed plausible, such as the slow out-diffusion of Sb through the In$_2$O$_3$ layer. Vasquez \textit{et al.} attributed the accumulation of elemental Sb in their work to the thermodynamically favorable formation of InCl$_3$ compared to SbCl$_3$.\textsuperscript{15} In their adsorption-desorption study on InP, Murrel \textit{et al.} observed mass fragments from InCl$_x$ (x=0-2), P$_y$ (y=1-4), and Cl but not Cl$_2$ or PCl$_x$.\textsuperscript{14} The lack of phosphorus chloride desorption fragments was attributed to the competition between surface chlorination and segregation of P at the InP/In chloride interface by diffusion.

The etching of III-V substrates and the generation of excess group V atoms extends to hydrogen halides, which are less aggressive than halogens. Su \textit{et al.} demonstrated that GaAs was etched by Cl$_2$ at room temperature, but the etching rate using HCl
was negligible below 670 K. Above this temperature, the etching products consisted of GaCl and As$_2$. A study of gas phase HF/H$_2$O etching of the native oxide of InSb(100) by Lie et al. showed that nucleophilic attack by HF on the oxide resulted in the removal of oxygen and the formation of In-rich fluoride films (80-90% In). A ~3 Å-thick excess elemental Sb layer was produced only when ~90% of the native oxide was removed and a <10 Å-thick fluoride film accumulated on the surface, suggesting that In atoms were preferentially fluorinated once the substrate was exposed to HF. Similarly, In-enrichment of the fluoride overlayer and As-enrichment of the layer directly in contact with the substrate were observed in gas phase HF/H$_2$O etching of native oxide-covered InAs and In$_{0.53}$Ga$_{0.47}$As(100) surfaces.

Differing reaction kinetics between group III and group V atoms with chlorine could impact the film growth mode in the first few ALD cycles. Although Cl has been shown to bond readily with both Ga and As on GaAs, the initial Cl$_2$ uptake was higher on Ga-rich surfaces. These experimental observations are supported by the ab initio study of Jenichen and Engler that showed there was no potential barrier for dissociative chemisorption of Cl$_2$ on a Ga-rich surface, but there was a small barrier (12 kcal/mole) on an As-rich surface. Paralleling the results of Simpson and Yarmoff for Cl$_2$ on GaAs(100), Murrell et al. observed an enhanced Cl$_2$ uptake on an In-rich InP(100) surface. Wang et al. found that I$_2$ bonded to both In- and Sb-rich InSb(100) surfaces, but InI$_2$ was the dominant reaction product and the rate of formation was higher on the In-rich surface. A study by Nooney et al. showed that dissociative adsorption of H$_2$ on GaAs(100) produced both Ga–H and As–H, but HCl dissociatively chemisorbed on Ga– and As–rich GaAs(100) surfaces asymmetrically, yielding Ga–Cl and As–H. The poisoning of surface nucleation sites due to preferential bonding of group III atoms with halogens could result in Volmer-Weber (island) or Stranski-Krastanov (layer plus island) growth below the desorption temperature.
of the halogen, instead of the Frank-van der Merwe (layer-by-layer) growth desired in ALD.

This paper investigates the reactions of titanium tetrachloride (TiCl$_4$) with the native oxide-covered InSb(100) surface. TiCl$_4$ is a model for metal chloride precursors and is commonly used to deposit TiO$_2$ and TiN by ALD. We first describe the effect of vacuum annealing on the native oxide-covered InSb(100) surface as a control as well as to establish a cut off processing temperature. This is particularly important for InSb which has a relatively low noncongruent melting point of 653 K.$^{23}$ Following annealing in vacuum, the effect of TiCl$_4$ exposure at room temperature and at temperatures approaching the cut off were investigated.

D.2 Experimental

A GaAs(100) wafer with a 2 µm-thick epitaxially-grown InSb(100) layer was cleaved into 1 cm$^2$ coupons. The samples were degreased by sonication in acetone (99.9%, Pharmco-Aaper) for 5 min and blown dry with nitrogen followed by the same procedure using methanol (100%, Mallinckrodt AR). Solvent-cleaned InSb(100) was covered with a 34.7±1.5 Å-thick (95% margin of error) native oxide layer measured using ellipsometry (J.A. Woollam Co. M-2000S) and modeled using a Cauchy dispersion relation for the refractive index. After solvent cleaning, samples were mounted on a hollow stainless steel holder using Mo clips on two corners and loaded into a reactor for annealing either in vacuum or in a TiCl$_4$ (99.7%, Air Products) ambient.

The reactor had a base pressure of 10$^{-10}$ Torr, achieved using a 500 L/s ion pump (Thermionics) and was connected to an x-ray photoelectron spectroscopy (XPS) chamber via an ultra high vacuum transfer tube. Clustering enabled sample processing, transfer, and surface analysis without air exposure. Samples were heated radia-
tively using a tungsten filament positioned parallel to the back side of the sample, while the sample holder was cooled using liquid N$_2$. A 0.5 mm type K thermocouple spot-welded to a $4 \times 4 \times 0.25$ mm Ta plate was brought into contact with the front surface of a sample for temperature measurement. Temperature was controlled using a Eurotherm 2404 controller. Since the thermocouple plate was positioned near the sample perimeter, the center of a sample could be 30°C higher than the measured temperature. The thermocouple temperature was calibrated using the characteristic H$_2$ thermal desorption peaks at 675 and 775 K obtained at a heating rate of 2.5 K/s from a Si(100) surface that was prepared by dipping in a 1:10 HF:water solution for 5 min.

Vacuum annealing at 500, 550, 600, and 650 K was done for 5 min each at a base pressure of $10^{-10}$ Torr. Reactive gas annealing was performed at sample temperatures from 470 to 560 K for 3 min with a TiCl$_4$ pressure of 1 to $3 \times 10^{-7}$ Torr. Samples were heated from room temperature to a set point of either 470 or 500 K at a rate of 2 K/s. In order to minimize contamination, the thermocouple was removed from the sample surface prior to a TiCl$_4$ dose once the temperature reached the set point. The heater current was kept constant during a TiCl$_4$ dose, which caused the sample temperature to drift upward by sixty degrees from the original set point. For this reason, sample temperatures are reported as ranges for the TiCl$_4$ experiments.

The TiCl$_4$ was delivered by vapor draw from a source maintained at 50°C, which generated a pressure of $\sim$41 Torr. TiCl$_4$ was metered into the chamber through a leak valve and directed at the sample by a doser. The doser assembly consisted of an 8 in-long, 0.25 in-diameter tube with a 0.5 in-diameter shroud that was positioned within 3 mm of the sample surface using a linear motion feedthrough. This design enhanced the gas flux to the surface by approximately 60 times (for TiCl$_4$ dosed at 500 K, $\leq 0.2$ sticking probability, and 500 L/s pumping speed$^{24}$), yielding total exposures
of about $1 - 3 \times 10^3$ L (1 L = $1 \times 10^{-6}$ Torr-s). Another set of samples was exposed to TiCl$_4$ for 3 min at room temperature followed by vacuum annealing at 500 K for 1 min. Prior to loading a sample, TiCl$_4$ was dosed into the reactor for at least 30 s to passivate the dosing lines and reactor walls in order to minimize the generation of HCl during the experiments from the reaction of TiCl$_4$ with residual moisture.

Surface analysis was performed using in situ XPS at room temperature. Photoelectrons were excited using a twin anode non-monochromatic x-ray source (Al/Mg) and energy analyzed using a double pass cylindrical mirror analyzer (Physical Electronics 549) at 50 eV pass energy. Al K$_\alpha$ x-rays (1486.6 eV) were used throughout this study. The binding energy (BE) scale was referenced to the Sb 3d$_{3/2}$ substrate peak assigned to 537 eV.$^{25}$ The elastic and inelastic electron scattering backgrounds were removed using a Shirley algorithm.$^{26}$ Peak deconvolution was performed using multipeak fitting packages included with Igor Pro (WaveMetrics, Inc., v.6) and custom procedures. Peak assignments were based on the chemical shift ($\Delta$BE) referenced to either the In or the Sb peak of the InSb substrate.$^{25,27–31}$ Surface topography was imaged ex situ using a Digital Instruments Multimode IIIa atomic force microscope (AFM) with a Nanoscope III controller in tapping mode and a Hitachi S-4500 field-emission secondary electron microscope (SEM) operated with a 15 keV accelerating voltage.

D.3 Results and Discussion

High resolution XPS spectra of a solvent-cleaned InSb(100) surface showed that the native oxide layer consisted of both In and Sb oxides (Fig. D.1a). The Sb 3d and In 3d spectra each contain two peak envelopes due to spin-orbit coupled states with a characteristic 3d$_{5/2}$ to 3d$_{3/2}$ branching ratio of 1.5.$^{32}$ Within the Sb 3d$_{3/2}$ envelope,
two states belonging to Sb$_2$O$_5$ at 539.7 eV ($\Delta$BE= +2.7 eV) and to Sb of the InSb substrate at 537 eV were resolved. The same states were resolved in the Sb 3d$_{5/2}$ envelope at 530.5 eV ($\Delta$BE= +2.9 eV) and at 527.6 eV, respectively. But in addition, there was a contribution from the O 1s state in the 530-532 eV BE range, which overlapped with the Sb$_2$O$_5$ peak. In the In 3d spectrum, the spin-orbit split peaks were broadened (FWHM 2.6 eV) by contributions from In$_2$O$_3$, which has a chemical shift of 0.4-1.4 eV, but was not resolved.

Annealing at 500 and 550 K did not result in significant changes in either the In or the Sb 3d spectra (Fig. D.1b and c). While the absolute intensity of both In and
Sb 3d peaks increased significantly after annealing to 550 K (Fig. D.1c), the ratios of In to Sb peaks and oxidized to substrate Sb peaks were constant, indicating that the increased signal was due to variations in sample alignment. Annealing at 600 K completely removed Sb$_2$O$_5$ because the peak at 539.7 eV on the starting surface was no longer present (Fig. D.1d). This is consistent with the onset of Sb$_2$O$_5$ desorption at 623 K reported in the literature\textsuperscript{15}. The partial removal of In$_2$O$_3$ after the 600 K anneal was reflected by the 0.4 eV shift to lower binding energy and the asymmetry of the In 3d peaks. An O 1s peak due to the remaining In$_2$O$_3$ was resolved at $\sim$530.5 eV as a shoulder on the Sb 3d$_{5/2}$ substrate peak. Complete removal of In$_2$O$_3$ was not expected based on its high melting point (1912°C) and relatively low vapor pressure.\textsuperscript{1,23} The In and Sb signals from the bulk substrate became more intense as the oxide was thinned by heating.

Increasing the annealing temperature to 650 K disrupted the InSb(100) surface structure. The intensity of the O 1s peak shown in Fig. D.1e was reduced but was not completely removed. A cross-sectional SEM image showed a rough surface morphology containing droplets and a 50% loss of the InSb film because there was only a $\sim$1 µm-thick layer remaining (Fig. D.2a). Top-down SEM images showed corrugations in the surface (Fig. D.2b), and the surface morphology was not homogeneous across the entire sample (not shown). The intensities of both In and Sb 3d photoelectrons were reduced significantly (Fig. D.1e). Shading of surfaces outside of the line of sight of the x-ray beam due to features that are on the order of the x-ray attenuation length ($\sim$100-1000 nm) could reduce the total analysis area and the XPS intensity.\textsuperscript{33} Thus, a 550-600 K cut-off temperature was established for vacuum annealing InSb(100) covered by native oxide, which is somewhat lower than the 653 K reported in the literature.\textsuperscript{23} An Sb$_4$ over-pressure is typically applied to prevent preferential loss of Sb and formation of In droplets when an InSb surface is annealed.
Figure D.2. SEM topographical image of an InSb(100) surface after solvent cleaning and annealing in vacuum at 650 K for 5 min at a base pressure of $10^{-10}$ Torr. Image (a) was taken at a grazing angle with a scale bar of 2.5 µm and image (b) was taken perpendicular to the surface with a scale bar of 500 nm.

Room temperature TiCl$_4$ exposure followed by annealing to 500 K partially etched the native oxide. Compared to the starting surface (Fig. D.3a), the peak due to the overlapping Sb 3d$_{5/2}$ (Sb$_2$O$_5$) and O 1s signals at 530.5 eV shifted by 0.2 eV to lower BE (Fig. D.3b). The comparable In and Sb 3d photoelectron substrate peak intensities for the spectra shown in Fig. D.3a and b yielded the difference spectrum shown in Fig. D.3(b-a). Partial removal of Sb$^{3+}$ and O from the oxide layer is evident from the decreased photoelectron intensities at 540.7 and 531.6 eV. In order to quantify the amount of oxygen removed, the O 1s peak before and after the TiCl$_4$ exposure was extracted from the Sb 3d$_{5/2}$ peak envelope. An oxidized Sb 3d$_{5/2}$ peak was generated from the Sb 3d$_{3/2}$ peak based on the 9.4 eV spin-orbit splitting characteristic of Sb 3d photoelectrons$^{25}$ and the 3:2 spin-orbit branching ratio of 3d$_{5/2}$ to 3d$_{3/2}$ photoelectrons. This peak was subtracted from a spectrum to resolve the O 1s peak. From the extracted O 1s peaks, an estimate of 27% of the oxygen was removed from the native oxide by the room temperature TiCl$_4$ exposure.
and 500 K vacuum anneal. The XPS intensity ratio of the removed O to Sb$^{5+}$ was 10.7 after normalization of the extracted O 1s and Sb 3d$_{5/2}$ signals using relative sensitivity factors. Since removal of Sb$_2$O$_5$ would warrant an O to Sb$^{5+}$ ratio of $\sim$2.5, a portion of the oxygen removed must have originated with the In oxide.

An analysis of the In 3d spectrum showed that the removal of oxygen bonded to In was not accompanied by the removal of In from the surface. The magnified In 3d difference spectrum [Fig. D.3(b-a)×4] showed that the photoelectron intensity increased at both 445.1 and 452.7 eV. These states are consistent with the formation of indium chlorides. A small, broad, and flat Cl 2p peak centered at about 197 eV was detected after the 298 K TiCl$_4$ exposure and 500 K anneal (Fig. D.4). Also a small Ti 2p$_{3/2}$ peak at 458.7 eV was produced in Fig. D.3(b-a), which is indicative of Ti$^{4+}$ (TiO$_2$) with a possible contribution from titanium chloride. The appearance of both indium chlorides and TiO$_2$ on the surface is consistent with ligand exchange, in which an In–O (Ti–Cl) bond was replaced by an In–Cl (Ti–O) bond. A large thermodynamic driving force exists for the electron deficient Ti in TiCl$_4$ to bond to O, liberating a Cl atom to bond to either In or Sb in the oxide layer. The reaction Ti–Cl + In–O $\rightleftharpoons$ Ti–O + In–Cl evolves 353 kJ/mole, based on bond dissociation energies ($D_{298K}^\circ$). A similar reaction with In replaced by Sb is also exothermic with 189 kJ/mole generated. Ligand exchange reactions involving Sb are also thermodynamically favorable, but lead to etching of Sb likely as SbCl$_3$, which has a vapor pressure of 1.1 Torr at 323 K. There was no evidence for preferential removal of one substrate oxide over the other because the native oxide was indium rich ($\sim$ 69% In$_2$O$_3$) and the oxide loss was 64% as In$_2$O$_3$ and 36% as Sb$_2$O$_5$.

Despite the large thermodynamic driving force and evidence for ligand transfer reactions leading to TiO$_2$ formation, the removal of oxygen from the surface suggests that there was an additional reaction pathway for TiCl$_4$. Owing to the strong Ti–O
Figure D.3. Sb 3d, In 3d, and Ti 2p core-level XPS spectra taken at 50 eV pass energy for InSb(100) (a) solvent cleaned, (b) exposed to TiCl$_4$ at 298 K for 3 min and annealed to 500 K for 1 min, (c) exposed to TiCl$_4$ at 470-530 K for 3 min, and (d) exposed to TiCl$_4$ at 500-560 K for 3 min. The (b-a) spectrum is a difference, and the difference in the In 3d range was magnified $\times$4 for clarity. The In 3d spectra in (c) and (d) were magnified by $\times$8. Component states are shown by solid lines below each of the spectra in (c) and (d).
Figure D.4. Cl 2p core-level spectra taken at 200 eV pass energy for InSb(100) samples (◦) exposed to TiCl₄ at 298 K for 3 min and annealed at 500 K for 1 min, (---) exposed to TiCl₄ at 470-530 K for 3 min, and (—) exposed to TiCl₄ at 500-560 K for 3 min.

bond (D₀^{298K} = 668 kJ/mole)¹, TiCl₄ could have chemisorbed dissociatively on the oxide surface and bonded to either In or Sb atoms via bridging O, forming In–O–TiCl₃ or Sb–O–TiCl₃. In this configuration, the TiCl₃ moiety would pull electron density away from In–O or Sb–O weakening these bonds. This could promote nucleophilic attack by Cl on In and Sb, eliminating a Cl atom from Ti and producing a molecular compound O=TiCl₂. We hypothesize that formation of titanium oxychloride is the most plausible pathway for O to leave the surface because the vacuum annealing results show that heating to 500 K did not measurably change the oxide states in the XPS spectra. TiOCl₂ has been identified spectroscopically as one of the gaseous species in the reactions of water with compounds containing Ti, Al, and Cl.³⁷ A volatile oxychloride TiOCl₂ was proposed in a quartz crystal microbalance study of TiCl₄ and H₂O ALD³⁸ as well as in an XPS and temperature programmed desorption
(TPD) study of TiCl$_4$ reactions with As$_2$O$_3$ on GaAs(100).$^{27}$ Oxygen removal via formation of titanium hydroxychlorides from the reaction of TiCl$_4$ with the naturally hydrophilic native oxide surface is plausible but is less likely. Titanium hydroxychlorides was proposed to be a short-lived intermediate formed when TiCl$_4$ reacted with hydroxyl terminated SiO$_2$ as well as GaAs(100) native oxide surface.$^{7,9,39}$ The reactivity and unstability of this compound, as indicated by the elusive detection of it,$^{39}$ however, advocate that oxide was being removed by the formation of TiOCl$_2$, which is stable enough to be pumped out of the system. While there are no data for indium oxychloride, O removal via formation of volatile antimony oxychloride is unlikely. SbOCl was detected in the solid phase products of the reaction between Sb$_2$O$_3$ and chlorinated flame retardants, such as chlorinated paraffin (C$_{27}$H$_{31}$Cl$_{25}$) and Diels-Alder adduct (C$_{15}$H$_6$Cl$_{12}$) at 473-773 K.$^{40}$ Pitt et al. reported that SbOCl decomposed stepwise into Sb$_4$O$_5$Cl$_2$ at 518 K, Sb$_3$O$_4$Cl at 683 K, and Sb$_2$O$_3$ at 748 K, evolving gaseous SbCl$_3$.$^{41}$ If formed, the stability and thermal decomposition of SbOCl would not have caused the removal of O atoms from the InSb native oxide surface in our experiments.

At elevated temperatures, TiCl$_4$ exposure promoted oxide etching. As shown in Fig. D.3c and d, peaks in the binding energy range expected for Sb$_2$O$_5$ and O 1s were absent from the Sb 3d spectra after TiCl$_4$ exposures at 470-560 K. Instead a single symmetric peak was obtained corresponding to Sb(0). In the temperature range 470-530 K, the overall In 3d photoelectron signal was significantly reduced from that of the native oxide-covered surface. The In 3d peak was also a single symmetric state and was shifted by +1.4 eV, which is within the range expected for In$_2$O$_3$ (Fig. D.3c). The absence of an O 1s peak, however, means that the oxidized In signal was the result of chloride formation. This is corroborated by the relatively strong Cl 2p signal shown in Fig. D.4 after dosing TiCl$_4$ at 470-530 K. Based on the chemical shift,$^{15,25}$
InCl$_x$ with $x \leq 2$ was present. Increasing the dosing temperature to 500-560 K induced indium chlorides to desorb (Fig. D.3d) and significantly reduced the Cl 2p signal (Fig. D.4). The relatively high vapor pressures of InCl (278 Torr)$^{42}$ and InCl$_3$ (1.6$\times$10$^{-4}$ Torr)$^{43}$ at 550 K caused indium chlorides to desorb alongside SbCl$_3$. Oxide removal likely proceeded via the same mechanism proposed above, producing volatile TiOCl$_2$.

Residual titanium was observed on surfaces after the high temperature TiCl$_4$ dose. As shown in Fig. D.3c, within the Ti 2p$_{3/2}$ peak envelope, peaks at 463.1 (\(\Delta E = +3.3\) eV) and 459.8 eV were due to oxidized Ti and Ti in the metallic state, respectively.$^{25,35,44}$ The same states were resolved in the Ti 2p$_{1/2}$ peak envelope, with a peak due to oxidized Ti at 457.4 eV and metallic Ti at 454.2 eV. Since the O 1s signal was absent, the higher oxidation states of Ti must also correspond to titanium chlorides.$^{35,44}$ From an XPS and thermal desorption study of clean W(110) exposed to TiCl$_4$, Sandell et al. reported Ti 2p$_{1/2}$ binding energies of 458.4 eV for adsorbed TiCl$_4$ and 454.7 eV for surface TiCl$_x$ ($x=1-3$).$^{44}$ Tiznado et al. reported a binding

**Figure D.5.** SEM topographical image of an InSb(100) surface after solvent cleaning and exposed to TiCl$_4$ at 500-560 K for 3 min. Image (a) was taken at a grazing angle with a scale bar of 2.5 µm and image (b) was taken perpendicular to the surface with a scale bar of 500 nm. Inset is a 2×2 µm AFM height image showing a step height of ~100 nm between points indicated by the arrows.
energy of 458.9 eV for Ti$^{+4}$ and 455.1 eV for Ti$^{+3}$ for an Ar sputtered Ni foil exposed to TiCl$_4$. Based on the binding energy of 457.4 eV, Ti could be bonded to one to four chlorine atoms. Molecularly adsorbed TiCl$_4$ was only stable up to 300 K on a W(110) surface and should not have been present after the TiCl$_4$ dose at 470-530 K. The intermediate shift of the titanium chloride peak could be due to the elemental Sb matrix on which it is bound. The higher electronegativity of Sb compared to Ti could take charge away from Ti causing a shift to higher binding energy. When the TiCl$_4$ dosing temperature was increased to 500-560 K, the peak due to titanium chloride shifted by 1 eV to lower binding energy. This indicates that the oxidation state of Ti was reduced, which is consistent with the smaller Cl 2p signal shown in Fig. D.4. This occurred without loss of Ti from the surface because the integrated Ti 2p peak intensity did not change with the higher dosing temperature.

Once the oxide was removed completely from the surface, TiCl$_4$ selectively chlorinated and etched In from the bulk InSb layer. This is consistent with the notably low In 3d photoelectron signal as well as the residual InCl$_x$ observed on samples dosed with TiCl$_4$ at 470-530 K and its complete removal when the dosing temperature was increased to 500-560 K (Fig. D.3c and d). A photoelectron signal from In bonded to Sb in the substrate was absent for TiCl$_4$ dosed at both 470-530 and 500-560 K. Thus, Sb must have been present in a metallic state, either bound to other Sb atoms or to Ti, and the Sb layer thickness should have been equal to or greater than the Sb 3d photoelectron sampling depth of $\sim$72 Å estimated from the electron inelastic mean free path. In contrast to annealing at 650 K, which resulted in the loss of approximately 1 µm of the InSb layer and produced a droplet surface morphology (Fig. D.2), gross InSb etching did not occur. Instead the surface morphology consisted of pits and grain boundaries as shown by the grazing angle and top down SEM images of samples exposed to TiCl$_4$ at 500-560 K (Fig. D.5). Based on the AFM section
analysis shown in the inset, the surface height modulation was on the order of 100 nm, consistent with the absence of the XPS signal from bulk InSb due to the relatively thick Sb layer. While Cl$_2$ could have resulted in substrate etching as reported in other III-V materials, the generation of Cl$_2$ from thermal decomposition of TiCl$_4$ is not expected. The Gibbs free energy for the decomposition of TiCl$_4$$_{(g)}$ to TiCl$_{x}$$_{(g)}$ (x≤3) and Cl$_2$$_{(g)}$ is positive between the TiCl$_4$ source temperature (323 K) and the substrate temperature (470–560 K). To illustrate the thermal stability of TiCl$_4$ in the gas phase, only 5% and 60% of the TiCl$_4$ dosed was converted to TiO$_2$ at 773 K and 973 K, respectively, in the presence of oxygen in a chemical vapor deposition process.

Based on the Gibbs free energies of formation, In chloride etching products where $D_{\text{In-Cl}}^0$ is 436 kJ/mole are more thermodynamically favorable than those of Sb where $D_{\text{Sb-Cl}}^0$ is 360 kJ/mole. A review of halogen reactions with III-V surfaces concluded that while there is preferential bonding of Cl to Group III atoms when a surface plane consists of both Group III and Group V atoms, such as GaAs(110), Cl bonds to the on-top atom when a surface plane consists exclusively of either a Group III or a Group V atom, such as GaAs(100). Thus, initially In should have been preferentially chlorinated, but as indium chlorides were removed exposing Sb planes, a portion of the available Sb should have been chlorinated, resulting in desorption because of the high volatility ($p_{\text{SbCl}_3}$=1.1 Torr at 323 K). The observed bulk accumulation of Sb must be due to a kinetically inhibited chlorination of Sb relative to In.

Owing to the electronic structure of Group III and Group V atoms, the normally four-fold coordination of In and Sb atoms in the bulk becomes three-fold coordination when a crystal plane is missing, such as on a surface. The lone pair of electrons on three-fold coordinated Sb could repel electronegative Cl, resulting in a higher activation energy for chlorination. A study of Cl$_2$ reactions on oxide-free GaAs surfaces
reported a higher rate of initial Cl uptake for Ga-rich surfaces compared to As-rich surfaces and a 50 Å elemental As overlayer was not reactive to Cl\(_2\).\(^{13}\) TiCl\(_4\) etching of the residual As\(_2\)O\(_3\) layer on GaAs(100) after treating with an aqueous HF dip stopped at the elemental As layer, and the surface was unreactive to further TiCl\(_4\) doses.\(^{27}\) These observations are consistent with a density functional theory calculation showing that chemisorption of HCl and Cl\(_2\) is barrierless on Ga-rich but not on As-rich GaAs surfaces.\(^{20}\)

The formation of a Ti-Sb alloy is another plausible kinetic barrier to chlorination of Sb. The peak area ratios of metallic Ti to elemental Sb normalized by their sensitivity factors\(^{34}\) were 0.43 and 0.46 in Fig. D.3c and d. The BE separation between the Sb 3d\(_{5/2}\) and Ti 2p\(_{3/2}\) peaks in the metallic state were 73.6 to 73.8 eV after the high temperature TiCl\(_4\) dose. These values are lower than the 74.2 eV BE separation expected for pure Sb and Ti by 0.4 to 0.6 eV,\(^{25}\) consistent with charge transfer from the more electropositive Ti to Sb. While these observations are not conclusive, they are consistent with the formation of the alloy TiSb\(_2\). Electron deficient Ti in TiCl\(_4\) could have been attracted to the electron lone pair on a surface Sb atom, leading to dissociative adsorption of TiCl\(_4\) on bare InSb forming Sb–TiCl\(_3\) and In–Cl bonds and chemically passivating Sb relative to In.

For preferential chlorination and bulk etching of In to occur, In must have been available to react with Cl despite the buried InSb/Sb interface as the elemental Sb overlayer or TiSb\(_2\) alloy evolved during etching. The high chlorination rate of In and desorption of indium chloride would have created a gradient in the chemical potential, inducing out-diffusion of In to the surface and segregation of Sb at the interface. A study on the self-diffusion in InSb reported lattice diffusion activation energies of 1.45 eV and 1.91 eV for In and Sb, respectively.\(^{48}\) In the presence of grain boundaries, however, short-circuit diffusion is thought to occur and diffusivities are 10\(^4\) times higher
than those for the lattice, lowering the diffusion activation energies to 0.84 and 1.1 eV for In and Sb, respectively.\textsuperscript{48} The higher rate of In and P segregation due to diffusion relative to the rate of interface reactions with Cl was cited as an explanation for the pressure-dependent thermal desorption spectra of InP(100) exposed to Cl\textsubscript{2}.\textsuperscript{14} At low dosing pressures, the reaction rate was slower than the diffusion rate resulting in the chlorination only of In and the segregation of P at the InCl\textsubscript{x}/InP interface. At high dosing pressures, however, the rates were comparable and the desorption peaks from InCl\textsuperscript{+} and P\textsuperscript{4+} mass fragments coincided, indicating that segregation did not occur. This implies that reactant flux is a plausible condition limiting the kinetics. Taking into account the approximately 60 times flux enhancement due to the dosing system geometry, the estimated TiCl\textsubscript{4} flux in our experiments was \(6.8 \times 10^{14}\) molecules/(cm\(^2\)-s). This flux is comparable to the typical atomic surface density of \(1 \times 10^{15}\) atoms/cm\(^2\), such that if a sticking probability of 1 is assumed, there were sufficient TiCl\textsubscript{4} molecules to react with every atom on the surface. Thus, the preferential chlorination and etching of In was not the result of limiting the reactant flux, but rather to the higher energy barrier to chlorinate Sb due either to its electronic structure or passivation by Ti and to the enhanced out-diffusion of In making it available to react with chlorine.

The results show that while TiCl\textsubscript{4} selectively chlorinated and etched In from InSb(100) in the range 470-560 K, TiO\textsubscript{2} nucleated and the surface was passivated with indium chloride with a room temperature TiCl\textsubscript{4} dose. An intermediate temperature range could consequently provide controlled oxide etching by TiCl\textsubscript{4} and prevent bulk etching, allowing nucleation and growth of a TiO\textsubscript{2} film. Hydroxylation of the surface could aid in overcoming the passivation of TiO\textsubscript{2} nucleation sites by chlorine bound to In and in achieving true two-dimensional growth. Surface hydroxilation is a requirement for deposition of TiO\textsubscript{2} on SiO\textsubscript{2} surfaces. In a review paper by Puurunen,
ligand transfer in which SiO–H(Ti–Cl) bonds were replaced by SiO–Ti bonds with the release of HCl was determined to be the dominant reaction path below 300\degree.\textsuperscript{39} Chlorine passivation via dissociative adsorption of TiCl\textsubscript{4}, forming Si–O–TiCl\textsubscript{x} and Si–Cl\textsubscript{1–x}, did not occur on surface siloxane (Si–O–Si) even after all hydroxyl groups on the surface were consumed.\textsuperscript{39} This is likely due to the relatively high Si–O bond dissociation energy\textsuperscript{1} of 799.6 kJ/mole. Based on our result, however, dissociative chemisorption of TiCl\textsubscript{4} on InSb oxide is the dominant path in the absence of surface hydroxyl, likely due to the relatively weak In–O (346 kJ/mole) and Sb–O (434 kJ/mole) bonds. In addition to optimizing the temperature and conditioning the surface for deposition, tuning of the ambient pressure by means of inert gases could potentially suppress uncontrolled desorption of chlorides leading to bulk etching. A higher TiCl\textsubscript{4} pressure is anticipated to result in a higher bulk InSb etching rate as observed for Cl\textsubscript{2} etching of GaAs.\textsuperscript{13} The facile chlorination of In and Sb in the oxide as well as the volatility of the intermediate TiOCl\textsubscript{2} produced in the reaction of TiCl\textsubscript{4} with InSb native oxide has the potential to be applied as an \textit{in situ} surface preparation method prior to deposition of high-k films. To date, success in controlled \textit{in situ} InSb native oxide removal is limited to molecular hydrogen cleaning\textsuperscript{49} and gas phase HF/H\textsubscript{2}O etching,\textsuperscript{18} the later producing similar results as TiCl\textsubscript{4} with less than 10 Å of an indium fluoride-rich overlayer and \(\sim\)3 Å of an elemental Sb layer left on the surface.

D.4 Conclusion

A cut-off temperature of 550-600 K was established for processing native oxide-covered InSb(100) in vacuum. Annealing at 600 K completely desorbed Sb\textsubscript{2}O\textsubscript{5}, but residual In\textsubscript{2}O\textsubscript{3} was stable on the surface. At 650 K, oxide was not completely removed but
preferential desorption of Sb ensued, bulk etching occurred, and In droplets formed.

Exposing native oxide surfaces to TiCl$_4$ at room temperature followed by annealing to 500 K partially removed both In and Sb oxides. About 25% of the oxygen in the native oxide was etched likely by the formation of volatile TiOCl$_2$. A submonolayer TiO$_2$ coverage and indium chlorides were detected, suggesting that TiCl$_4$ reacted with the InSb surface via a ligand transfer mechanism in which an In–O (Ti–Cl) bond was replaced by an In–Cl (Ti–O) bond. A similar mechanism occurred on Sb oxide, but SbCl$_3$ desorbed upon annealing to 500 K. The etching reaction prevailed when TiCl$_4$ was dosed with the substrate temperature maintained between 470-560 K. The TiCl$_4$ exposure at elevated temperatures not only completely removed native oxide but also preferentially etched In from the InSb substrate via formation of volatile indium chlorides. The bulk etching produced a rough surface with at least a 72 Å-thick Sb layer on the surface. The accumulation of a relatively thick Sb layer indicates that the kinetic barrier to chlorinate Sb is higher than the one for In. A repulsive interaction between chlorine ligands and the electron lone pair on tri-coordinated Sb surface atoms could contribute to this barrier. The Sb layer was in the form of elemental Sb or a Ti-Sb alloy (TiSb$_2$), as indicated by a Ti to Sb ratio of 0.43-0.46. The bonding of Sb to Ti could also chemically passivate Sb to chlorination. Grain boundaries and modulations in the surface topography on the order of ∼100 nm that were observed with SEM and AFM likely promoted out-diffusion of In to the surface, making In available for chlorination despite the formation of a buried InSb/Sb interface.

D.4.1 Acknowledgement

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REFERENCES


[40] Bogdanova, V. V.; Fedeev, S. S.; Lesnikovich, A. I.; Klimvtsova, I. A.; Sviridov, V. V. Polym. Degrad. Stabil. 1989, 11, 205

[41] Pitts, J. J.; Scott, P. H.; Powell, D. G. J. Cell. Plast. 1969, 6(1), 35


[45] Roine, A. HSC Chemistry Ver. 4.1.; Outokumpu Research Oy: Pori, Finland, 1999


Appendix E

Passivation of InGaAs interface by atomic layer deposition of Al$_2$O$_3$ and post deposition annealing
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E.1 Experimental

An InP(100) wafer with a 1 µm epitaxially grown In$_{0.53}$Ga$_{0.47}$As(100) layer (n-type, S doped to 1-4 × 10$^{17}$ cm$^{-3}$, IQE) was cleaved into 1 cm$^2$ coupons. Surface preparation consisted of either a degreasing procedure, which is designated as Nox, or degreasing followed by etching in aqueous HF solution, which is designated as LHF. The degreasing procedure consisted of sonication in acetone (99.9%, Pharmco-Aaper) for 5 min and blown dry with nitrogen followed by the same procedure using methanol (100%, Mallinckrodt AR), ultra pure water rinse (UPW, 18 MΩ-cm resistivity from in house ultra pure water facility), and blown dry with ultra pure N$_2$. Solvent-cleaned In$_{0.53}$Ga$_{0.47}$As(100) was covered with a 12.7±0.2 Å-thick (95% margin of error) native oxide layer measured using ellipsometry (J.A. Woollam Co. M-2000S) and modeled using a Cauchy dispersion relation for the refractive index. The liquid phase HF etching procedure consisted of immersing a sample in hydrofluoric acid (49%, Ashland Chemical, Cleanroom Electronic Grade) for 1 min, rinsing with ultra pure water, and drying with ultra pure N$_2$. Samples were loaded into a vacuum chamber for surface analysis or Al$_2$O$_3$ deposition within 5 min of being removed from solution.

ALD of Al$_2$O$_3$ films was carried out at 170 °C in a custom built reactor which is clustered with a surface analysis chamber by X-ray photoelectron spectroscopy (XPS). The clustered reactor system enables surface analysis between ALD cycles without air contamination. Trimethylaluminum (TMA, Al(CH$_3$)$_3$, Hi-κ grade, Rohm and Haas) and ultra pure water vapor were pulsed into the ALD reactor in a carrier gas of ultra pure nitrogen, which was also used to purge the reactor between reactant
pulses. One ALD cycle consisted of a 1 s TMA pulse, 30 s purge, 0.1 s H\textsubscript{2}O pulse, and 30 s purge. A growth rate of 1.1 Å/cycle was determined \textit{ex situ} by ellipsometry of Al\textsubscript{2}O\textsubscript{3} films deposited on Si(100).

The effect of post Al\textsubscript{2}O\textsubscript{3} deposition annealing to interface composition was investigated by exposing samples to forming gas (FGA) or ammonia (NH\textsubscript{3}) after depositing a 10 nm thick Al\textsubscript{2}O\textsubscript{3}. A 10 nm thick Al\textsubscript{2}O\textsubscript{3} was necessary to draw a parallel relationship between interface composition and interface quality probed electrically in a separate publication.\textsuperscript{1} The FGA step consisted of a ramp to 350 °C for 3 h followed by a soak at 400 °C for 1 h in a flowing mixture of N\textsubscript{2} and H\textsubscript{2} gas at atmospheric pressure. The ammonia annealing was done by alternating pulses of ammonia and nitrogen in an ALD system for 2 h at 300°C. After the FGA or NH\textsubscript{3} annealing, the 10 nm thick Al\textsubscript{2}O\textsubscript{3} films were thinned down to ~2.5 nm to enable XPS analysis of the InGaAs/Al\textsubscript{2}O\textsubscript{3} interface. Al\textsubscript{2}O\textsubscript{3} back-etching procedure involved immersing a sample in a 49% HF diluted with UPW at a ratio of 1:1000 by volume. For select samples, NH\textsubscript{3} annealing was performed after depositing 10 nm Al\textsubscript{2}O\textsubscript{3} and a Ni(15 nm)/Au(20 nm) blanket film on top of the Al\textsubscript{2}O\textsubscript{3} film using an electron beam evaporator. The blanket metal was lifted off and Al\textsubscript{2}O\textsubscript{3} film was back-etched prior to XPS analysis of this sample. Ni/Au blanket film was lifted off by immersing a sample in an aqua regia solution containing HCl:HNO\textsubscript{3}:H\textsubscript{2}O at ratio of 3:1:2 by volume (XX% HCl from bla and XX% HNO\textsubscript{3} from bla) for 30 s, rinsing in UPW, and drying in ultra pure N\textsubscript{2}. Sample labels reflect the sequence of processes done prior to surface analysis, which could consist of surface cleaning (Nox or LHF), dielectric film deposition (Aox), post-dielectric deposition annealing (FGA or NH\textsubscript{3}), and blanket metal deposition (M). For example, the label "LHFAoxMNH\textsubscript{3} back-etched" denotes that the sample was degreased, etched in liquid phase HF, subjected to Al\textsubscript{2}O\textsubscript{3} ALD and Ni/Au blanket deposition, annealed in NH\textsubscript{3}, and back-etched in aqua regia and diluted HF.
Surface analysis was performed using XPS at room temperature. Photoelectrons were excited using a twin anode non-monochromatic X-ray source (Al/Mg) and energy analyzed using a double pass cylindrical mirror analyzer (Physical Electronics 549) at 50 eV pass energy. Al Kα X-rays (1486.6 eV) were used throughout this study. The binding energy (BE) scale was referenced to the As 3d₃/₂ substrate peak assigned to 42 eV.² The elastic and inelastic electron scattering backgrounds were removed using a Shirley algorithm.³ Peak deconvolution was performed using multipeak fitting packages included with IGOR PRO (WaveMetrics, Inc., v.6) and custom procedures. Peak assignments were based on the chemical shift (ΔBE) referenced to the In, Ga, and As peaks of the substrate.²,⁴⁻⁸ Results of XPS peak fitting are presented in E.1.

A physical description of the interface was obtained by modeling the surface as a stack of the following homogeneous layers: an As-terminated substrate, a mixed InGaAs interfacial oxide, and an Al₂O₃ film. Since the structure of III-V crystals in the [100] direction consists of alternating group III and group V atomic planes, the intensity of photoelectrons originating from In, Ga, and As atoms of the bulk substrate was expressed as the summation of signals from each In-Ga and As plane.⁹ The exponential attenuation of photoelectron intensities due to thin film overlayers, which in this case consisted of interfacial oxide and Al₂O₃ film, was accounted for using standard equations in literature.¹⁰ A set of nonlinear equations for In 3d₅/₂, Ga 2p₃/₂, and As 2p₃/₂ photoelectron intensities from the substrate and the interfacial oxide, and Al 2p photoelectron intensities from the Al₂O₃ film were generated based on the model. Photoelectron intensities, which is the XPS peak areas, were normalized using empirical atomic sensitivity factors from literature¹¹ and were fed to the model from experimental data.¹¹ Literature values for the photoelectron inelastic mean free paths (IMFP)¹² and oxide densities¹³ were used. The coverage of As on the substrate termination plane, the composition, thickness, and atomic coverages of In, Ga, and
As in the interfacial oxide, and the thickness of Al₂O₃ film were solved for each sample using the fsolve algorithm in Matlab (version 7.8.0.347).

E.2 Results

E.2.1 Solvent cleaned surface

After solvent cleaning, the In₀.₅₃Ga₀.₄₇As(100) surface was covered with a mixed oxide layer consisting of In, Ga, and As (Fig. E.1a). XPS peaks were fit with components at binding energies of 446.8 eV (+1.4 eV) in the In 3d spectrum indicative of In₂O₃, at 1119.7 eV (+1.3 eV) in the Ga 2p₃/₂ spectrum indicative of Ga₂O₃, and at 1328.4 eV (+4.5 eV) and 1327.0 eV (+3.1 eV) in the As 2p₃/₂ spectrum indicative of As₂O₅ and As₂O₃ (E.1). The peak shifts relative to the substrate peaks at 445.4 eV for In, 1118.4 eV for Ga, and 1323.9 eV for As are shown in parentheses. The oxide and substrate binding energies shifts are close to literature values.²,⁴–⁸,¹⁴,¹⁵

From quantitative XPS calculations, the native oxide was 8±1.4 Å thick and contained 21% In, 27% Ga, and 52% As with a 95% margin of error of ±10%. The thickness extracted from XPS was smaller than the 12.7±0.2 Å measured using ellipsometry, likely due to the assumptions of a homogeneous oxide, IMFP, and oxide density in the XPS modelling, as well as the use of Cauchy dispersion relation for the refractive index in the ellipsometry measurements. The oxide composition is consistent with stoichiometric oxidation of the substrate, but a concentration gradient of the oxide constituents across the substrate/oxide and oxide/air interface is expected thermodynamically and kinetically. Based on the quaternary phase diagram,¹⁶ As₂O₃ is thermodynamically unstable in contact with InGaAs substrate and oxide constituents formed in the order of increasing O-content are In₂O₃/Ga₂O₃, As₂O₃, and InAsO₄/GaAsO₄/As₂O₅. The final composition and distribution of the
Table E.1. Binding energy (chemical shift with respect to substrate peaks) in eV of InGaAs chemical states present after a processing step. Binding energies for InGaAs substrate in the In 3d$_{5/2}$, Ga 2p$_{3/2}$, and As 2p$_{3/2}$ regions are 445.4, 1118.4, 1323.9 eV, respectively. Sample labels reflect the sequence of processes done prior to surface analysis, which could consist of surface cleaning (Nox for solvent-cleaned or LHF for liquid phase HF etched), Al$_2$O$_3$ deposition using ALD (Aox), post-dielectric deposition annealing in forming gas (FGA) or NH$_3$, and blanket metal deposition (M). Samples with back-etched label denotes that a 10 nm thick Al$_2$O$_3$ film was deposited onto that sample prior to metal deposition and, or annealing, and the Al$_2$O$_3$ film was thinned down using diluted HF prior to XPS analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>In 3d$_{5/2}$</th>
<th>Ga 2p$_{3/2}$</th>
<th>As 2p$_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In$_2$O$_3$</td>
<td>Ga$_2$O$_3$</td>
<td>As$_2$O$_5$</td>
</tr>
<tr>
<td>Nox</td>
<td>446.8 (+1.4)</td>
<td>1119.7 (+1.3)</td>
<td>1328.4 (+4.5)</td>
</tr>
<tr>
<td>Nox + 1 Al$_2$O$_3$ ALD cycle</td>
<td>446.6 (+1.2)</td>
<td>1119.7 (+1.3)</td>
<td>1328.4 (+4.5)</td>
</tr>
<tr>
<td>NoxAox (20 ALD cycles)</td>
<td>446.6 (+1.2)</td>
<td>1119.7 (+1.3)</td>
<td>1328.2 (+4.3)</td>
</tr>
<tr>
<td>NoxAoxFGA back-etched</td>
<td>446.6 (+1.2)</td>
<td>1119.7 (+1.3)</td>
<td>1327.8 (+3.9)</td>
</tr>
<tr>
<td>NoxAoxNH$_3$ back-etched</td>
<td>446.6 (+1.2)</td>
<td>1119.7 (+1.3)</td>
<td>1328.2 (+4.3)</td>
</tr>
<tr>
<td>LHF</td>
<td>446.8 (+1.4)</td>
<td>1119.8 (+1.4)</td>
<td>-</td>
</tr>
<tr>
<td>LHF + 15 Al$_2$O$_3$ ALD cycles</td>
<td>-</td>
<td>-</td>
<td>1327.0 (+3.1)</td>
</tr>
<tr>
<td>LHFAox back-etched</td>
<td>-</td>
<td>-</td>
<td>1327.6 (+3.7)</td>
</tr>
<tr>
<td>LHFAoxFGA back-etched</td>
<td>-</td>
<td>1119.7 (+1.3)</td>
<td>-</td>
</tr>
<tr>
<td>LHFAoxNH$_3$ back-etched</td>
<td>-</td>
<td>1119.9 (+1.5)</td>
<td>1328 (+4.1)</td>
</tr>
<tr>
<td>LHFAoxMNH$_3$ back-etched</td>
<td>-</td>
<td>1119.6 (+1.2)</td>
<td>-</td>
</tr>
</tbody>
</table>
oxide is also affected by the availability of O to oxidize the In, Ga, and As atoms, which is expected to be highest at the oxide/air interface. In an angle resolved XPS study of the native oxide-covered surface (not shown), Ga$_2$O$_3$ was present at decreasing concentration and As$_2$O$_5$ to As$_2$O$_3$ proportion was increasing from the InGaAs/oxide interface approaching the oxide/O-rich air interface, consistent with the thermodynamic and kinetic arguments. The presence of ternary oxides such as InAsO$_4$ and GaAsO$_4$, where In and Ga are in a $+3$ oxidation state and As is in a $+5$ oxidation state, and hydroxides such as In(OH)$_3$, where In is in a $+3$ oxidation state, are plausible but the similar core level chemical shifts do not allow unambiguous distinction between the ternary and binary oxides and hydroxide. The substrate was stoichiometric, with an In fraction of $0.53 \pm 0.07$ consistent with the supplier specification, and was terminated on the As plane with a coverage of $1.05 \pm 0.5$ monolayer at a 95% margin of error.

InGaAs native oxide was drastically removed by the first ALD cycle of TMA and water. Comparing Fig. E.1a to b, peaks due to Ga$_2$O$_3$ and As$_2$O$_5$ were significantly reduced relative to the bulk substrate peak after the first ALD cycle. The removal of As$_2$O$_5$ was also evident in the decreased peak intensity although to a lesser extent. There was no significant change in the In$_2$O$_3$ peak, other than a 0.2 eV shift to lower BE. Continued ALD cycles of TMA and water only further removed As$_2$O$_5$ and As$_2$O$_3$ as evident in the decreased intensity of these peaks and a 0.2 eV shift to lower BE after 20 ALD cycles (Fig. E.1c and E.1). Signals from In 3d, Ga 2p, and As 2p photoelectrons were attenuated, most pronounced after the 20$^{th}$ cycles (Fig. E.1c), due to the thin Al$_2$O$_3$ film deposited.

The quantitative XPS analysis results showed that InGaAs oxide constituents were not removed stoichiometrically by the ALD process. The ratios of In$^{+3}$, Ga$^{+3}$, As$^{+3}$, and As$^{+5}$ peaks to that of Ga and As in the substrate, which are directly proportional
Figure E.1. In 3d, Ga 2p$_{3/2}$, As 2p$_{3/2}$ core level XPS spectra with the fitted components for In$_{0.53}$Ga$_{0.47}$As(100) samples (a) after solvent cleaning (Nox), (b) after 1 ALD cycle of TMA and water, and (c) after 20 ALD cycles of TMA and water.
to the amount of that particular oxide constituent on the surface, are plotted versus
the number of ALD cycle in Figs. E.2a and b. The first ALD cycle preferentially
removed approximately two thirds of the Ga$_2$O$_3$ and half of the As$_2$O$_5$. The re-
moval of Ga$_2$O$_3$ and As$_2$O$_3$ stopped after one and ten ALD cycles, respectively, while
As$_2$O$_5$ removal continued even after 15 ALD cycles. Although As$_2$O$_5$ was reduced
more drastically in the first ALD cycle compared to As$_2$O$_3$, both were removed at
approximately the same rate afterward. The different stages in removal of the oxide
constituents is consistent with the enrichment of the topmost portion of the oxide
layer with As$_2$O$_5$ and some Ga$_2$O$_3$, which could be in the form of the ternary oxide
GaAsO$_4$, and the distribution of Ga$_2$O$_3$ and As$_2$O$_3$ closer to the interface with the
substrate. Little information can be extracted from the In 3d spectrum since there
was no significant change in the peak area ratio (Fig. E.2a). Based on the inelastic
mean free paths,\textsuperscript{12} In 3d photoelectrons originated from a larger depth than the Ga
2p and As 2p photoelectrons, making it less surface sensitive.

Despite the oxide-ALD precursor reaction, the ALD process did not significantly
affected the InGaAs substrate. As shown in Fig. E.2c, the substrate was terminated
on the As plane with a coverage of 0.7±0.13 monolayer which is within the margin
error of that in the solvent cleaned surface. The fraction of In in the substrate
(In$_x$Ga$_{1-x}$As) was slightly reduced to 0.44±0.03 and 0.42±0.03 after the first and
twentieth ALD cycle (Fig. E.2c).

With the removal of InGaAs oxide, Al$_2$O$_3$ was grown on the surface. The total
thickness of the interfacial layer consisting of substrate oxides decreased by about 1.5
Å, on average, and there was a concomitant growth of about 3 Å of Al$_2$O$_3$ on top
of the interfacial layer after the first ALD cycle (Figure E.2d). The interfacial layer
thickness leveled out at 4±0.8 Å after the 10\textsuperscript{th} ALD cycle, after which the Al$_2$O$_3$
growth was linear at a rate of 1±0.2 Å per cycle. A 18.7±3.4 Å thick Al$_2$O$_3$ film was
deposited at the end of the 20\textsuperscript{th} ALD cycles.

The drastically improved electrical performance of InGaAs/Al\textsubscript{2}O\textsubscript{3} interface after post dielectric deposition annealing in forming gas and NH\textsubscript{3} led to investigation of the effect of annealing on interface composition.\textsuperscript{1} After the deposition of 10 nm-thick Al\textsubscript{2}O\textsubscript{3} film on a solvent cleaned InGaAs surface, samples were annealed in either forming gas or ammonia and the Al\textsubscript{2}O\textsubscript{3} film was thinned down to <3 nm for XPS analysis. Shown together with the nonannealed spectrum as a reference (Fig. E.3a), annealing in forming gas (Fig. E.3b) and NH\textsubscript{3} (Fig. E.3c) produced qualitatively similar changes in the interfacial layer composition. The Ga\textsubscript{2}O\textsubscript{3} peak at 1119.7 eV (\(\Delta BE=1.3\) eV) significantly increased for both anneals. Peaks due to As\textsubscript{2}O\textsubscript{5} at 1327.8 eV (\(\Delta BE=3.9\) eV) for FGA annealed and at 1328.2 eV (\(\Delta BE=4.2\) eV) for NH\textsubscript{3} annealed surfaces were increased. The As\textsubscript{2}O\textsubscript{5} to As substrate peak area ratio increased from 0.20±0.07 to 0.46 and 0.31 after FGA and NH\textsubscript{3} anneals, respectively. Peaks due to As\textsubscript{2}O\textsubscript{3} at 1326.4 eV (\(\Delta BE=2.6\) eV) for forming gas annealed was constant and at 1326.8 (\(\Delta BE=3\) eV) for NH\textsubscript{3} annealed surface was slightly decreased, as evident by the decreased peak area ratio for As\textsubscript{2}O\textsubscript{3} to As substrate from 0.45±0.21 to 0.20 after NH\textsubscript{3} anneal. The As\textsubscript{2}O\textsubscript{5} and As\textsubscript{2}O\textsubscript{3} peaks in the forming gas annealed sample were shifted 0.4 eV to lower BE compared to the reference (NoxAox). Photoelectron signals from nitrogen were absent from the NH\textsubscript{3} annealed sample (data not shown).

Based on the XPS peak areas and results of modelling the surface, the interfacial layer after FGA was 4.2 Å thick, consisting of 9\% In oxide, 56\% Ga oxide, and 35\% As oxide, and the substrate was terminated by 0.8 monolayer of As and had an In fraction of 0.44. The interfacial layer after NH\textsubscript{3} annealing was 5.3 Å thick, consisting of 6\% In oxide, 40\% Ga oxide, and 54\% As oxide, and the substrate was terminated by 1.3 monolayers of As and had an In fraction of 0.44. The thicker interfacial oxide and higher As content in the interfacial oxide of the NoxAoxNH\textsubscript{3} sample compared to
Figure E.2. Quantitative XPS analysis for In$_{0.53}$Ga$_{0.47}$As(100) samples after solvent cleaned and exposed to 1 to 20 cycles of ALD Al$_2$O$_3$ showing (a) XPS peak area ratios between Ga$_2$O$_3$ (□) and In$_2$O$_3$ (∇) to the Ga and In peak of the substrate, (b) XPS peak area ratios between As$_2$O$_3$ (♦) and As$_2$O$_5$ (◊) peaks to As peak of the substrate, (c) the fraction of In in the substrate (△) and the coverage of As terminating the substrate(▲) in monolayer (ML), and (d) interfacial layer thickness (◦) and Al$_2$O$_3$ thickness (■) in Å. In (d) a linear regression of Al$_2$O$_3$ thickness versus number of ALD cycles above 10 cycles revealed a slope of 1±0.2 Å/cycle. Other lines in graphs are only to guide eye.
In 3d$_{5/2}$, Ga 2p$_{3/2}$, As 2p$_{3/2}$ core level XPS spectra with the fitted components for an In$_{0.53}$Ga$_{0.47}$As(100) sample after (a) solvent cleaning and exposed to 15 cycles of ALD Al$_2$O$_3$ (NoxAox), and for samples processed similarly as in (a) but with a 10 nm thick Al$_2$O$_3$ followed by annealing in (b) forming gas (NoxAoxFGA) and (c) NH$_3$ (NoxAoxNH$_3$). Spectra (b) and (c) were acquired after thinning the ∼10 nm-thick Al$_2$O$_3$ film to 14 and 19 Å using a 1:1000 HF:H$_2$O solution.

The NoxAoxFGA sample could be due to oxidation of the interface after back-etching the Al$_2$O$_3$ film. Only approximately 14 Å of Al$_2$O$_3$ was left on the surface after back-etching the NoxAoxNH$_3$ sample, compared to the ∼19 Å thick Al$_2$O$_3$ film on the NoxAoxFGA back-etched sample.

E.2.2 Liquid phase HF etched surface

Liquid HF immersion of the native oxide removed all of the As$_2$O$_5$ and most of the In$_2$O$_3$ and Ga$_2$O$_3$ as shown by the XPS spectra in Fig. E.4a. The As$_2$O$_3$ present on the surface at 1326.9 eV ($\Delta$BE = 3.0 eV) in the As 2p$_{3/2}$ spectrum was most
likely the result of the re-oxidation of the elemental As layer due to air exposure after aqueous HF etching. Based on the XPS modeling and peak fitting, a $4.3 \pm 1.5$ Å thick overlayer was present containing $91 \pm 7\%$ As in a $+3$ oxidation state on top of $1.5 \pm 0.1$ monolayers of As on the substrate. The In fraction in the substrate was $0.44 \pm 0.1$, which was lower but within the 95% margin of error of the solvent-cleaned surface.

The deposition of Al$_2$O$_3$ by 15 ALD cycles of TMA and water completely removed the interfacial In$_2$O$_3$ and Ga$_2$O$_3$ and reduced the As$_2$O$_3$ close to the noise level as shown by the in situ XPS spectra in Fig. E.4b. Relatively small XPS peaks belonging to As$_2$O$_3$ at 1327 eV and As sub-oxide at 1325.4 eV binding energies were still present. The interfacial oxide after 15 ALD cycles was only $1 \pm 0.3$ Å thick, and the InGaAs substrate was terminated by $1 \pm 0.1$ monolayer of As with an In fraction of $0.44 \pm 0.05$. The Al$_2$O$_3$ film was $18.7 \pm 1.2$ Å thick, which was comparable to the Al$_2$O$_3$ film grown by 20 ALD cycles on the solvent-cleaned sample (NoxAox).

In order to assess the effect of thinning the Al$_2$O$_3$ in dilute HF and air exposure between the etching and XPS scan, an additional $\sim 85$ Å of Al$_2$O$_3$ was deposited after the XPS scan in Fig. E.4b and the $\sim 10$ nm-thick Al$_2$O$_3$ film was back-etched to approximately 17 Å. Oxidation of the interfacial oxide was evident in Fig. E.4c. The As$_2$O$_3$ peak, which was originally at 1327 eV, shifted 0.6 eV to higher BE giving a chemical shift of $\Delta$BE$=+3.7$ eV, which is between that expected for As$_2$O$_5$ and As$_2$O$_3$. The interfacial oxide thickness increased slightly to $\sim 1.8$ Å, but the substrate termination and In fraction were essentially constant.

Modulation of interfacial oxide composition was also found after the same Al$_2$O$_3$ deposition, annealing, and back-etching procedure performed on liquid phase HF prepared InGaAs (Fig. E.4d-e). The interfacial layer, which initially consisted of As$_2$O$_3$ and As sub-oxides (Fig. E.4b), consisted of Ga oxide after the forming gas anneal. This is evident in the presence of a Ga$_2$O$_3$ peak at 1119.7 eV ($\Delta$BE$ = +1.3$
Figure E.4. In 3d, Ga 2p$_{3/2}$, As 2p$_{3/2}$ core level XPS spectra with the fitted components for In$_{0.53}$Ga$_{0.47}$As(100) samples (a) after solvent cleaning and etching in 49% HF (LHF), followed by (b) 15 cycles of ALD Al$_2$O$_3$, (c) sample (b) with additional 85 cycles of ALD to deposit 10 nm-thick Al$_2$O$_3$ (LHF Aox), (d) deposition of 10 nm-thick Al$_2$O$_3$ and annealing in forming gas (LHF AoxFGA), (e) deposition of 10 nm-thick Al$_2$O$_3$ and annealing in NH$_3$ (LHF AoxNH$_3$), and (f) deposition of 10 nm-thick Al$_2$O$_3$, 15 nm-thick Ni and 20 nm-thick Au blanket, and annealing in NH$_3$ (LHF AoxMNH$_3$). Spectra (c) thru (e) were acquired after thinning the $\sim$10 nm Al$_2$O$_3$ film to $\sim$2.5 nm using a procedure described in the experimental section. Spectra (f) was acquired after etching the Ni/Au blanket film and thinning the Al$_2$O$_3$ film using procedures described in the experimental section. The y-axis scale for the Ga 2p$_{3/2}$ and As 2p$_{3/2}$ spectra of liquid phase HF etched sample (a) are 0.4 and 0.2 times the y-axis scale of other samples.
eV) and the absence of the As oxides peaks in Fig. E.4d. For the NH$_3$ annealed sample, interfacial layer consisted of both Ga and As oxides. Interfacial Ga$_2$O$_3$ was evident by an XPS peak at 1119.9 eV ($\Delta$BE = +1.5 eV, Fig. E.4e). As oxides peaks were found at 0.8 eV higher binding energies compared to the unannealed sample. The higher oxidation state As was at 1328 eV, which chemical shift ($\Delta$BE=+3.9) is between that of As$_2$O$_5$ and As$_2$O$_3$, and the lower oxidation state As was at 1326.2 eV, which chemical shift ($\Delta$ BE = +2.3) is lower than that of As$_2$O$_3$. Photoelectron signals from nitrogen was absent from the NH$_3$ annealed sample (data not shown).

From the quantitative XPS analysis result, the interfacial layer thickness was reduced to $\sim$0.4 Å and the substrate was terminated by 1.3 monolayer of As and had an In fraction of 0.44 after FGA. The interfacial layer after NH$_3$ was $\sim$1.6 Å and the substrate was terminated with 1.4 monolayer of As and has an In fraction of 0.47. The interfaces remained essentially oxide-free after reactive annealing and compare closely with the interfaces formed in the initial stage ($\leq$15 cycles) of Al$_2$O$_3$ film growth.

Motivated by a contrasting electrical performance of capacitor stacks when post dielectric deposition annealing was performed before or after metal electrode deposition, XPS analysis was conducted on one sample in which NH$_3$ annealing was performed after liquid phase HF, deposition of 10 nm thick Al$_2$O$_3$ film, and deposition of Ni(15 nm)/Au(20 nm) blanket film (LHFAoxMNH$_3$). Prior to the XPS analysis, the blanket Ni/Au film was removed and the 10 nm Al$_2$O$_3$ film was thinned down using procedures described in the experimental section. The result shown in Fig. E.4f revealed that the InGaAs/Al$_2$O$_3$ interface consisted of Ga$_2$O$_3$, As$_2$O$_3$, and As sub-oxides. While the interfacial oxide was slightly thicker ($\sim$2.1 Å), the substrate was essentially the same as that on the sample annealed without metal blanket as it was terminated by one monolayer of As and had an In fraction of 0.47.
Figure E.5. In 3d$_{5/2}$, Ga 2p$_{3/2}$, As 2p$_{3/2}$ core level XPS spectra with the fitted components for an In$_{0.53}$Ga$_{0.47}$As(100) sample after (a) solvent cleaning, etched in 49% HF, and exposed to 15 cycles of ALD Al$_2$O$_3$ (LHFAox), and for samples processed similarly as in (a) but with a 10 nm-thick Al$_2$O$_3$ followed by annealing in (b) forming gas (NoxAoxFGA) and (c) NH$_3$ (NoxAoxNH$_3$). Spectra (b) and (c) were acquired after thinning the ∼10 nm Al$_2$O$_3$ film to ∼2.5 nm using a 1:1000 HF:H$_2$O solution.
E.2.3 Correlating chemical and electrical characterization

In Fig. E.6, the compositions of the interfacial layer between the substrate and the Al₂O₃ film were extracted from quantitative XPS peak fits and are plotted as a function of the surface recombination velocity (SRV) measured on capacitor devices reported in a separate publication.¹ In parts a and b, the Al₂O₃ was deposited on native oxide and in parts c and d the Al₂O₃ was deposited after aqueous HF etching. The atomic coverages shown on the vertical axes do not correspond to surface atomic density since it was obtained by multiplying the atomic density of the various oxide constituents to the overall thickness of the interfacial oxide instead of multiplying it with an assumed thickness of a monolayer. The atomic coverages are means to directly compare how much of each oxide constituents was present at the interfaces of different samples. The SRV values shown on the horizontal axes were obtained from a separate set of samples where both a 10 nm Al₂O₃ film was deposited and the surfaces were patterned with metal electrodes to make devices. In contrast to XPS data in which forming gas and NH₃ annealing was performed on InGaAs/Al₂O₃ stack without depositing metal gate (except for LHFAOxMNH₃), the SRV values for annealed sample corresponds to annealing samples after metal gate deposition. This was justified by the essentially same interface obtained on LHFAoxNH₃ and LHFAoxMNH₃. Each SRV value is an average calculated from measurements done on 3 capacitor devices with error bars denotes the 95% margin of error. The XPS data shown for NoxAox and LHF Aox are averaged from two samples and the error bars represent one standard deviation. For both the solvent cleaned and liquid phase HF prepared surfaces, the SRV values decreased drastically from 30-40 cm/s before annealing to less than 5 cm/s after annealing. The forming gas anneal had a more pronounced effect on the native oxide surface, reducing the SRV from 34.4±3.7 cm/s
to 1±0.3 cm/s, whereas the NH₃ anneal had the largest effect on the HF-cleaned surface, reducing the SRV from 28.9±13.4 cm/s to ~1.5 cm/s. The SRV decreased with increasing Ga₂O₃ (Fig. E.6a and c) although the magnitude of change was significantly higher in the solvent cleaned surface. In addition, the SRV was reduced despite the presence of a ~1 ML As layer terminating the surface and despite the slight increased in the As coverages after annealing (Fig. E.6b and d). The substrate stoichiometry remained constant for both native oxide and liquid HF-cleaned surfaces after annealing in either gas.

E.2.4 Acknowledgement

Funding for this project was provided by Intel Corp. The authors thank Dr. Willy Rachmady for fruitful discussions.
FIGURE E.6. XPS composition analysis plotted against surface recombination velocity (SRV in cm s$^{-1}$) for solvent cleaned prepared samples, (a) and (b), and liquid phase HF etched samples, (c) and (d), showing interfacial layer coverages of In in In$_2$O$_3$ state ($\triangledown$), Ga in Ga$_2$O$_3$ state ($\square$), and As in oxide states ($\bullet$), the fraction of In in the sub surface InGaAs ($\triangle$), and the coverage of As layer terminating the substrate ($\blacktriangle$) in monolayer (ML).
REFERENCES


APPENDIX F

EFFECT OF DEEP-LEVEL DEFECTS ON SURFACE RECOMBINATION VELOCITY AT THE INTERFACE BETWEEN SILICON AND DIELECTRIC FILMS

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Effect of Deep-Level Defects on Surface Recombination Velocity at the Interface Between Silicon and Dielectric Films

Babak Imangholi, Fee Li Lie, Harold G. Parks, Senior Member, IEEE, and Anthony J. Muscat

Abstract—The surface recombination velocity (SRV) characteristic of deep-level defects at Si interfaces with dielectric thin films was obtained from conductance measurements on metal–insulator–semiconductor capacitor (MISCAP) devices. The dielectrics in contact with Si were thermal SiO₂ (Tox), chemical SiO₂, and atomic layer deposition (ALD) Al₂O₃, which were annealed and exposed to a low flux of X-rays. A modified conductance technique was developed in which a large ac signal was superimposed on a dc bias and the surface potential was swept across the band gap of a MISCAP from near accumulation to deep depletion. The frequency-dependent energy loss due to all defects across the band gap and their correlations were measured using the effective equivalent conductance. A model containing one resistor and one capacitor was sufficient to describe the frequency-dependent energy losses due to defects with similar activities. The total SRV was 112 ± 19 cm/s for Si/Tox, 1045 ± 150 cm/s for Si/Chemical SiO₂/ALD-Al₂O₃, and 578 ± 96 cm/s for Si/ALD-Al₂O₃ interfaces. After forming gas annealing at 400 °C, the SRV decreased to ~1 cm/s for both Si/Tox and Si/Chemical SiO₂/ALD-Al₂O₃ and 47 ± 6 cm/s for Si/ALD-Al₂O₃. Vacuum annealing improved the Si/Chemical SiO₂/ALD-Al₂O₃ interface but had an adverse effect on Si/ALD-Al₂O₃. Soft X-ray exposure increased the SRV of both Si/Chemical SiO₂/ALD-Al₂O₃ and Si/ALD-Al₂O₃.

Index Terms—Defect, interface, metal–insulator–semiconductor capacitor (MISCAP) device, surface recombination velocity (SRV).

I. INTRODUCTION

DEFECTS at the interface between a dielectric layer and a semiconductor are often caused by structural imperfections when two dissimilar materials are bonded together. The energy states of defects, including vacancies and interstitials, strongly influence the performance of semiconductor devices. States below and above the charge neutrality level [1] modify the surface potential and pin the Fermi level at a different energy than that defined by the bulk semiconductor, affecting device biasing [2], [3]. Moreover, defect states above the Fermi level allow electron–hole (e–h) carriers to recombine nonradially generating heat [4]–[7] and drawing current [2]. The impact of these processes depends on both the density and the activity of interface states [1]–[3], [8].

In the case of Fermi level pinning, a trap density of $N_{tr} = 10^{12}$ cm$^{-2}$ [9] generates an electrical field $\xi = \left(\frac{eN_{tr}}{2e}\right) \approx 10^{9}$ V/cm at a Si/SiO₂ interface based on the permittivity $\varepsilon$ of Si, assuming that all of the traps are charged. If the Si is lightly doped to a concentration of $\sim 10^{14}$–$10^{16}$ cm$^{-3}$, this field results in a depletion region thickness $w \sim 100$ nm [9]. The band bending associated with these charged defects is expected to be $\Delta \Phi = \xi w \sim 1$ eV, which is about the Si band gap energy. In practice, band bending at Si/SiO₂ interfaces is much smaller [9] since only a fraction of the defects are charged. This indicates that the trap or defect density incompletely characterizes a semiconductor interface and that other parameters, such as the capture cross-section and activation energy, are typically needed to describe the extent of Fermi level pinning [1] and the magnitude of the nonradiative recombination coefficient [4]–[7], [10]. Surface recombination velocity (SRV), denoted by $S$ (in centimeters per second), is a measure of defect activity at an interface independent of the doping density and material thickness [4]–[7], [10]–[13]. The coefficient $S$ quantifies how defects contribute to the capture and emission processes of e–h carriers from conduction and valence bands [14], [15] and how strongly these defects are correlated [16]. Characterization of $S$ at an interface is consequently a more representative measure of interface quality than relying only on the trap density.

At a semiconductor interface, $S$ is determined by measuring the nonradiative recombination rate of e–h carriers through the trap centers [4]–[7], [10]. Following Schroder [11], $S = \nu_{th}N_{tr}\sigma_{tr}$ for a defect with one midgap energy state (parameter definitions are included in Appendix A). The capture cross section can be expressed as $\sigma_{tr} = \sigma_{tr}e^{-E_{c}/kT}$, where $\sigma_{tr}$ is the capture cross-section at infinite temperature, and $E_{c}$ is the activation energy of the trap. Thus, the SRV becomes $S = \nu_{th}N_{tr}\sigma_{tr}e^{-E_{c}/kT}$. Details of the positions of traps in the band gap and the amount of energy transferred to lattice vibrations (phonons) as heat are embedded in $\sigma_{tr}$ and $E_{c}$ [11], [13]. At interfaces containing defects with multiple energy levels, the total SRV, $S_{tot}$, is not simply a superposition of $S$ from individual states because defect states can be correlated. Correlations account for filling and emptying of one trap energy level by other traps [16]. This strongly impacts the performance of interfaces with the same number of defects, but having different capture cross-sections and activation...
energies. Defect correlations are complicated processes, and a detailed discussion of them can be found in the classic paper by Sah and Shockley [16]. Although S values of individual traps are not comparable, the net effect of defect correlations manifests itself in changes in the nonradiative lifetime of e–h carriers \( \tau \) and, consequently, in \( S_{\text{total}} \) [16], since \( \tau = d/S_{\text{total}} \), where \( d \) is the active sample or confinement thickness [5]–[7]. Values of \( S_{\text{total}} \) can be compared for different interfaces.

Since the operation of a device influences the value of \( S_{\text{total}} \) [11], high e–h carrier densities and changes in surface potential are important considerations. In devices with high e–h carrier densities, quasi-Fermi levels are used to define the excess carriers generated in the conduction and valence bands [2]. In this case, the semiconductor is no longer in thermal equilibrium, and defects located below the Fermi level at steady-state are active and contribute to \( S_{\text{total}} \) [17]. \( S_{\text{total}} \) varies as well when the surface potential is changed by an external voltage, as in the operation of a CMOS device [2]. The external voltage moves energy bands toward or away from the Fermi level, activating or deactivating defects distributed across the band gap [11], [18]. The dynamics of a device are consequently important in measuring and understanding \( S_{\text{total}} \). There are various techniques for characterizing interface traps to determine SRV [11]. The most commonly used methods are time-resolved photoluminescence decay (TRPLD), capacitance–voltage (C–V) curves, charge pumping, and deep-level transient spectroscopy (DLTS) [11]. Short overviews of these techniques are discussed here.

TRPLD is a sensitive technique that allows straightforward measurement of \( S_{\text{total}} \) for direct band gap semiconductors [4]–[7]. For indirect and short band gap semiconductors, radio frequency photoconductive decay (RFPCD) is an alternative [10], [19]. In both techniques, when the initial nonlinear radiative and Auger recombination responses have fully relaxed (low e–h carrier densities), the decay lifetime is related to \( S_{\text{total}} \). In both TRPLD and RFPCD, the Fermi level position and the semiconductor band edge profile are not affected by low e–h carrier densities [20]. Measurement of \( S_{\text{total}} \) includes only the activity and correlation of defects located above the Fermi level. Moreover, the presence of a net charge at an interface [21], [22] or an applied external potential [18] can bend the bands toward or away from the Fermi level, repelling one type of carrier away from the interface and drastically reducing the SRV [10]. This introduces ambiguities into the measurement of \( S_{\text{total}} \) due to external effects.

Low- and high-frequency capacitance–voltage (C–V) measurements are used routinely to characterize dielectric–semiconductor interface traps. In the C–V technique, the capacitance change is measured as the voltage is swept from accumulation to depletion and back [11]. C–V curves are typically analyzed using the Terman method to extract the interface trap density, fixed oxide charge, and substrate doping concentration, among other parameters. A C–V measurement alone cannot be used to monitor the dynamics of carriers and, consequently, the capture cross-section of defects and \( S \).

Furthermore, thinning a gate oxide to scale a device increases the gate insulator capacitance, rendering the high frequency Terman method almost insensitive to voltage shifts that are inversely proportional to insulator capacitance [11].

Charge pumping [11] and deep-level transient spectroscopy (DLTS) [11]–[13], [23] are well-established techniques for measuring defect density and capture cross-section, hence \( S \). Charge pumping, however, requires the fabrication of a complete MOSFET device [11], [24], [25]. Furthermore, in MOS-DLTS characterization, the experimental setup is very demanding in cases where capacitance changes must be measured for short relaxation times (\( < 1 \mu s \)), either due to a high doping density or to the presence of interface traps with large capture cross-sections [11]–[13], [23]. Furthermore, leakage current affects MOS capacitance values, which adds to the complexity of analyzing data for thin gate oxides.

Conductance is one of the most practical and sensitive characterization techniques, and the measurement and analysis of the data are straightforward [9], [11]. A conductance technique has been used to characterize defect density and capture cross-section in leaky gates as thin as 1.5 nm [26]–[28]. The advantages and limitations of conductance measurements in metal–insulator–semiconductor capacitor (MISCAP) devices with tunneling gate dielectrics are discussed in detail in [26].

In this paper, we report measurements of the deep level SRV using an unconventional conductance technique that employs a large ac signal swept across the band gap to probe defect activity. The measured \( S_{\text{total}} \) is independent of Fermi level pinning, surface charges, metal–semiconductor work function difference, and external surface potential. The deep-level characterization of \( S_{\text{total}} \) allows unambiguous comparison of different dielectric–semiconductor interfaces prepared by a variety of methods and deposition techniques. This paper is organized as follows. Section 2 describes the large ac signal conductance technique. Section 3 details the chemical process flow and fabrication of MISCAP devices. Section 4 presents results and discussion. Section 5 concludes and discusses future work.

II. LARGE AC SIGNAL CONDUCTANCE TECHNIQUE

Using conductance to measure the density of traps and the capture cross-section was first proposed by Nicollian and Goetzberger in 1967 [29]. They showed that the capture and emission of majority carriers by traps is a lossy process and can be modeled by a resistor \( R_t \) and a capacitor \( C_t \) for single-level traps in a MISCAP device [Fig. 1(a)]. The capacitance \( C_t \) represents the capability of a trap to hold an electron or hole for some time after capturing it. In practice, the trap conductance \( G_f(\omega) \) is measured as a loss of energy versus frequency \( f \) by superimposing a small ac signal on a dc bias and filling and emptying traps [11]. The measured conductance is modeled to extract parameters of traps [Fig. 1(b)]. Following Schroeder [11], the normalized conductance to gate area of a MISCAP \( G_f(\omega)/\omega \) (F cm\(^{-2}\)) for interface defects with a single-level midgap energy and no fluctuation in surface potential is

\[
G_f(\omega)/\omega = \frac{\varepsilon_0\varepsilon_f D_t}{1 + \left(\omega\tau_6\right)^2}
\]

where \( D_t = e^2C_t \) is the trap density, \( \omega = 2\pi f \), and \( \tau_6 = R_tC_t \) is the time constant of the trap. The maximum \( G_f(\omega)/\omega \) occurs at \( \omega = 1/\tau_6 \). The defect density is extracted from the peak maximum as
Fig. 1. MISCAP device equivalent circuits [11, 20]. (a) MISCAP with no substrate resistance and oxide leakage. (b) Simplified circuit of (a). (c) MISCAP device with series resistance \( r_p \) and oxide leakage conductance \( G_{ox} \). (d) Simplified circuit of (c). Parameter definitions are included in Appendix A.

\[ D_n = 2G_p(\omega_{\text{max}})/\omega_{\text{max}}. \]

The SRV of traps with energy \( E_{\text{th}} \) measured with respect to the intrinsic Fermi level \( (E_F) \) of the semiconductor is

\[ S_{\text{SRV}} = \frac{D_n}{\tau_n N_d} = D_n \tau_n k_\text{B} E_{\text{th}} e^{-E_{\text{th}}/k_\text{B} T}. \]

Expressing the temperature dependence of the capture cross-section explicitly, the single energy SRV becomes

\[ S_{\text{SRV}} = D_n \tau_n k_\text{B} \sigma_{\text{int}} e^{-\frac{E_{\text{th}}}{k_\text{B} T}}. \]

where \( \sigma_{\text{int}} \) is the capture cross-section at infinite temperature, and \( E_{\text{th}} \) is the activation energy of the traps [11].

Defect states in a semiconductor are correlated, and this affects how the surface recombination velocities of traps combine at specific energy levels given by (3) to obtain the total. The number and duration of intermediate stops at trap states that an electron makes when traversing from the conduction band to the valence band depend on the cross-sections and activation energies of individual states, as well as on the populations and Coulomb interactions of the defects treated as a whole. The total SRV includes all of these effects and depends not only on the activity, but also on the occupancy of defect states. In short, the total SRV depends on the way that a device is operated. For example, the \( S_{\text{SRV}} \) values determined by the small ac signal conductance method across the band gap cannot be linearly combined to obtain the total SRV because each energy level is only interrogated locally, making it insensitive to correlations among defects. Fig. 2(a) depicts a 1-D energy level diagram at a dielectric–semiconductor interface containing three defect states. With small ac signal conductance, each interface trap is probed individually, as shown for state 2, by pinning the Fermi level at the energy of the trap and sweeping the voltage within \( \pm k_\text{B} T \) of \( E_{\text{th}} \) to fill and empty the state.

Large ac signal conductance probes all defect energy states simultaneously as they fill and empty, including correlations. The SRV is representative of a device during operation since the density of defect states is convoluted with the activity or cross-section of these states and their correlations. Information on the number of defects and the activity at a particular energy level are inaccessible, but all of the processes that produce cooperative behavior are included. This is accomplished by applying a dc bias to pin the Fermi level in the middle of the band gap, \( E_{\text{FB}} \), and superimposing a large ac signal with amplitude \( \pm (E_{\text{FB}}/2e) \), which sweeps the surface potential from accumulation to deep depletion, as shown in Fig. 2(b) and (d).

Using large ac signal conductance, the filling and emptying processes for each interface trap depend on the occupancy of other traps. The complicated equivalent circuit shown in Fig. 2(c) is simplified in Fig. 2(f) to include only one effective \( R_{\text{tr}} \), and one \( C_{\text{tr}} \) to model each group of correlated defects. An interface may have several groups of correlated defects. As shown in Fig. 2(c) and (d), applying a large ac signal simultaneously exposes all defects to the majority carriers. Consequently, filling and emptying a trap energy level is influenced by the occupancy of other filled and empty traps located within the band gap [16]. This process is phenomenologically equivalent to an ideal TRPLD and RFPACD measurement where the Fermi level is unpinned and close to the valence band so that all defects are active. In this case, the decay of carriers in the low-density regime accurately represents the SRV of all defects across the band gap [16]. In practice, such an ideal time-resolved decay measurement is not easy to achieve because of
charges near the interface that bend the bands [10], [21]. The large ac signal conductance method overcomes this obstacle by manipulating the surface potential and measuring losses across the band gap in frequency space.

Although the large ac signal conductance method probes the bulk semiconductor within the depletion depth, interface traps dominate bulk traps in high-quality substrates and in devices with a high surface-to-probe-depth ratio [4]-[7]. Devices can consequently be treated as 1-D structures with a conductance that is only related to interface traps.

The effective values $R_{te}$ and $C_{te}$ describe only the activity of defects that are correlated and that have similar time constants. As a result, the conductance peak versus frequency is described by (1) using effective $R_{te}$ and $C_{te}$ for correlated defects with similar time constants. Therefore, the SRV of correlated traps with comparable activities is

$$S_{te} = D_{te} \sigma_{te} / N_{d} = D_{te} v_{th} \sigma_{te} e^{-E_{g}/kT}$$

(4)

where $\sigma_{te}$ and $E_{g}$ are the effective capture cross-section and the effective position of the correlated defects with similar activities. The capture cross-section $\sigma_{te}$ does not necessarily represent individual cross-sections with similar time constants since it includes the probability of the capture and emission of e-h carriers from correlated traps. The SRV in conventional units of velocity is determined by integrating the defect density across the band gap. The total defect density is

$$\int_{E_g}^{E_F} N_{d} dE = D_{te} v_{th} 2E_i \approx D_{te} v_{th}$$

(5)

where the band gap energy is $E_g \approx 2E_i$. Hence, the total SRV is

$$S = E_g D_{te} v_{th} \sigma_{te} e^{-E_{g}/kT} = N_{d} v_{th} \sigma_{te} e^{-E_{g}/kT} = N_{d} v_{th} \sigma_{te} e^{-E_{g}/kT}$$

(6)

where $\sigma_{te}$ is the effective capture cross-section at infinite temperature, and $E_{g}$ is the effective activation energy of correlated defects.

The large ac signal conductance $G_p(\omega)/\omega$ versus $\omega$ based on an impendence $R(\omega) + iX(\omega) = R + iX$ across the MISCAP circuit in Fig. 1(d) is given in (7), shown at the bottom of the page, where $G_L = \int_{-\infty}^{+\infty} G_L(w) dw + \int_{-\infty}^{+\infty} G_L(w) dw$ is the leakage conductance averaged over the ac voltage sweep. In a MISCAP device with no defects, $R(\omega) = r_s + G_0/(G_L^2 + C_m^2 \omega^2)$ and $X(\omega) = -C_m \omega/(G_L^2 + C_m^2 \omega^2)$, where $C_m$ is the equivalent capacitance of $C_{ox}$ and $C_0$ in series. In this case, $G_L$ is zero, as expected. The semiconductor capacitance $C_0$ in Fig. 2(e) and (f) is a function of the ac signal frequency and amplitude. $C_0$ is fixed and reproducible for a sample; also, it does not contribute to frequency-dependent energy losses, allowing a straightforward separation and determination of conductance $G_p(\omega)/\omega$ versus $\omega$ in a MISCAP device. Each peak that appears in $G_p(\omega)/\omega$ versus $\omega$ represents a group of correlated defects with comparable activities or time constants. Deconvoluting the conductance data into individual peaks using effective $R_{te}$ and $C_{te}$ values yields the corresponding surface recombination velocities. The total SRV, $S_{total}$, is found by linearly combining the individual surface recombination velocities from each peak.

The limitations of characterizing traps using the large ac conductance method are similar to small ac conductance [9], [11]. For thick oxide films, the magnitude of the dc bias and the amplitude of the ac signal are irrelevant as long as the band gap is swept from deep depletion to near accumulation since the Fermi level cannot be pinned above the conduction or below the valence band. For thin oxides, the dc bias and the amplitude of the ac signal are critical due to leakage and breakdown of the dielectric [9], [11], [26]. The best approach is to pin the Fermi level of a MISCAP device near the midgap and apply the minimum ac amplitude required to sweep the Fermi energy from the conduction to the valence band and vice versa. An initial C–V measurement defines the gate voltages corresponding to accumulation and deep depletion [9], [11], and the dc bias and ac amplitude are set at half of the difference. This way, defects can be investigated across the band gap. However, the amplitudes of the dc bias and the ac signal can be adjusted to measure SRV at a device interface, where the range of active defects is limited by the device operation.

$$G_p(\omega) = \frac{C_0^2 \omega \left( 1 - G_L (R - r_s) (R - r_s) + G_L X \right)}{\left( 1 - 2G_L (R - r_s) + G_L^2 \left( (R - r_s) X + X^2 \right) + C_m^2 \omega^2 \left( C_m (R - r_s)^2 \omega^2 + X (2 + C_m X) \right) \right)}$$

(7)
MISCAP devices were fabricated on Si(100) using different preparation steps and two dielectric films [Fig. 3(c)–(e)]. C–V curves were measured following the procedure described by Norton [30] [Fig. 3(b)], yielding the doping density $N_d$ and the oxide capacitance $C_{ox}$. The leakage conductance $G_l$ was obtained by $I–V$ measurements in dc mode, as suggested by Vogel et al. [26]. Both the C–V curves and the large ac signal conductance were determined by measuring the real and imaginary parts of the impedance across the MISCAP devices and fitting to the equivalent circuits shown in Figs. 3(b) and 1(d), respectively.

III. DEVICE FABRICATION AND EXPERIMENTAL SETUP

MISCAP devices containing SiO2 and Al2O3 dielectric layers were fabricated on Si(100) substrates (Sumitomo Corporation, p-type, $10^{18}$ cm$^{-3}$). The sample preparation, dielectric, and annealing process choices are summarized in Table I. All samples were initially prepared by immersing in piranha solution containing 3:1 v/v H2SO4 (98%, General Chemical); H2O2 (28%, General Chemical) for 5 min, rinsing with ultrapure water (18 MΩ) for 5 s, immersing in 49% hydrofluoric acid (HF) (Ashland chemical) for 1 min, and blow drying with ultrapure N2. Thermal SiO2 layers approximately 100 nm thick were grown at 950 °C in a furnace using water vapor. Chemical SiO2 layers that were 1.5–2.5 nm thick were grown by immersing samples in piranha for 5 min, rinsing with ultrapure water for 5 s, and blow drying with ultrapure N2.

<p>| Table 1: MISCAP Surface Preparation and Dielectric Film Processing and Analysis Stepsa |</p>
<table>
<thead>
<tr>
<th>Sample</th>
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<th>HF</th>
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<th>Second Dielectric</th>
<th>Anneal</th>
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aThe abbreviations are Tox (thermal SiO2), Cox (chemical SiO2 grown by piranha last), Aox (aluminum oxide Al2O3 deposited by ALD), FGA (forming gas annealing), VA (vacuum annealing), X (XPS analysis), p (piranha), and h (HF). Processing details are given in the text.

Both the gate and runway of the MISCAP devices were fabricated on top of the dielectric film, as shown in Fig. 3(a). Each MISCAP structure contained eight gates around the perimeter of a runway or base with a much larger surface area. Two
different gates with areas of 0.034 and 0.075 mm$^2$ and a runway with an area of $\sim64$ mm$^2$ were fabricated by depositing a 25-nm-thick titanium adhesion layer followed by a 25-nm-thick gold layer through a shadow mask using an e-beam evaporator (BOC Edwards Auto 306). The reproducibility of the surface preparation and deposition processes was monitored on duplicate samples fabricated on different days using XPS and electrical measurements. A 1-MHz impedance meter (Agilent 4284A) was used for $C-V$ and large ac signal conductance characterization. $C-V$ characterization was used to measure doping density ($\sim10^{14}$ cm$^{-3}$), series resistance ($r_s \sim 1$ k$\Omega$), and oxide capacitance on each sample. The low doping density yielded a small interface trap time constant $\tau_i$, which, in turn, made the Agilent 4284A impedance meter suitable for detecting defects with large capture cross-sections [9]. The impedance of MISCAP devices was measured at both 800 kHz and 1 MHz to derive the series resistance [Fig. 3(b)] and the $C-V$ curves using Norton’s approach [30]. The $C-V$ curves were scanned in the forward direction from negative to positive gate voltage followed by the reverse direction from positive to negative gate voltage.

The large ac signal conductance was determined from (7) using impedance values measured on MISCAP devices from 20 Hz to 1 MHz. The parameters $D_{tr}$ and $\tau_{tr}$ were obtained from (1) for each group of correlated defects by fitting conductance data using IGOR PRO (WaveMetrics, Inc., v.6). The $G_p/\omega$ versus $\omega$ curves were fit with no more than three types of defect groups ($D_{tr1.2.3}$ and $\tau_{tr1.2.3}$), using a $\chi^2$ test to achieve the best fit. Fitting with too many groups produced negative time constants and fitting with too few drastically increased $\chi^2$. Each group of defects was numbered based on the approximate frequency range, from low to high. The peak frequency ($\omega_p = 1/\tau_{tr}$), trap density ($D_{tr}$), capture cross-section ($\tau_{tr}$), and SRV ($S_{tr}$) for each group of defects was extracted from the peak fits. Error bars are one standard deviation obtained from eight gates on each sample. After FGA, the lowest frequency peak of $G_p/\omega$ shifted lower in frequency, often below 20 Hz, which is the cutoff of the Agilent 4284A LCR meter. When this occurred, the peak maximum was fixed at 20 Hz for extracting parameters.

**IV. EXPERIMENTAL RESULTS AND DISCUSSION**

$C-V$ curves were measured for the following three different oxide layers: 1) Tox [Fig. 4(a)]; 2) a stack consisting of both a chemical SiO$_2$ buffer layer in contact with Si and ALD Al$_2$O$_3$ [Fig. 5(a)]; and 3) ALD Al$_2$O$_3$ [Fig. 6(a)]. $C-V$ data were used to determine the dielectric constant ($\varepsilon$), doping density ($N_d$), measured flatband voltage ($V_{FBM}$), and fixed oxide charge ($Q$) [11], which are given in Table II. The ideal flatband voltage ($V_{FBM}$) was calculated based on the gate metal (Ti) work function and the measured doping density $N_d$. The measured flatband voltage ($V_{FBM}$) was set equal to the voltage on an experimental $C-V$ curve that produced the same capacitance as the ideal flatband voltage. The errors shown are one standard deviation and were obtained from measurements on multiple gates in MISCAP devices from multiple samples. The capacitance in the depletion region was lower for samples treated by FGA.

This was caused primarily by thickening of the oxide, which has been observed previously with Si-dielectric interfaces [32]. These samples were not used for averaging ideal and measured flatband voltages since gold and titanium interdiffused during heating, forming an alloy of unknown composition.

The hysteresis in the $C-V$ curves is attributed to fast mobile ions inside the dielectric films [30], and the flatband voltage offset is due to fixed charges both inside the dielectric films and at the metal–dielectric interface [11]. The existence of mobile ion charges at the metal–dielectric interface was unavoidable in our experiments because devices were exposed to an uncontrolled laboratory environment at multiple points in the process flow. Since the electrical measurements could not distinguish between an interface trap and a fixed charge located near an interface [9], [33], thick oxide films of 10–100 nm were chosen.
Fig. 6. (a) Normalized $C-V$ curves for Aox, AoxFGA, AoxVA, AoxFGAX, and AoxVAX; f denotes the forward bias sweep direction and b the backward or reverse bias direction. Large ac signal conductance data and peaks fit for (b) Aox, AoxVA, and AoxFGA and (c) AoxVAX and AoxFGAX. $G_f/\omega$ was not normalized to gate area. The insets expand the scales to show the highest frequency peaks. Data lower range was limited to $f = 20 \text{ Hz}$ by the instrument response. Therefore, the maximum conductance at low frequency was fixed at 20 Hz.

The effect of mobile ions and fixed charges was most pronounced for Tox films grown using water vapor, where the flatband voltage offset was $\approx 4 \text{ V}$. FGA minimized the mobile ion charges, which reduced the hysteresis [30], and the slope of the $C-V$ curve was sharper, indicating that the quality of the Si/SiO$_2$ interface also improved [Fig. 4(a)]. However, a kink appeared at $\approx 4 \text{ V}$, which was most pronounced in reverse bias. The width of the kink depended on the $C-V$ scan time, and the kink was further stretched sweeping in the forward direction, confirming that it is related to mobile ions. Since both fixed and mobile ion charges do not change occupancy as the gate voltage changes [9], the data suggest that mobile ions must have diffused into the vicinity of the Si/SiO$_2$ interface and acted to separate the less reproducible metal–dielectric interface from the better controlled and reproducible semiconductor–dielectric interface. For devices containing thin dielectric films (e.g., $\approx 2 \text{ nm}$), the electrical potential generated by charges at the metal–dielectric interface can overlap with the wave functions of e–h carriers in the semiconductor [20], affecting SRV measurements. There are fixed oxide charges inside the dielectric layer that are located near the semiconductor interface, and these are included in the SRV measurements [9], [33].
as interface traps. This is better understood since the kink was located in the depletion region of the C–V curve of the p-type Si/SiO$_2$ MISCAP devices, where a positive voltage was applied to the gate; consequently, positive mobile ions must have been pushed toward the Si/SiO$_2$ interface. The shape of the reverse trace has the same signature as single-level acceptor traps located within the band gap, whereas the shape of the forward trace indicates that traps were close to the conduction band edge and retained the same charge over the nonconstant capacitance portion of the C–V curve; the shallow slope in the depletion region of the FGA-treated Si sample is a result of rapid dc sweeping (−0.4 V·s$^{-1}$), pushing the C–V curve slightly into deep depletion [11], rather than an indication of interface traps. We did not investigate whether mobile ions were the source of the traps or whether they were bound to Si or O at the interface, creating new chemical moieties with midgap energy levels. The kink in the C–V curve disappeared at voltages below 2 V, indicating that either positive mobile ions were expelled from the interface or bonds to Si or O were broken as a result of the applied electric field.

The large ac signal conductance method was investigated on Tox samples over a range of dc voltages and ac amplitudes. The responses of $G_p/\omega$ for two biasing regimes, i.e., $d_c = -8$ V, $\omega = 7$ V and $d_c = -11$ V, $\omega = 12$ V, are shown in Fig. 4(b). The close match proves that large ac signal conductance is independent of the dc bias and the ac signal amplitude when the Fermi level is swept from deep depletion to near accumulation.

The potential for spurious peaks to emerge due to the large ac amplitudes used was investigated by fabricating a MISCAP device on a glass microscope slide. This MISCAP structure forms only an oxide capacitance $C_{ox}$ with negligible $r_s$, $C_G$, $R_{ox}$, $C_{sh}$, and $G_s$. The large ac conductance was measured by applying the same dc and ac voltages used on the Tox samples. The peak in $G_p/\omega$ appeared above $10^7$ Hz with an amplitude of less than ±0.5 pF, as shown in the inset of Fig. 4(b). Since this peak is one to two orders of magnitude smaller than the peaks observed for the SiO$_2$ and Al$_2$O$_3$ samples studied, it defines the noise floor of this method using our setup. The peaks in $G_p/\omega$ for the semiconductor samples, consequently characterized by the frequency-dependent energy losses of interface traps in the SiO$_2$ and Al$_2$O$_3$ film stacks.

The large ac signal conductance data for the Tox and ToxFAGA samples are shown in Fig. 4(c). Using the circuit given in Fig. 1(d) as a model, the data were fit using

$$G_p(\omega) = \frac{\varepsilon \omega \tau_{r1} D_{r1}}{1 + (\omega \tau_{r1})^2} = \frac{\varepsilon \omega \tau_{r2} D_{r2}}{1 + (\omega \tau_{r2})^2} + \frac{\varepsilon \omega \tau_{r3} D_{r3}}{1 + (\omega \tau_{r3})^2}$$

where the numbered subscripts refer to the approximate frequency ranges of the peaks; in this case, only subscripts 1 and 2 or two sets of correlated defect groups were present since there were no peaks in the kilohertz range. The fit results are given in Table III, namely, frequency (effective trap time constant), effective trap density, effective capture cross-section, and SRV. The SRV values for each group of correlated defects reported in the table is the average of the values measured on all of the gates from all of the samples, namely, $S_{total,j} = \sum_{j=m}^{n} S_{rd,j}/N_{gate}$ for defect group $j$, where $N_{gate}$ is the total number of gates on all samples processed in the same way; the standard deviation was computed based on these values. Since each group of correlated defects was uncoupled from the others by the large ac signal method, the total SRV for each group $j$ was obtained by summing the SRV from each of the three groups, namely, $S_{total,j} = S_{rd,j} + S_{rd,j} + S_{rd,j}/N_{gate}$, the standard deviation was computed based on these values. For the Tox sample, the high-frequency peak at 1.5 MHz had a defect density ($D_{rd}$) that was an order of magnitude smaller than the low-frequency peak at 360 Hz, but it displayed the highest overall activity because the capture cross-section ($\sigma_{rd}$) was over three orders of magnitude larger. This produced an SRV of 111 ± 19 cm$^{-2}$/s for the high frequency defect group and 0.8 ± 0.1 cm$^{-2}$/s for the low frequency group. Although smaller in number, the high frequency group accounted for the entire $S_{total,j}$ value of 112 ± 19 cm$^{-2}$/s. The time constants associated with these two sets of traps were ~0.7 μs for the high frequency group and ~2.8 μs for the low frequency group. Annealing Tox in forming gas reduced the height of the large ac conductance peaks and shifted them to lower frequency, as shown in Fig. 4(c). The high-frequency peak decreased to near the noise level, reducing the total SRV almost two orders of magnitude from 112 ± 19 cm$^{-2}$/s to 1.3 ± 0.3 cm$^{-2}$/s for ToxFAGA. The trap density and the cross-section for the low-frequency peak also changed. As a result, only $S_{total,j}$ should be used for comparison, rather than the SRV from individual peaks due to possible changes in the type of traps and the way they are correlated ($\sigma_{rd}$, $E_{rd}$). The measured $S_{total,j}$ quantifies the lower electrical activity of the Si/SiO$_2$ interface after FGA. This agrees qualitatively with the C–V results.

Both vacuum annealing and FGA of a SiO$_2$–Al$_2$O$_3$ dielectric film stack reduced hysteresis in the C–V curves, as shown by a comparison of CoxAuOXA and CoxAuOFGA to CoxAox

<table>
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<th>TABLE II</th>
<th>AVERAGED VALUES OF C–V DEVICE PARAMETERS$^b$</th>
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<tr>
<td>Sample</td>
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<tr>
<td>Tox</td>
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<tr>
<td>Aox</td>
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</tr>
</tbody>
</table>

$^b$The abbreviations are Tox (thermal SiO$_2$), Cox (chemical SiO$_2$ grown by piranha last), Aox (aluminum oxide Al$_2$O$_3$ deposited by ALD), FGA (forming gas annealing), VA (vacuum annealing), and P (piranha). Processing details are given in the text.
### Table III

**Large AC Conductance Results for Dielectric Films on Silicon**

| Sample  | \( \varepsilon_r \) | \( N_{SiO_2} \) | \( \sigma_{SiO_2} \) | \( N_{Al_2O_3} \) | \( \sigma_{Al_2O_3} \) | \( \varepsilon_r \) | \( N_{SiO_2} \) | \( \sigma_{SiO_2} \) | \( N_{Al_2O_3} \) | \( \sigma_{Al_2O_3} \) |
|---------|----------------|-------------|----------------|-------------|----------------|----------------|-------------|----------------|-------------|----------------|----------------|
| Tox     | 3.58 ± 0.02    | 17.8 ± 0.5  | 2.3 ± 0.2      | 0.0 ± 0.1   | -              | 1.5 ± 0.1      | 53.3 ± 0.3  | 1.1 ± 0.1     | 113.1 ± 1.9  | 127.3 ± 1.9  |
| Tox/Al  | 24.3 ± 0.3     | 0.8 ± 0.06  | 7.6 ± 0.5     | 1.3 ± 0.3   | -              | -              | -           | -             | -           | -              |
| CoxOxVAX| 84.5 ± 0.01    | 21.2 ± 0.4  | 4.0 ± 0.01    | 2.5 ± 0.5   | 8.2 ± 0.4     | 5.8 ± 0.3      | 53.1 ± 1    | 0.6 ± 0.05    | 102.3 ± 1.1  | 80.3 ± 0.3   |
| CoxAxVAX| 81.2 ± 0.02    | 0.8 ± 0.01  | 2.5 ± 0.1     | 35.9 ± 2.0  | 2.7 ± 0.05    | 3.4 ± 0.2      | 19.6 ± 0.1  | 0.6 ± 0.08    | 65.7 ± 0.3   | 38.6 ± 0.4   |
| CoxAxVAX| 51.7 ± 0.3     | 1.2 ± 0.5   | 2.3 ± 0.3     | 0.4 ± 0.1   | -              | -              | -           | -             | -           | -              |
| Cox     | 39.0 ± 0.01    | 17.5 ± 0.3  | 3.3 ± 0.6     | 48.2 ± 0.7  | 7.3 ± 0.3     | 29.3 ± 0.5     | 34.9 ± 0.5  | 0.3 ± 0.03    | 67.8 ± 0.11  | 10.0 ± 0.01  |
| AoxVAX  | 1050 ± 0.05    | 150 ± 0.4   | 95 ± 0.5      | 231 ± 4.2   | 6.3 ± 0.9     | 9.1 ± 0.7      | 125 ± 0.2   | 1.3 ± 0.06    | 189 ± 0.11   | 156 ± 0.01   |
| AoxOxVAX| 297 ± 0.23     | 2.3 ± 0.06  | 4.7 ± 0.01    | 7.4 ± 0.1   | 0.3 ± 0.2     | 10.2 ± 0.1     | 15.3 ± 0.6  | 0.6 ± 0.05    | 27.0 ± 0.14  | 21.0 ± 0.1   |
| Aox     | 39.0 ± 0.15    | 3.8 ± 0.9   | 5.7 ± 1.9     | 4.4 ± 1.5   | -              | 0.7 ± 0.07     | 44.1 ± 0.1  | 1.5 ± 0.03    | 124.7 ± 1.3  | 134 ± 0.11   |
| Aox     | 85.2 ± 0.21    | 3.2 ± 0.3   | 3.7 ± 0.04    | 5.7 ± 0.1   | 5.5 ± 0.7     | 6.8 ± 0.09     | 17.9 ± 0.2  | 0.8 ± 0.08    | 23.2 ± 0.3   | 58.6 ± 0.4   |
| Aox     | 3.1 ± 0.4      | 1.4 ± 0.6   | 1.7 ± 0.1     | 0.5 ± 0.3   | 3.5 ± 0.7     | 0.6 ± 0.1      | 2.9 ± 0.2   | 1.6 ± 0.4     | 4.3 ± 0.1    | 45.4 ± 0.6   |

The abbreviations are Tox (thermal SiO₂), Cox (chemical oxide SiO₂ grown by piranha last), Aox (aluminium oxide Al₂O₃ deposited by ALD), FGA (forming gas annealing), VA (vacuum annealing), X (XPS analysis). Each group of defects was numbered depending on the approximate frequency range, from low to high. The error bars reflect one standard deviation and were obtained by sampling different gates on each sample. The \( N_{SiO_2} = \varepsilon_r \varepsilon_0 E_d \) and \( E_d \approx 1 \text{eV} \) is used.

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In Fig. 5(a), the stack was composed of a chemical SiO₂ buffer layer in contact with Si and an ALD Al₂O₃ capping layer. The thermal treatments reduced the concentration of mobile ion charges, and the VA reduced the concentration of fixed charges (Table II). Similar to the Tox film, a kink appeared between 0 and 1.7 V in the \( C-V \) curve after FGA, but in this case, it was the same in both forward and reverse scans. The kink is indicative of the presence of charge traps in the upper half of the Si band gap close to the conduction band edge. It was not possible by the \( C-V \) method to identify whether these traps were located at the Si/SiO₂ interface, the SiO₂/Al₂O₃ interface, or both since the chemical SiO₂ layer was so thin (≈2 nm) [33]. The slopes of the \( C-V \) curves in Fig. 5(a) are similar, which makes it difficult to distinguish between them and quantify differences.

The large ac signal conductance method classifies defects based on the recombination velocity or time constant of the electrical activity. Since frequency space spans six orders of magnitude, there is ample sensitivity to distinguish between different groups of defects. Fig. 5(b)–(d) shows the large ac signal conductance curves for CoxAox, CoxAoxVA, CoxAoxFGA, and CoxAoxVAX. The parameters extracted by fitting these curves with (8) are given in Table III. Annealing in vacuum reduced defect activity since \( S_{total} \) decreased from 1045 ± 150 cm/s for CoxAox to 408 ± 47 cm/s for CoxAoxVA due largely to a reduction in the activity of the high-frequency state at 0.3–0.5 MHz. FGA completely removed this state, and \( S_{total} \) dropped by three orders of magnitude to 0.4 cm/s. Heating provided the thermal energy needed to overcome the activation barriers to make new bonds and to mass transport. VA was done at a higher temperature, but for a shorter time than FGA. The higher temperature could have produced a restructuring of the interface and new bond formation, but it was insufficient to completely eliminate trap states. Both a longer heating time and a source of monovalent H atoms were successful. If the defect states at the Si/SiO₂ interface were either lone Si or O dangling bonds, then based on a simple bond formation calculation, they were terminated with H after FGA since Si(s) + (1/2)H₂(g) → Si—H(s) releasing 0.8 eV and O(g) + (1/2)H₂(g) → O—H(g) releasing 2 eV. The O—H can go on to react via SiO—H + Si—OH → Si—O—Si + H₂O. Although the chemical composition of defects and the detailed mechanism for defect elimination cannot be extracted from the large ac signal conductance measurements, the SRV provides a quantitative measure of the electrical activity at the interface. For example, exposing a vacuum annealed surface to X-rays and high-energy electrons during XPS was sufficient to degrade the interface since the activity of all three groups of defects increased, which resulted in \( S_{total} \) increasing from 408 ± 47 cm/s on CoxAoxVA to 855 ± 62 cm/s on CoxAoxVAX. The approximately factor of two change in activity is entirely due to XPS analysis since the clustered apparatus used for this portion of the processing prevented air exposure.

The \( C-V \) curves for the samples with an ALD Al₂O₃ dielectric film in direct contact with Si have similar shapes and slopes, as shown in Fig. 6(a). Both vacuum and FGA reduced the hysteresis by eliminating a portion of the mobile ion charges; compare the curves for AoxVA and AoxFGA to that for Aox. In contrast to the SiO₂ layers, annealing left the depletion range free of kinks and VA did not significantly reduce the fixed oxide charges, as it did with the chemical SiO₂ buffer layer (Table II). Since the chemical nature of the fixed oxide charges is unknown, it is not clear whether these charges remained the same or were removed, but new fixed oxide charges were created as result of VA. The \( C-V \) curves were not as sharp and were shifted to more negative voltages when XPS analysis was done; compare AoxVAX to AoxVA and AoxFGAX to AoxFGA.

FGA had a pronounced affect on \( S_{total} \) for Al₂O₃ in direct contact with Si, as it did with the two SiO₂ films, but VA
The $S_{\text{total}}$ of $112 \pm 19$ cm/s for the thermally prepared Si/SiO$_2$ interface using large ac signal conductance is close to the $\sim 100$ cm/s measured by Ikari et al. using photothermal reflection microscopy [38]. In that measurement, band bending resulting from fixed and mobile ion charges was flattened because of the high e-h carrier density [10, 20]. This allowed quasi-Fermi levels to form, activating all defects across the band gap, which makes this measurement directly comparable to the SRV obtained by large ac signal conductance. In contrast, the $S_{\text{total}}$ of $578 \pm 96$ cm/s for the Si/Al$_2$O$_3$ interface using large ac signal conductance is much higher than the $\sim 2$ cm/s reported by Hoex et al. using time-resolved decay of e-h carriers [21]. The low carrier density in that measurement, however, means fixed oxide charges created a field that preferentially repelled one type of carrier from the interface, reducing the recombination rate at defects centers. The result obtained by field-effect passivation is consequently not comparable to the SRV obtained by the large ac signal conductance method, which measures only chemical passivation. Hoex et al. discuss both chemical and field-effect passivation approaches and show by simulation that the SRV for the Si/Al$_2$O$_3$ interface is $\sim 100$ cm/s, which increases when band bending due to fixed charges is reduced [39]. The simulation accounts for defects across the band gap, which are activated by illumination, generating an e-h carrier density close to the doping density.

Annealing generally improved the Si/oxide surfaces since $S_{\text{total}}$ was lower, which agrees with the standard practice in Si/SiO$_2$ device fabrication [3], [9], [36]. FGA had a more pronounced effect than VA on the three oxide layers in contact with Si. The interface that chemical SiO$_2$ made with Si after FGA was comparable electrically to the one made by Tox. Moreover, $S_{\text{total}}$ for both CoxAoxFGA and ToxFGA was close to the $\sim 0.4$ cm/s value measured for hydrogen-terminated Si(100) [10]. The SRV reported by Yablonsvitich et al. was measured by the RFPCD technique, while the Si samples were immersed in an aqueous 49% HF solution. This approach ensured that no band bending occurred at the surface and that the decay measurement was unaffected by separation of e-h carriers [10]. Only defects located above the Fermi level were accounted for by this measurement. Since the main defects at Si/SiO$_2$ interfaces are related to Si dangling bonds, which can be passivated by monovalent hydrogen, Si-H bonds create energy levels that are near the band edges with very low activity [3], [9]. As a result, the SRV measurement for H-terminated Si as well as RFPCD is directly comparable to that for ToxFGA and CoxAoxFGA by large ac signal conductance. Similarly the nature of interface defects at Si/Al$_2$O$_3$ interfaces are like those at Si/SiO$_2$ [3], [36], [37] and Si dangling bonds at Si/Al$_2$O$_3$ interfaces can be passivated by hydrogen [3], [40], [41]. $S_{\text{total}}$ confirms improvement in Aox and AoxVAX interfaces after FGA treatment. The only exception found was that VA degraded the interface quality of Si/Al$_2$O$_3$. This must be related to the abruptness of the interface between Si and Al$_2$O$_3$ preventing thermal accommodation during VA and, hence, increasing the number of defects when no hydrogen was present [36]. Ultimately, the Si/Al$_2$O$_3$ interface contained more active defects than either Si/Tox or Si/chemical SiO$_2$ interfaces, even after FGA [3].

**Fig. 7.** Surface recombination velocity ($S_{\text{total}}$) at the interface of Si for various dielectric film stacks and processing (Table III). These values are compared with surface recombination velocity at Si(100)-terminated hydrogen (Si-H), submerged in 49% HF (solid horizontal line) [10].

degraded the interface. The large ac signal conductance curves for Aox, AoxVA, and AoxFGA processes are shown in Fig. 6(b) and those for AoxVAX and AoxFGAX in Fig. 6(c). The parameters given in Table III were obtained from fitting with three defect groups as for CoxAox. $S_{\text{total}}$ was $578 \pm 96$ cm/s for Aox, which decreased to $47 \pm 6$ cm/s after annealing in hydrogen (AoxFGA) but increased to $1250 \pm 130$ cm/s after annealing in vacuum (AoxVA). Hydrogen should passivate Al dangling bonds, if they exist, as well as Si at the interface, since Al(s) + (1/2)H$_2$(g) $\rightarrow$ Al–H(s) releases 0.7 eV. Although the Si–O bond strength is higher than that for Al–O, Al could compete with Si for O at the interface, producing Si dangling bonds, without H to serve as a passivation. The interface quality after VA (AoxVA) was further degraded by X-ray exposure [3] during XPS since $S_{\text{total}}$ increased to $1348 \pm 121$ cm/s (AoxVAX). In contrast to the SiO$_2$ layers, FGA repaired all of the damage done by X-ray exposure with Al$_2$O$_3$ contacting Si, as $S_{\text{total}}$ was $48 \pm 3$ cm/s (AoxFGAX).

The SRV for all processes and interfaces is plotted in Fig. 7, together with the result for H-terminated Si(100) [10]. Thermal SiO$_2$ produced the lowest recombination velocity and provided the best Si surface passivation compared to chemical SiO$_2$ and ALD Al$_2$O$_3$: $S_{\text{total}}$ increased in the order Tox $< Aox < CoxAox$. This corroborates the results of previous investigations of Tox [3], [9] and chemical SiO$_2$ [34], [35] layers, as well as ALD Al$_2$O$_3$ [3], [36], [37], which show that defects are related primarily to Si dangling bonds and are Si/SiO$_2$-like. The defect density for the Si/Al$_2$O$_3$ (Aox) interface was $\sim 1$–2 orders of magnitude greater than that for Si/chemical SiO$_2$ (CoxAox) [3], [36], [37] in these studies, and the CoxAox defect density was $\sim 1$–2 orders of magnitude greater than that for Si/Tox [3], [9], [34], [35]. The differences in the defect density can affect not only the effective trap density ($N_{\text{tr}}$), but also the effective capture cross-section ($\sigma_{\text{tr}}$), since defects are correlated [16]. The effective capture cross-section of the most active state was much larger for CoxAox than for Aox. This explains why the SRV for CoxAox is larger than for Aox, even though the effective trap density for CoxAox is smaller than for Aox.
Radiation-induced defects have been extensively investigated at Si interfaces with oxides [3, 19]. S$_{\text{SRV}}$ clearly confirms and quantifies the degradation of Si/chemical SiO$_2$ and Si/O$_x$O$_2$ after X-ray exposure during XPS characterization; compare CoxAOxVA and AoxVA to CoxAOxVAX and AoxVAX in Fig. 7.

V. SUMMARY AND CONCLUSION

The large ac signal conductance technique was used to probe the density and activity of deep-level defects across the band gap, yielding an SRV characteristic of the interfaces that Si made with dielectric layers. The SRV measurement by this method is not affected by the choice of semiconductor and dielectric materials, the semiconductor doping density, and the band bending due to fixed oxide charges, mobile ion charges, charged interface defects, and work function differences between the gate metal and the semiconductor substrate. The agreement between the theoretical fit and the experimental data demonstrates that a model based on one resistor and one capacitor represented correlated defects with similar activity. The SRV values based on large ac signal conductance at Si interfaces with SiO$_2$ and Al$_2$O$_3$ film stacks were in good agreement with literature values obtained by other methods. In large ac signal conductance, the dc and ac voltages can be adjusted to mimic a device interface during operation, characterizing SRV more specifically for that device. In semiconductors with a high doping density or a large defect capture cross-section, the time constant shifts, requiring an impedance measurement at high frequencies, which is a relatively easy task with current conventional high-frequency impedance meters (e.g., 40–110 MHz, 4294A Agilent Technologies). This makes large ac signal conductance a practical method for investigating a wide range of interfaces in various types of devices. Future work will focus on measuring the SRV as a function of temperature to quantify the capture cross-section $\sigma_{\text{SRV}}$ and activation energy $E_a$. This would determine the impact of temperature on the performance of a semiconductor–dielectric interface.

APPENDIX

DEFINITION OF VARIABLES

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<th>Variable</th>
<th>Definition</th>
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<tr>
<td>$A_G$</td>
<td>gate area (cm$^2$)</td>
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<td>$C$</td>
<td>MOS capacitance (F) and (F cm$^{-2}$)$^1$</td>
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<td>$C_{\text{SRV}}$</td>
<td>effective capacitance of correlated traps (F) and (F cm$^{-2}$)$^1$</td>
</tr>
<tr>
<td>$d$</td>
<td>e-h confinement thickness (cm)</td>
</tr>
<tr>
<td>$D_{\text{SRV}}$</td>
<td>interface trap density (cm$^{-2}$ eV$^{-1}$)</td>
</tr>
<tr>
<td>$D_{\text{IT}}$</td>
<td>effective correlated interface traps density (cm$^{-2}$ eV$^{-1}$)</td>
</tr>
<tr>
<td>$\Delta\Phi$</td>
<td>interface–bulk differential potential (eV)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>electron and unit of charge (e)</td>
</tr>
</tbody>
</table>

$^1$The parameter is normalized to gate area, $A_G$.

$E_a$ activation energy of correlated defects (eV)

$E_{\text{SRV}}$ activation energy of single level traps (eV)

$E_i$ semiconductor intrinsic Fermi level (eV)

$E_{\text{IT}}$ interface trap energy measured from $E_i$ (eV)

$E_{\text{TR}}$ effective correlated interface traps energy measured from $E_i$ (eV)

$G_p$ interface trap and correlated interface trap conductance (\ohm$^{-1}$) and (\ohm$^{-1}$ cm$^{-2}$)$^1$

$G_{\text{IT}}$ averaged leakage conductance (\ohm$^{-1}$)

$\kappa$ Boltzmann constant (m$^2$ kg s$^{-2}$K$^{-1}$)

$\kappa$ Oxide dielectric constant

$N_d$ doping density (cm$^{-3}$)

$N_{\text{IT}}$ effective correlated interface traps density (cm$^{-3}$)

$\omega$ angular frequency (s$^{-1}$)

$Q$ fixed oxide charge (C) and (C cm$^{-2}$)$^1$

$R_p$ parallel leakage resistor ($\Omega$)

$R_s$ series resistance ($\Omega$)

$R_{\text{IS}}$ interface trap resistance ($\Omega$)

$R_{\text{TR}}$ effective correlated interface traps resistance ($\Omega$)

$R_{\text{MISCA}}$ resistivity ($\Omega$)

$\sigma_{\text{IT}}$ interface trap capture cross-section (cm$^2$)

$\sigma_{\text{TR}}$ effective correlated interface traps capture cross-section (cm$^2$)

$\sigma_{\text{SRV}}$ effective correlated interface traps capture cross-section at infinite temperature (cm$^2$)

$S_{\text{SRV}}$ surface recombination velocity of an interface trap (cm s$^{-1}$ eV$^{-1}$)

$S_{\text{TR}}$ surface recombination velocity of correlated traps (cm s$^{-1}$ eV$^{-1}$)

$S_{\text{TOT}}$ total surface recombination velocity of all correlated interface traps (cm s$^{-1}$)

$\tau$ non-radiative e-h carrier lifetime (s)

$\tau_{\text{IT}}$ interface trap time constant (s)

$\tau_{\text{TR}}$ effective correlated interface traps time constant (s)

$T$ Absolute temperature (K)

$\tau_{\text{e-h}}$ thermal velocity of e-h carriers

$V_{\text{BD}}$ ideal flat band voltage (V)

$V_{\text{mV}}$ measured flat band voltage (V)

$\delta$ depletion width (cm)

$X$ MISCA reactance ($\Omega$)

$\xi$ electric field (V cm$^{-1}$)

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We would like to thank W. Rachmady and B. Turko of Intel for the useful discussions and for suggesting the on-top MISCAP device.

REFERENCES


[4] G. W. Hofft and C. Van Opdorp, “Determination of bulk minority-carrier lifetime and surface/interface recombination velocity from...
Harold G. Parks (M’64–SM’89) received the B.S. degree from Lowell Technological Institute, Lowell MA, in 1964, the M.S. degree from Syracuse University, Syracuse, NY, in 1969, and the Ph.D. degree from Rensselaer Polytechnic Institute, Troy, NY, in 1980, all in ion electrical engineering. From August 1969 to February 1990, prior to coming to the University of Arizona, he was a member of Technical Staff with the Corporate Research and Development Center, General Electric Company, Schenectady, NY. During 1990–1995, he was the Director of a task leader for the University of Arizona SEMATECH Center of Excellence for Contamination/Defect Assessment and Control. He was a founding member and a Principal Investigator for the Wafer Engineering and Defect Science Center, an NSF/IUCRC including six wafer manufacturers and seven universities, during 1995–2002. He was the University of Arizona Site Director of a Principal Investigator for the Center for Microcontamination Control, an NSF/IUCRC, during 2003–2006. He is currently an Associate Professor in the Department of Electrical and Computer Engineering, University of Arizona, Tucson, which he joined in February 1990. He is a coauthor of the book Advanced CMOS Process Technology, Vol. 19, VLSI Electronics Microstructure Science Series, Norman G. Einspruch Editor (New York: Academic Press Inc., 1989). His current research interests include prognostic cells for reliability enhancement, semiconductor device characterization and modeling, test structures, contamination control and yield enhancement, semiconductor reliability, and semiconductor processing.

Dr. Parks was an Associate Editor (1991–1995) and an Editor (1996–1999) for the IEEE Electron Device Letters under the tenure of Dr. J. R. Brews as Editor and Editor-in-Chief. He served as the IEEE Electron Devices Society Administrative Committee (EDS ADCOM) representative to the Editorial Board of the IEEE Circuits and Devices Magazine (1999–2006) and to the IEEE EDS ADCOM Publication Committee (2004–2007).

Anthony J. Muscat received the Ph.D. degree in chemical engineering from Stanford University, Stanford, CA, in 1993. He is currently a Professor with the Department of Chemical and Environmental Engineering, University of Arizona, Tucson, and holds the APS Professorship for Technology and Entrepreneurship in the College of Engineering. His research interests include the surface chemistry and physics of electronic device fabrication, materials processing using supercritical CO₂, and the synthesis of quantum dots.

Dr. Muscat is currently an Associate Editor for the IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING.
APPENDIX G

CHARACTERIZATION OF DEFECT STATES AT N-TYPE Ga$_{0.47}$In$_{0.53}$As AND Al$_2$O$_3$ INTERFACES USING SURFACE RECOMBINATION VELOCITY
Characterization of defect states at the interface of $n$-type Ga$_{0.47}$In$_{0.53}$As with Al$_2$O$_3$ layers using surface recombination velocity

G.1 Introduction

Efficient semiconductor devices are realized by making interfaces with low defect densities$^1$. The best semiconductor interfaces are produced by molecular beam epitaxy (MBE)$^2$ and metal organic vapor phase epitaxy (MOVPE)$^2$, but these are too expensive for high volume production. Atomic layer deposition (ALD) is a lower cost alternative that is easier to integrate in manufacturing$^3$-$^5$. ALD is currently used in the microelectronics industry to deposit oxides with high dielectric permittivities on Si, forming high-$\kappa$ gate stacks that support continued scaling of field-effect transistors$^6$. This development also provides an opportunity to replace Si in the channel region of these devices with a III-V compound semiconductor to increase the charge mobility and achieve faster switching speeds. Methods must now be demonstrated that use ALD to deposit high-$\kappa$ films on III-V substrates with low defect densities$^4$-$^5$.

Zhao et al. investigated the device performance of $n$-type In$_{0.53}$Ga$_{0.47}$As with Al$_2$O$_3$, HfO$_2$, and LaAlO$_3$ films deposited by ALD$^7$. They concluded that the interface between In$_{0.53}$Ga$_{0.47}$As and Al$_2$O$_3$ was the best based on a midgap defect density of $1.17 \times 10^{12}$/cm$^2$-eV and capacitance-voltage (C-V) curves with low dispersion. The dielectric constant reported for Al$_2$O$_3$ was 8.1 and for HfO$_2$ was 17. McIntyre et al. studied the interface quality of In$_{0.53}$Ga$_{0.47}$As(100)/Al$_2$O$_3$ fabricated by in situ thermal desorption of an As cap in the ALD chamber prior to Al$_2$O$_3$ deposition$^5$. This process resulted in an atomically abrupt interface confirmed by transmission electron microscopy (TEM) and scanning transmission electron microscope (STEM) without oxidation of the substrate during Al$_2$O$_3$ growth based on x-ray
photoelectron spectroscopy (XPS). C-V and conductance-voltage measurements of metal-oxide-semiconductor (MOS) capacitors using a Pt electrode showed temperature and frequency-dependent inversion behavior indicative of an unpinned semiconductor/oxide interface. The experimental performance is consistent with the work of Kim et al. who theoretically simulated an ideal In$_{0.53}$Ga$_{0.47}$As(100)/Al$_2$O$_3$ interface using density functional theory calculations to predict a weak perturbation of the substrate electronic structure by avoiding oxidation. Kim et al. also investigated the effect of hydrogen annealing before and after metal deposition on an n-type In$_{0.53}$Ga$_{0.47}$As(100)/Al$_2$O$_3$ interface fabricated using an As cap. They report that hydrogen annealing was effective in passivating border traps in the oxide in addition to some of the midgap states. The C-V measurements show a reduction of both the frequency dispersion in accumulation and the stretch-out through depletion as well as suppression of the inversion carrier response. At high frequency where the Terman condition was likely to have been satisfied, the dielectric constants extracted for Al$_2$O$_3$ from the C-V curves reported in some of these papers appears to be anomalously low, in the range of 6.

Xuan et al. investigated the interface quality in p-type In$_{0.53}$Ga$_{0.47}$As(100)/Al$_2$O$_3$. Electrical characterization based on C-V measurements showed that the conventional Fermi-level pinning phenomenon on III-V's is overcome. Yet a small frequency dispersion at the accumulation capacitance was related to the relatively high $D_\text{it}$ at the valence band edge. This effect is different than tunneling of the electrons into border traps in the ALD Al$_2$O$_3$ layer, which is typically observed for n-type In$_{0.53}$Ga$_{0.47}$As(100)/Al$_2$O$_3$.

In this paper the interface between n-type Ga$_{0.47}$In$_{0.53}$As and Al$_2$O$_3$ deposited by ALD was investigated using both C-V curves and large AC signal conductance (LSC) on metal-insulator-semiconductor capacitor (MISCAP) devices. In the LSC
method, a large AC signal is applied to a MISCAP device at different frequencies in order to modulate the Fermi energy from the conduction to the valence band. The modulation causes simultaneous filling and emptying of traps across the band gap. Deconvolution of the conductance data in frequency space yields peaks corresponding to trap states that are correlated from which a value of the deep-level surface recombination velocity (SRV) is extracted. Summing the SRV values representative of groups of correlated trap states yields the SRV characteristic of a semiconductor-dielectric interface. The total SRV obtained in this way is independent of band banding, fixed oxide charges, external potential, metal work function, doping density, and material thickness.

Al\(_2\)O\(_3\) is a model high dielectric permittivity layer because the surface reactions during ALD are understood, permitting inferences about the effect of interface chemistry on the electrical response. Alumina was deposited directly on native oxide as well as on HF-last surfaces. The changes in the electrical behavior due to forming gas and ammonia annealing are compared as are changes due to the sequence of the annealing and metal deposition steps. Each interface is quantified using the total SRV obtained by the LSC method. These SRV values are compared to Si/thermal SiO\(_2\), Si/ALD Al\(_2\)O\(_3\), Si passivated by hydrogen, and MOVPE epitaxial Ga\(_{0.47}\)In\(_{0.53}\)As/InP interfaces. Dielectric constants were obtained from C-V curves at various frequencies and are compared to the values expected for bulk Al\(_2\)O\(_3\) films. The frequency dispersion and the deviation of the dielectric constant from bulk values are commonly related to border traps or slow states located in the Al\(_2\)O\(_3\) layer near the interface with the semiconductor that can exchange charge carriers with the substrate. When the high frequency Terman condition is satisfied, the deviation of the dielectric constant from bulk values is shown to be the result of oxide traps that reside in the Al\(_2\)O\(_3\) film, but which are far enough away from the interface that no charge carriers are
exchanged with the substrate. Exposure to ambient light before capping with metal is shown to degrade device behavior.

In section G.2, the procedure to fabricate Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices and the experimental setup for electrical characterization are described. We present the experimental data in section G.3, including C-V and conductance-frequency curves, as well as the assumptions and conditions necessary to extract values representative of groups of correlated defect states. In section G.3, the C-V and LSC data are analyzed and used to explain the electrical response of the MISCAP devices. In the concluding section G.5, the major results obtained from the electrical measurements on the MISCAP devices are summarized, and different interfaces are compared quantitatively based on the SRV. Variable definitions are listed in Appendix G.5.2.

G.2 Device Fabrication and Experimental Setup

As shown in Fig. G.1a and b, MISCAP device structures were built on a 1 µm n-type Ga$_{0.47}$In$_{0.53}$As(100) film (Si doped to $\sim 1 \times 10^{18}$ cm$^{-3}$, IQE Inc.), which was grown epitaxially on an InP(100) substrate. Sample labels reflect the sequence of process steps, which consisted of surface cleaning, dielectric film deposition, post-deposition annealing, and metal deposition steps. Surface preparation consisted of either immersion in the solvents acetone and methanol to degrease the sample which is designated Nox because it is preserved the $\sim$1 nm-thick native oxide or immersion in the solvents followed by immersion in a 49% aqueous HF solution (Ashland chemical) for 1 min and drying with ultrapure N$_2$ which is designated liquid HF (LHF). A 10 nm-thick Al$_2$O$_3$ film (Aox) was deposited by ALD using pulses of trimethylaluminum (TMA) (Hi-k grade, Rohm and Haas) and water vapor at 170°C$^{15}$. The post-Al$_2$O$_3$ deposition anneals investigated were forming gas annealing (FGA)$^{12}$ and ammonia
annealing (NH$_3$). The forming gas annealing process consisted of a ramp to 350°C for 3 h followed by a soak at 400°C for 1 h in a flowing mixture of N$_2$ and H$_2$ gas at atmospheric pressure. The ammonia annealing was done by alternating pulses of ammonia and nitrogen in an ALD system for 2 h at 300°C. A Ni(15 nm)/Au(20 nm) metal gate was deposited using standard procedures in an electron beam evaporator through a shadow mask, forming a gate area of $43 \times 43 \mu$m$^2$ and a larger runway area of about 9 mm$^2$. The sample label NoxAoxMFGA, for example, indicates that the processing sequence was degreasing, depositing an Al$_2$O$_3$ film, metalizing with Ni/Au, and FGA annealing.

In high quality semiconductor substrates with a large surface to volume ratio (gate size to depletion depth), both C-V and LSC methods probe states at the semiconductor surface (dangling bonds or fast states) and $\sim$3 nm into the oxide films (border traps or slow states)$^{12,16}$, including the Al$_2$O$_3$. Therefore, the depth probed electrically includes any interfacial oxide at the III-V surface as well as traps in the oxide films. A schematic of the NoxAox interface including the oxide layers is shown in Fig. G.1c. C-V and LSC curves were acquired at frequencies from 100 Hz to 30 MHz using HP4284A and HP4285A calibrated impedance meters$^{17}$. Details of the equivalent circuit, the mathematical description, and the data fitting procedure were published previously$^{12}$. The measurement setup is shown schematically in Fig. G.1d. The C-V curves for two standard capacitances with nominal values of 5 pF and 20 pF, which are similar to the values for MISCAP devices in depletion and accumulation, are shown in Fig. G.2 over the same frequency and DC voltage range used for the MISCAP device measurements. These results indicate that the parasitic dispersion due to the experimental apparatus was negligible compared to the dispersion observed for the C-V curves of all MISCAP devices.

Approximately 2 nm of Al$_2$O$_3$ was deposited on both Nox and LHF samples in
Figure G.1. Schematics of a) the NoxAox stack where an $\text{Al}_2\text{O}_3$ dielectric layer was deposited by ALD on the native oxide of the $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ surface, b) the LHFAox stack where the native oxide was removed with aqueous HF and an $\text{Al}_2\text{O}_3$ layer was deposited by ALD on the As oxide covering the $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ surface, c) the physical location of interface traps including fast states created by dangling bonds at the semiconductor surface and slow states or border traps due to defects in the oxides within approximately 3 nm from the semiconductor surface\textsuperscript{16}, and d) the setup to measure C-V curves and large AC signal conductances in which the gate and pad are fabricated on the top surface\textsuperscript{12}.
Figure G.2. C-V curves for standard capacitors with nominal values of 5 pF and 20 pF over the same frequency and DC voltage ranges used to measure MISCAP devices in order to evaluate the background parasitic dispersion. The values differ by less than 2% from 1 kHz to 30 MHz.
order to obtain a closed film and build a model interface with the Ga$_{0.47}$In$_{0.53}$As semiconductor for quantitative XPS analysis$^{15}$. The first TMA pulse removed most of the oxides present before Al$_2$O$_3$ was deposited yielding an interface containing approximately 5 Å of native oxide on the NoxAox samples and 2 Å of arsenic oxide as As$_2$O$_3$ on the LHFAox samples. XPS measurements were only performed on non-device samples using a similar preparation process as the device samples to avoid degradation of the interface by x-rays$^{12}$.

G.3 Results

The C-V curves for the NoxAox series of processes in the left panel and those for the LHFAox series in the right panel of Fig. G.3 show significant stretch out and dispersion unless an anneal was performed in forming gas or ammonia after metallization (i.e. MFGA and MNH$_3$). The ideal C-V curve$^{18}$ shown for each process was computed using the 30 MHz data. The 30 MHz curves were chosen because the capacitance in accumulation was constant above 10 MHz for the MFGA and MNH$_3$ curves in each series, confirming that the Terman condition was established. This was validated by the LSC data shown in Fig. G.4 because there are no conductance peaks above 10 MHz. There was dispersion in the capacitance in accumulation up to 30 MHz for the FGAM and NH$_3$M curves, and the Terman condition could not be established for these devices because frequencies above 30 MHz were unavailable. The interface quality of these devices is only qualitatively discussed and the dielectric constants and SRV values are estimates. In all of the C-V curves recorded, forward scans were done from depletion to accumulation and backward scans from accumulation to depletion. Performing a bias stress test at room temperature for scan times from 5 min to 1 h confirmed that the hysteresis in all of the C-V curves was due
to positive fast mobile ions\textsuperscript{12,16}. The lower frequency C-V curves were normalized to the accumulation capacitance of the 30 MHz curve to qualitatively compare interface properties. For all of the FGA and NH\textsubscript{3} annealing processes, the Ni and Au interdiffused in the electrode regions based on visual observations forming an alloy of unknown composition, yet the work function of the alloy was similar to that for Ni and Au (Φ\textasciitilde5.2 eV)\textsuperscript{19}. Therefore, the shift observed in all of the C-V curves relative to the ideal C-V curve in Fig. G.3 is attributed only to fixed oxide charges\textsuperscript{18} in the Al\textsubscript{2}O\textsubscript{3}.

Table G.1 shows the doping density ($N_d$), ideal flat band voltage ($V_{fbi}$), measured flat band voltage ($V_{fbm}$), fixed oxide charges ($Q_f$), physical oxide thickness ($t_{ox}$), equivalent oxide thickness (EOT), and oxide capacitance ($C_{ox}$) determined from the C-V data at 30 MHz. The error bars reported define the 95% confidence intervals and were obtained from measurements on 10 gates on each MISCAP device, except for the NoxAoxM and LHFAoxM devices where averaging extended over four MISCAP devices with 10 gates on each MISCAP device. The dielectric constants $\kappa_{30}$ and $\kappa_1$ were obtained from the capacitance in accumulation from each C-V curve at 30 MHz and 1 kHz. The $\kappa_{30}$ values ranged from 6 to 14 and the $\kappa_1$ values from 10 to 18. The surface recombination velocities varied between 1 and 79 cm/s.

The SRV values were obtained by fitting peaks to the LSC data as shown in Fig. G.4. The capture cross-section of a group of correlated defects was determined from the peak position, excluding the doping density from calculation. The density of each group of traps was determined by the peak height. The effective trap density ($N_{tr}$), conductance frequency ($\omega$), effective capture cross-section ($\sigma_{tr}$), and surface recombination velocity for each group of correlated traps ($S_{tr}$) are shown in Table G.2 in Appendix G.5.2. Changes in defect activity and density reflect the effect of the processes on the GaInAs/oxide interface and in the oxide within \textasciitilde3 nm of this
Figure G.3. Normalized C-V curves for Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices. All C-V curves were normalized to the oxide capacitance, $C_{ox}$, in accumulation of the 30 MHz curves. All C-V curves were recorded by forward scanning (f) from depletion to accumulation followed by backward scanning (b) from accumulation to depletion. Both forward and reverse bias curves are shown at the following frequencies: 1 kHz (○), 10 kHz (□), 100 kHz (△), 1 MHz (<), 10 MHz (▽), 20 MHz (⊳), 30 MHz (-). The ideal C-V curves are indicated by the heavy continuous red line. The dielectric constants at 1 kHz and 30 MHz as well as the surface recombination velocity are included with 95% margins of error from Table G.1, where the processing sequences are defined that were used to fabricate the MISCAP devices.
<table>
<thead>
<tr>
<th>Process</th>
<th>$N_d(10^{17})$</th>
<th>$V_{fbh}$</th>
<th>$V_{fbm}$</th>
<th>$Q_f (10^{11})$</th>
<th>$t_{ox}$</th>
<th>EOT</th>
<th>$C_{ox}$</th>
<th>$\kappa_{30}$</th>
<th>$\kappa_1$</th>
<th>SRV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NoxAoxM</td>
<td>17.3 ± 11.9</td>
<td>0.71 ± 0.02</td>
<td>0.23 ± 0.07</td>
<td>25.1 ± 7.1</td>
<td>11 ± 1</td>
<td>4.2 ± 1.7</td>
<td>0.73 ± 0.27</td>
<td>10 ± 1.5</td>
<td>11.8 ± 1.8</td>
<td>34.4 ± 3.7</td>
</tr>
<tr>
<td>NoxAoxMFGA</td>
<td>10.5 ± 1.7</td>
<td>0.7 ± 0.0</td>
<td>0.56 ± 0.02</td>
<td>8.8 ± 0.95</td>
<td>90.5</td>
<td>3.4 ± 0.2</td>
<td>0.88 ± 0.06</td>
<td>12 ± 0.8</td>
<td>13 ± 0.8</td>
<td>1 ± 0.3</td>
</tr>
<tr>
<td>NoxAoxMNH$_3$</td>
<td>8.2 ± 1.2</td>
<td>0.69 ± 0.0</td>
<td>0.55 ± 0.08</td>
<td>7.7 ± 4.2</td>
<td>90.11</td>
<td>4.2 ± 0.3</td>
<td>0.73 ± 0.05</td>
<td>10.4 ± 0.7</td>
<td>11.6 ± 0.9</td>
<td>3.5 ± 0.8</td>
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<td>NoxAoxFGAM</td>
<td>32 ± 7.1</td>
<td>0.7 ± 0.0</td>
<td>0.44 ± 0.0</td>
<td>18.0 ± 2.0</td>
<td>90.11</td>
<td>3.5 ± 0.4</td>
<td>0.87 ± 0.09</td>
<td>12.3 ± 1.2</td>
<td>14.4 ± 1.6</td>
<td>6.8 ± 0.9</td>
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<tr>
<td>NoxAoxNH$_3$M</td>
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<td>0.7 ± 0.0</td>
<td>0.23 ± 0.0</td>
<td>40 ± 2.5</td>
<td>90.11</td>
<td>2.9 ± 0.2</td>
<td>1.06 ± 0.07</td>
<td>15 ± 1</td>
<td>17.6 ± 1.2</td>
<td>6.1 ± 0.5</td>
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<td>LHFAoxM</td>
<td>10.7 ± 7.4</td>
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<td>0.40 ± 0.41</td>
<td>15.6 ± 15.5</td>
<td>10.2 ± 0.8</td>
<td>4.1 ± 1.2</td>
<td>0.76 ± 0.22</td>
<td>10 ± 1.3</td>
<td>11.5 ± 1.8</td>
<td>28.9 ± 13.4</td>
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<td>0.68 ± 0.0</td>
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<td>90.10</td>
<td>6.4 ± 0.3</td>
<td>0.56 ± 0.05</td>
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<td>35.3 ± 2.2</td>
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<td>0.72 ± 0.0</td>
<td>-0.96 ± 0.03</td>
<td>59.8 ± 5.8</td>
<td>90.116</td>
<td>3.5 ± 0.3</td>
<td>0.88 ± 0.08</td>
<td>13 ± 1.2</td>
<td>14.4 ± 2.3</td>
<td>79.2 ± 28.2</td>
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Abbreviations: Nox (native oxide), LHF (liquid phase HF), Aox (ALD Al$_2$O$_3$), FGA (forming gas annealing in hydrogen), NH$_3$ (annealing in ammonia), M (metal deposition), $N_d$ (doping density), $V_{fbh}$ (ideal flat band voltage), $V_{fbm}$ (measured flat band voltage), $t_{ox}$ (total physical oxide thickness and the ‘$\diamond$’ indicates thickness before FGA and NH$_3$), EOT (equivalent oxide thickness with respect to SiO$_2$), $C_{ox}$ (oxide capacitance), $\kappa_{30}$ (dielectric constant at 30 MHz), $\kappa_1$ (dielectric constant at 1kHz), and SRV (total surface recombination velocity). Error bars are 95% margins of error obtained by averaging data from 10 gates on each MISCAP device, except for the NoxAoxM and LHFAoxM devices where averaging extended over four MISCAP devices with 10 gates on each MISCAP device. Processing details are given in the text.
interface. The combined effect of all defects was obtained by summing the individual SRV values to obtain the total SRV, and this single value represents the activity and density of all interface traps. The total SRV values are reported in Table G.1.

The formation of inversion regions in the C-V curves of the NoxAoxMFGA and NoxAoxMNH₃ processes occur at frequencies below 1 MHz as shown in Fig. G.3. Achieving inversion in a C-V curve of a high quality MISCAP interface requires an interface with no midgap states and a fast generation-recombination lifetime of minority carriers to be able to follow the ac displacement current. The ac probe frequency for full inversion is related to the generation-recombination lifetime of minority carriers, \( \tau \), by

\[
f(v_g) = \frac{en_iW(v_g)}{\tau C(v_g)} \times \frac{1}{v^{18}},
\]

where \( e \) is the unit charge, \( n_i \) (m\(^{-3}\)) is the intrinsic carrier density, \( W(v_g) \) (m) is the depletion width, \( C(v_g) \) (F m\(^{-2}\)) is the MISCAP capacitance, \( v_g \)(V) is the applied bias gate voltage, and \( v \)(V) is the applied ac probe voltage amplitude. The probe frequency for achieving inversion varies as the space charge density, depletion width, and MISCAP capacitance vary with the gate voltage. The highest ac frequency for formation of a full inversion region can be estimated by letting \( W(v_g) \sim W_0 \sim 100 \) nm, which is the maximum depletion width for the Ga\(_{0.47}\)In\(_{0.53}\)As/Al\(_2\)O\(_3\) MISCAP devices with an average substrate doping of \( N_d \sim 10^{24} \) m\(^{-3}\) from Table G.1. The MISCAP capacitance was \( C(v_g) \sim C_{ox} \sim 0.01 \) Fm\(^{-2}\), and the applied ac probe voltage used to obtain the C-V curves was \( v \sim 26 \) mV. The intrinsic carrier density in Ga\(_{0.47}\)In\(_{0.53}\)As is \( n_i \sim 6 \times 10^{17} \) m\(^{-3}\), and we assume that the generation-recombination lifetimes are similar in the material, \( \tau_g \sim \tau_r \sim \tau^{18} \). In a highly doped direct-band gap semiconductor with low SRV, the recombination lifetime \( \tau_r \sim \left( \frac{SRV}{W_0} + BN_d \right)^{-1} \sim 1/BN_d^{21,22} \). In the MISCAP devices at room temperature, \( \tau \sim 2 \) nsec based on the radiative recombination coefficient \( B \sim 5 \times 10^{-16} \) m\(^{-3}\)s\(^{-1}\) in Ga\(_{0.47}\)In\(_{0.53}\)As\(^{20}\). Substituting into the equation for \( f(v_g) \), a probe frequency of \( f(v_g) \sim 10 \) kHz is needed to obtain full inversion. In all of the processes.
Figure G.4. Large AC signal conductance for Ga0.47In0.53As/Al2O3 MISCAP devices: a) NoxAox series where Al2O3 was deposited on top of native oxide and b) LHF Aox series where Al2O3 was deposited on an HF-last surface. The process sequences used to label the samples are defined in the text as well as in the note in Table G.1. The curves included in each series are ⊗ NoxAoxM and LHF AoxM, ○ NoxAoxM- FGA and LHF AoxMFGA, □ NoxAoxMNH3 and LHF AoxMNH3, △ NoxAoxFGAM and LHF AoxFGAM, and ♦ NoxAoxNH3M and LHF AoxNH3M. The insets shown for low and high frequency ranges highlight trends in the curves.
with low SRV, full inversion was achieved at frequencies at or below 10 kHz in the C-V curves. The formation of a full inversion layer was observed above 1 kHz by Zhao et al. for high quality Ga$_{0.47}$In$_{0.53}$As interfaces with Al$_2$O$_3$, HfO$_2$, and LaAlO$_3$ films at a substrate doping of $\sim 5 \times 10^{22}$ m$^{-3}$. This confirms the above approach where the generation-recombination lifetime of minority carriers is scalable and only depends on the doping density.

G.4 Discussion

Comparing the $\kappa$ of thin films that satisfy the Terman frequency condition with the dielectric constant of bulk Al$_2$O$_3$ is indicative of the integrity of the Al$_2$O$_3$ deposited by ALD as a high permittivity dielectric. The dielectric constant extracted from the C-V curves is dominated by the Al$_2$O$_3$ layer because its thickness of $\sim$10 nm is much larger than that of the native or As oxide layers, which are both $<$0.5 nm thick. The natural frequency dispersion of Al$_2$O$_3$ is negligible in the frequency range where the C-V curves and LSC signals were measured$^{23}$. Defect-free, amorphous Al$_2$O$_3$ deposited by ALD is consequently expected to have a dielectric constant in the same range as birefringent crystalline Al$_2$O$_3$, which is $9.3 \leq \kappa \leq 11.5$ accounting for the variation along the different crystal axes$^{24}$. For the non-annealed samples, the dielectric constant range for frequencies from 1 kHz to 30 MHz was $\sim$10-11.8 for NoxAoxM and $\sim$10-11.5 for LHFAoxM, which are similar to the bulk values. The SRV is a measure of the interface quality in a MOS device$^{12}$, and values of $34.4 \pm 3.7$ cm/s and $28.9 \pm 13.4$ cm/s were measured for NoxAox and LHFAox, respectively. These interfaces were far from ideal based on the SRV of $\sim$1 cm/s or lower measured on a hydrogen-passivated crystalline Si surface submerged in 49% HF$^{13}$ and on a thermal SiO$_2$ film on Si that was processed with a FGA$^{12}$. Although comparison
of SRV values between materials with different bandgaps is problematic because the wider the band gap, the more defects could be present\textsuperscript{12}, the SRV values measured for Ga\textsubscript{0.47}In\textsubscript{0.53}As are well above those for the best quality interfaces made on Si, which has a wider bandgap. The increase in $\kappa$ at lower frequencies for both of the nonannealed Ga\textsubscript{0.47}In\textsubscript{0.53}As samples is due to the response of border traps, which yield larger values of $\kappa$ in $n$-type substrates\textsuperscript{11}. The relatively small variation of $\kappa$ with frequency and the high values of the SRV indicate that the majority of the traps at the interface in these devices were due to fast states. In NoxAoxM and LHFAoxM quantifying fixed oxide charges based on the shift in the C-V curves from the ideal is ambiguous due to these fast states, which cause the C-V curves to stretch out\textsuperscript{18}. Note: border traps are present but the majority of traps are dangling bonds at the interface.

FGA and NH\textsubscript{3} annealing processes improved the interfaces containing native oxide and reduced the C-V stretchout, dispersion, and shift from the ideal curves as shown in Fig. G.3 for NoxAoxMFGA and NoxAoxMNH\textsubscript{3}. The SRV values of 1±0.3 cm/s for NoxAoxMFGA and 3.5±0.8 cm/s for NoxAoxMNH\textsubscript{3} are lower than the value for NoxAoxM, indicating that the electrical performance of the interfaces in these samples was improved and behaved similarly to a high quality passivated Si/SiO\textsubscript{2} interface\textsuperscript{12}. The conductance curves in Fig. G.4 shifted below 100 kHz and were attenuated after reactive annealing. The hydrogen passivation using a furnace appeared to be more effective than the hydrogen and nitrogen introduced by NH\textsubscript{3} in an ALD chamber.

In III-V compound semiconductors with covalent bonding, it has been shown that monovalent hydrogen is more effective at passivating dangling bonds, while nitrogen is more effective at passivating broken bonds with ionic character\textsuperscript{16}. Ga\textsubscript{0.47}In\textsubscript{0.53}As, Al\textsubscript{2}O\textsubscript{3}, and the oxide located at the interface between these two materials form chemical bonds which are partially covalent and partially ionic. The low SRV values and
relatively ideal C-V curves measured in NoxAoxMFGA and NoxAoxMNH$_3$ indicate that fast state traps due to the dangling bonds of Ga$_{0.47}$In$_{0.53}$As that are covalent were effectively passivated with monovalent hydrogen. The effect of FGA and NH$_3$ annealing on the chemical composition of native oxides is under investigation by XPS, but the formation of Ga-H and As-H due to annealing processes and the change in the chemical composition of native oxide in the presence of hydrogen have been observed$^{25,26}$.

The C-V curves for NoxAoxMFGA and NoxAoxMNH$_3$ are slightly shifted to the left or the more negative voltage side compared to the ideal C-V curves to compensate for positive fixed oxide charges$^{18}$ in the Al$_2$O$_3$. This shift is larger for the NoxAoxMNH$_3$ sample than the NoxAoxMFGA sample due to the effectiveness of the furnace hydrogen passivation. The dielectric constant range for frequencies from 1 kHz to 30 MHz was $\sim$12-13 for NoxAoxMFGA and $\sim$10.4-11.6 for NoxAoxMNH$_3$. For both processes, the dielectric constants increase at lower frequencies due to tunneling of electrons to border traps in n-type substrates$^{11}$. The values of dielectric constants obtained at high frequency when the Terman condition is satisfied are within the range of the bulk material to within measurement error. The dielectric dispersion of both samples was narrow and combined with the low SRV values shows that hydrogen effectively passivated defects at the interface and within the Al$_2$O$_3$ layer. The deposition of Al$_2$O$_3$ by ALD on the native oxide of Ga$_{0.47}$In$_{0.53}$As formed an oxide layer with a low density of defects with primarily covalent character.

Forming gas annealing of an Al$_2$O$_3$ film deposited on an HF-last surface (LH-FAoxMFGA) reduced the C-V stretch out compared to the nonannealed surface (LH-FAoxM) and lowered the SRV from 28.9$\pm$13.4 cm/s to 4.4$\pm$0.5 cm/s. Yet the dispersion in the C-V curves was large and the dielectric constants varied over $\sim$6-10 for probe frequencies from 30 MHz (Terman frequency condition) to 1 kHz. The disper-
sion is attributed to frequency- and voltage-dependent border traps that contribute a capacitance, $C_{bt}$, which is in parallel with $C_{ox}$ (Fig. G.5). By virtue of reaching the high frequency Terman condition at 30 MHz, the dielectric constant is determined only by the capacitance of the oxide, $C_{ox}$, but $\kappa$ is $6.2 \pm 0.3$ at 30 MHz, which is well out of the range expected for bulk Al$_2$O$_3$.

To explain this result we propose that another capacitance was present due to charges in the oxide, $C_{oc}$, that depend on voltage and polarity, but not frequency (Fig. G.5). Biasing an ideal MISCAP device in accumulation yields a capacitance that only accounts for $C_{ox}$ formed across the dielectric$^{18}$. In the absence of oxide charges, $C_{ox} = \frac{Q}{v_g}$, where $Q$ is the charge that accumulates at the gate with the same polarity based on the definition of capacitance$^{27}$ and $v_g$ is the gate voltage. Charge in the oxide, $Q_{oc}$, alters the capacitance. The modified oxide capacitance, $C'_{ox}$, can be modeled by applying Gauss' law to obtain the net accumulated charge inside of a parallel plate capacitor, accounting for the charge in the oxide and the polarity. Therefore, $C'_{ox} = \frac{Q \pm Q_{oc}}{v_g}$, where the sign in the numerator is chosen to account for the polarity of the oxide charge in the dielectric. Rearranging yields $C'_{ox} = \frac{Q}{v_g} \pm \frac{Q_{oc}}{v_g} = C_{ox} \pm C_{oc}$, indicating that the capacitance $C_{oc}$ is in parallel with $C_{ox}$.

On an $n$-type substrate, negative (positive) charge in the oxide decreases (increases) the capacitance in accumulation $C'_{ox}$ and correspondingly the value of $\kappa$.

In a MISCAP device, the total charge in the oxide is comprised of trapped, fixed, and mobile charges that are sufficiently far away from the interface that there is no exchange of charge carriers with the underlying semiconductor$^{16,18}$. Trapped charge that is close enough to shift the C-V curves away from the ideal are known as fixed oxide charges$^{18}$. Therefore, the polarity of fixed oxide charges is a good indication of the polarity and the chemical composition of trapped charges in the bulk oxide. Based on the slight shift of the C-V curves for the LHFAoxMFGA sample to the right (more
positive side) of the ideal curve, the fixed oxide charge is negative. This contribution reduces the capacitance in accumulation, explaining the low value of $\kappa$ that was measured. The fixed oxide charge density reported in Table G.1 for LHFAoxMFGA can not be used to correct for $C_{oc}$ because the fixed oxide charge does not account for all of the charge in the bulk.

Ammonia annealing an Al$_2$O$_3$ film deposited on an HF-last surface (LHFAoxMNH$_3$) reduced the C-V stretch out and dispersion compared to the nonannealed and forming gas samples. The SRV of 1.5±0.3 cm/s is comparable to the lowest value measured in this study for the native oxide sample that was annealed in forming gas (NoxAoxMFGA). The dispersion in the C-V curves for LHFAoxMNH$_3$ was caused by electron tunneling from the $n$-type semiconductor substrate to border traps at low frequencies. The $\kappa$ $\sim$10.2 at 30 MHz is within the range of the bulk dielectric constant for Al$_2$O$_3$ compared to the sample processed in forming gas where $\kappa$ $\sim$6.2 due to the charging of defects in the oxide. The C-V curves for LHFAoxMNH$_3$ are shifted to the left of the ideal curve, indicating that the fixed oxide charge was positive, similar to NoxAoxMFGA and NoxAoxMNH$_3$. There is ionic as well as covalent bonding in Al$_2$O$_3$ as in HfO$_2$. The electronegativity of Al is larger than Hf but close so the ionic bonds due to oxygen vacancies in Al$_2$O$_3$ should be similar to those observed in HfO$_2$. Nitrogen from the NH$_3$ annealing was effective in passivating oxygen vacancies in the Al$_2$O$_3$ that are negatively-charged, leaving residual defects that are primarily covalent with a positive polarity.

The nature of the oxide defects in the non-annealed sample LHFAoxM is ambiguous since both the C-V curves and the SRV measurements were dominated by the activity of fast states at the Ga$_{0.47}$In$_{0.53}$As interface with Al$_2$O$_3$. It is not clear whether these defects were positive, negative, or had both polarities, but by isolating defects of a particular type by reactive annealing, some insight is gained. As discussed above,
Figure G.5. MISCAP equivalent circuit. An ideal MISCAP device with no substrate resistivity contains only an oxide capacitance, $C_{ox}$, and semiconductor capacitance, $C_S$, in series\textsuperscript{18}. In accumulation, $C_S$ approaches infinity\textsuperscript{18}. The frequency- and voltage-dependent capacitance due to border traps, $C_{bt}$, is in parallel with $C_{ox}$ and causes the frequency dispersion in C-V curves in accumulation\textsuperscript{11}, and hence dielectric values at low frequencies. The voltage- and polarity-dependent, but frequency-independent capacitance due to oxide charging, $C_{oc}$, is also in parallel with the oxide capacitance $C_{ox}$. $C_{oc}$ accounts for defects in the $\text{Al}_2\text{O}_3$ that are not in electrical contact with the underlying semiconductor. The polarity reverse (forward) biased $C_{oc}$ due to negative (positive) oxide charges reduces (increases) the capacitance measured in accumulation, and hence the dielectric constant measured at the high frequency Terman condition.
introducing monovalent hydrogen by an FGA process passivated defects that had covalent bonding character, leaving defects in the Al₂O₃ layer that had primarily ionic character with a negative polarity. Introducing both hydrogen and nitrogen by an NH₃ annealing process passivated defects with both covalent and ionic bonding character. This must mean that deposition of Al₂O₃ by ALD on HF-last Ga₀.₄₇In₀.₅₃As created covalent and ionic defects with both positive and negative polarities.

The oppositely-charged defects were approximately balanced for the LHFAoxM process, lowering the oxide charge capacitance, $C_{oc}$, so that the dielectric constant at 30 MHz was largely unaffected at the Terman frequency condition. The NoxAoxM process yielded relatively few ionic-type defects because the FGA had much more impact than NH₃ annealing, leading one to conclude that the starting interface plays an important role in bond and defect formation in oxides deposited by ALD.

Annealing in forming gas or ammonia before metal deposition did not improve the interface. The C-V stretch out and frequency dispersion is larger for the NoxAoxFGAM, NoxAoxNH₃M, LHFAoxFGAM, and LHFAoxNH₃M MISCAP devices than in the corresponding processes where the annealing was done after metal deposition (Fig. G.3). The oxides of samples annealed before metal deposition were exposed to fluorescent light, whereas metal covered the oxides below the electrodes of samples annealed after metal deposition. The chemical bond energies between H and Ga, In, As, O, and Al fall within the ∼200-2000 nm (E∼6.2-0.62 eV) emission range of a typical fluorescent lamp¹ as shown in Fig. G.6. Nitrogen forms an ionic bond in Al₂O₃ and therefore its binding energy is roughly the same order as the nitrogen bond energy in HfO₂ or ∼0.4 eV¹⁶,²⁹. This binding energy also falls within the emission range of a typical black body thermal emitter, i.e., an incandescent lamp or daylight. Although more energy is typically required to break a bond using light than the bond energy, which depends on the difference in energies between the antibonding and bonding orbitals,
and this is complicated further by interface formation and by the bulk substrate, the electrical results suggest that the light exposure between annealing and metallization degraded the interface by breaking the bonds that had formed between H and N and the constituents of the interface, leaving unsatisfied bonds. Evidence for light-initiated oxidation on a hydrogen-passivated silicon surface has been reported previously\textsuperscript{32,33}, which indirectly confirms our conclusion.

The hypothesis that interfaces were degraded by light exposure was independently tested by fabricating two nonpatterned LHFAoxM samples, annealing one in forming gas and the other in ammonia, stripping the metal layer off, exposing to light, and re-metallizing both through a shadow mask. The blanket Ni/Au layer was stripped off with a 3:1:2 HCl:HNO\textsubscript{3}:H\textsubscript{2}O solution (aqua regia) for 1 min, rinsing in ultra pure water, and drying with N\textsubscript{2}. The Al\textsubscript{2}O\textsubscript{3} layer was not etched during the metal striping process as verified by monitoring the oxide thickness with ellipsometry. Removing
the metal exposes the repaired interfaces to light. The stretch out and frequency dispersion in the C-V curves as well as the reappearance of high frequency conductance peaks above 100 kHz in the LSC data shown in Fig. G.7 confirms that the interfaces were degraded by light exposure. An \( \sim 10 \) nm-thick \( \text{Al}_2\text{O}_3 \) oxide layer was used in these processes to ensure that only the \( \text{Ga}_{0.47}\text{In}_{0.53}\text{As}/\text{Al}_2\text{O}_3 \) interface was probed\(^{12,16,18} \). The intensity and duration of light exposure was not quantified or controlled in these experiments. Frequency dispersion is observed above 10 MHz, and the LSC peaks indicate that the defect activity approached the nonannealed devices. Defect activity above 30 MHz could not be confirmed because these higher frequencies were unavailable. It is not clear whether the 30 MHz responses accurately achieved the high frequency Terman condition to assure unambiguous measurements of dielectric constants and SRV values. The fits to the LSC peaks in Fig. G.7 deviate from the data at high frequencies. There are two possible reasons for this slight deviation: a) LSC peaks above 30 MHz which would contribute tails in this range or b) changes in the trap density and capture cross-section induced by the probing voltage. Mathematically the higher frequency LSC peaks on a log scale include more frequency intervals and, hence, all of the LSC peaks in frequency space are required to obtain accurate fits and SRV values. Also in the LSC measurement and the fitting procedure, it is assumed that the density and capture-cross section of traps does not change. But changes in both the density and capture cross-section can occur due to the high-electric field Fowler-Nordheim stress\(^{18,34} \) or avalanche injection\(^{18} \) in thin oxides, and these effects are inevitable during C-V and LSC measurements. Accurate SRV values may be larger than those reported, yet even with all of the limitations and qualifications, the C-V and LSC measurements up to 30 MHz were sufficient to confirm the adverse effect of light exposure on these interfaces for electrical device function.
Figure G.7. Normalized C-V curves (top) and LSC signal (bottom) for MISCAP devices fabricated using LHFAoxMFGAM and LHFAoxMNH₃M processes (defined in Table G.1). All C-V curves were normalized to the oxide capacitance in accumulation at 30 MHz. The probe frequencies were 1 kHz (○), 10 kHz (□), 100 kHz (△), 1 MHz (⊳), 10 MHz (▽), 20 MHz (⊲), 30 MHz (-), and the ideal C-V curve is shown by a solid line.
In all of the MISCAP devices exposed to light, a discussion of the fixed oxide charges and the dielectric constants at 30 MHz is challenging and leads to indefinite conclusions due to the large stretch out by fast states and the lack of a true high frequency Terman condition\textsuperscript{18}. But the dispersion in accumulation of all of the C-V curves was caused by tunneling of electrons from the semiconductor to border traps, which respond to the probe frequency by increasing the capacitance in accumulation at low frequencies in $n$-type substrates\textsuperscript{11}.

G.5 Summary and Conclusion

The electrical behavior of the interfaces formed between Ga$_{0.47}$In$_{0.53}$As and an Al$_2$O$_3$ film deposited by ALD depended on the native or residual oxide present, the reactive annealing step, and light exposure. The variation of the dielectric constant with frequency over a narrow range and the large SRV values for NoxAoxM indicates that without annealing defects were primarily covalent with a positive polarity due to dangling bonds in the interfacial region of the semiconductor-native oxide-deposited oxide stack. Annealing in forming gas (NoxAoxMFGA) improved this interface more than annealing in NH$_3$ (NoxAoxMNH$_3$). Removing the native oxide in the LHFAoxM sample produced both covalent and ionic defects with both positive and negative polarities, respectively, and annealing in NH$_3$ (LHFAoxMNH$_3$) had a more pronounced impact in repair of the interface than annealing in forming gas (LHFAoxMFGA). The ionic defects were most likely due to oxygen vacancies in the Al$_2$O$_3$ film. Although the band gap of GaInAs is much narrower than that of Si, which makes defect repair easier, reactive annealing with or without native oxide present produced interfaces comparable to thermally-prepared and reactive annealed Si/SiO$_2$ with SRV values in the vicinity of $\sim$1 cm/s. Fabrication of NoxAoxMFGA eliminates one processing step
compared to fabrication of LHFAoxMNH$_3$. Yet the thinner As oxide starting surface after HF treatment may be more advantageous than one containing a buffer native oxide in scaling down devices, similar to Si/SiO$_x$/Al$_2$O$_3$ due to the low dielectric constant of SiO$_x$.$^{35}$

The low value of the dielectric permittivity extracted from C-V curves at the high frequency Terman condition for the HF-last starting surface that was annealed in forming gas (LHFAoxMFGA) is due to trapped and fixed oxide charges in the Al$_2$O$_3$ film. This effect was explained by proposing a frequency-independent, but polarity-dependent capacitance in parallel with the oxide capacitance that can increase or decrease the capacitance in accumulation, and hence the value of the dielectric constant. A capacitance due to charges in the oxide film also can explain the low values of the dielectric permittivity measured previously for Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices.$^{5,7,9}$

Even after forming gas and NH$_3$ annealing, exposure of Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ stacks to ambient light appreciably degraded the interfaces. This result agrees with previous work by McIntyre et al.$^5$ and Kim et al.$^9$, who fabricated a Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ sample by in situ desorption of an As protective layer in forming gas at ambient pressure and 460°C followed by ALD deposition of Al$_2$O$_3$. However, after this process, metal deposition and post-FGA annealing were used to improve the interface quality in their Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices.

One aspect of obtaining values of the surface recombination velocity is that they provide a means of quantitatively comparing Ga$_{0.47}$In$_{0.53}$As passivated by ALD Al$_2$O$_3$ to Ga$_{0.47}$In$_{0.53}$As passivated by lattice-matched InP grown by MOVPE. The SRV values of as-deposited ALD Al$_2$O$_3$ in NoxAoxM (34.4 ± 3.7 cm/s) and in LHFAoxM (28.9 ± 13.4 cm/s) samples are comparable to the SRV of 45 cm/s in a GaInAs/InP heterojunction.$^{14}$ The latter SRV was measured based on external quantum efficiency
**Figure G.8.** Compendium of surface recombination velocities for different interfaces, including Si/SiO$_2$, Si/SiO$_2$/Al$_2$O$_3$ and Si/Al$_2$O$_3$\(^{12}\), Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ (this work), and Ga$_{0.47}$In$_{0.53}$As/InP\(^{14}\). The abbreviations are Tox (thermal SiO$_2$), Cox (chemical SiO$_2$ grown by piranha last), Aox (aluminum oxide Al$_2$O$_3$ deposited by ALD), FGA (forming gas annealing), NH$_3$ (NH$_3$ annealing), VA (vacuum annealing), X (XPS analysis), p (piranha), LHF (liquid HF), and Nox (native oxide).
at high carrier density generation where the semiconductor energy bands are flat and quasi-Fermi levels are formed, activating all defects across the band gap\textsuperscript{14}. This indicates that passivation of surface defects by lower cost ALD methods are as efficient as a more expensive MOVPE method for Ga\textsubscript{0.47}In\textsubscript{0.53}As.

A compendium of SRV values for different Si and GaInAs interfaces and process flows is shown in Fig. G.8. Included are Si passivated by hydrogen in solution\textsuperscript{13}, Si passivated by SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} films after vacuum and post-FGA annealing processes\textsuperscript{12}, results from this work for GaInAs passivated by native oxide and Al\textsubscript{2}O\textsubscript{3} before and after reactive annealing, and a MOVPE-grown GaInAs/InP heterojunction\textsuperscript{14}. The lowest published surface recombination velocity value of 0.25 cm/s for Si(111)-H\textsuperscript{13} is free from the effects of band bending and is a suggested baseline for quantifying an ideal surface passivation where all dangling bonds are satisfied with no mid-gap energy states. Other surfaces and interfaces after passivation can be compared to Si(111)-H, independent of semiconductor material, passivation layer, and methods of passivation, based on the value of the deep-level surface recombination velocity\textsuperscript{12}.

G.5.1 Acknowledgment

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## G.5.2 Definition of Variables

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<tr>
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<td>Radiative recombination coefficient (m$^{-3}$s$^{-1}$)</td>
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<td>$V_{fb\text{bi}}$</td>
<td>ideal flat band voltage (V)</td>
</tr>
<tr>
<td>$V_{fb\text{bm}}$</td>
<td>measured flat band voltage (V)</td>
</tr>
<tr>
<td>$v_g$</td>
<td>bias gate voltage (V)</td>
</tr>
<tr>
<td>$v$</td>
<td>ac probe voltage (V)</td>
</tr>
<tr>
<td>$W$</td>
<td>depletion width (cm)</td>
</tr>
<tr>
<td>$W_0$</td>
<td>maximum depletion width (cm)</td>
</tr>
</tbody>
</table>

* The parameter is normalized to gate area, $A_G$. 
Table G.2. Large AC Conductance Results for Ga$_{0.47}$In$_{0.53}$As/Al$_2$O$_3$ MISCAP devices$^c$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\omega_1$ (kHz)</th>
<th>$N_{tr1}$ (10$^{15}$ cm$^{-2}$)</th>
<th>$\sigma_{tr1}$ (10$^{-25}$ cm$^2$/s)</th>
<th>$S_{tr1}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NoxAoxM</td>
<td>4.1 ± 1.1</td>
<td>6.7 ± 3.6</td>
<td>4.9 ± 2.7</td>
<td>0.10 ± 0.10</td>
</tr>
<tr>
<td>NoxAoxMFGA</td>
<td>13.3 ± 0.7</td>
<td>4.3 ± 1.5</td>
<td>2.3 ± 1.0</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>NoxAoxMNH$_3$</td>
<td>2.8 ± 0.4</td>
<td>4.0 ± 0.7</td>
<td>7.1 ± 1.4</td>
<td>0.10 ± 0.00</td>
</tr>
<tr>
<td>NoxAoxFGAM</td>
<td>2.3 ± 0.4</td>
<td>3.3 ± 0.5</td>
<td>1.6 ± 0.7</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>NoxAoxNH$_3$M</td>
<td>1.8 ± 0.2</td>
<td>3.7 ± 0.2</td>
<td>1.0 ± 0.2</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>LHFAoxM</td>
<td>0.9 ± 1.1</td>
<td>1.2 ± 0.9</td>
<td>1.8 ± 2.4</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>LHFAoxMFGA</td>
<td>13.0 ± 3.4</td>
<td>2.9 ± 0.2</td>
<td>63.0 ± 1.4</td>
<td>0.7 ± 0.20</td>
</tr>
<tr>
<td>LHFAoxMNH$_3$</td>
<td>1.4 ± 0.5</td>
<td>5.0 ± 2.5</td>
<td>4.3 ± 2.0</td>
<td>0.11 ± 0.00</td>
</tr>
<tr>
<td>LHFAoxFGAM</td>
<td>2.0 ± 0.2</td>
<td>1.9 ± 0.1</td>
<td>1.8 ± 0.4</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>LHFAoxNH$_3$M</td>
<td>2.6 ± 0.2</td>
<td>1.8 ± 0.2</td>
<td>2.4 ± 0.6</td>
<td>0.02 ± 0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\omega_2$ (kHz)</th>
<th>$N_{tr2}$ (10$^{15}$ cm$^{-2}$)</th>
<th>$\sigma_{tr2}$ (10$^{-25}$ cm$^2$/s)</th>
<th>$S_{tr2}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NoxAoxM</td>
<td>78.5 ± 68.4</td>
<td>15.7 ± 1.9</td>
<td>9 ± 4.5</td>
<td>5.1 ± 2.0</td>
</tr>
<tr>
<td>NoxAoxMFGA</td>
<td>9.8 ± 5.2</td>
<td>3.6 ± 0.7</td>
<td>1.7 ± 0.7</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>NoxAoxMNH$_3$</td>
<td>21.8 ± 4.6</td>
<td>3.3 ± 0.6</td>
<td>5.4 ± 1.4</td>
<td>0.61 ± 0.1</td>
</tr>
<tr>
<td>NoxAoxFGAM</td>
<td>166.0 ± 26.3</td>
<td>16.7 ± 1.5</td>
<td>10.8 ± 2.5</td>
<td>6.6 ± 0.9</td>
</tr>
<tr>
<td>NoxAoxNH$_3$M</td>
<td>150.5 ± 4.8</td>
<td>20.0 ± 1.2</td>
<td>8.0 ± 1.0</td>
<td>5.9 ± 0.5</td>
</tr>
<tr>
<td>LHFAoxM</td>
<td>50.8 ± 44.5</td>
<td>79.7 ± 37.4</td>
<td>10.0 ± 6.8</td>
<td>3.0 ± 2.4</td>
</tr>
<tr>
<td>LHFAoxMFGA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LHFAoxMNH$_3$</td>
<td>9.0 ± 2.9</td>
<td>3.6 ± 1.2</td>
<td>2.6 ± 1.1</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>LHFAoxFGAM</td>
<td>14.5 ± 4</td>
<td>17.4 ± 1.7</td>
<td>12.6 ± 1.6</td>
<td>8.1 ± 0.3</td>
</tr>
<tr>
<td>LHFAoxNH$_3$M</td>
<td>202.4 ± 7.3</td>
<td>17.0 ± 1.9</td>
<td>18.8 ± 3.0</td>
<td>11.8 ± 0.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\omega_3$ (MHz)</th>
<th>$N_{tr3}$ (10$^{14}$ cm$^{-2}$)</th>
<th>$\sigma_{tr3}$ (10$^{-25}$ cm$^2$/s)</th>
<th>$S_{tr3}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NoxAoxM</td>
<td>141.1 ± 11.3</td>
<td>5.0 ± 1.0</td>
<td>16.0 ± 4.7</td>
<td>28.8 ± 6.8</td>
</tr>
<tr>
<td>NoxAoxMFGA</td>
<td>0.2 ± 0.2</td>
<td>1.5 ± 0.7</td>
<td>0.3 ± 0.2</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>NoxAoxMNH$_3$</td>
<td>1.0 ± 0.4</td>
<td>3.2 ± 0.6</td>
<td>2.5 ± 0.9</td>
<td>2.7 ± 0.8</td>
</tr>
<tr>
<td>NoxAoxFGAM</td>
<td>13.1 ± 2.0</td>
<td>60.1 ± 10.7</td>
<td>0.01 ± 0.0</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>NoxAoxNH$_3$M</td>
<td>11.2 ± 0.6</td>
<td>68.9 ± 4.5</td>
<td>0.01 ± 0.0</td>
<td>0.2 ± 0.0</td>
</tr>
<tr>
<td>LHFAoxM</td>
<td>12.1 ± 6.3</td>
<td>3.0 ± 1.9</td>
<td>24.2 ± 18.8</td>
<td>25.7 ± 16.3</td>
</tr>
<tr>
<td>LHFAoxMFGA</td>
<td>1.7 ± 0.1</td>
<td>1.2 ± 0.2</td>
<td>8.5 ± 0.8</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td>LHFAoxMNH$_3$</td>
<td>0.2 ± 0.1</td>
<td>5.7 ± 2.4</td>
<td>0.7 ± 0.3</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>LHFAoxFGAM</td>
<td>19.2 ± 2.4</td>
<td>4.4 ± 0.3</td>
<td>16.6 ± 2.2</td>
<td>27.2 ± 2.2</td>
</tr>
<tr>
<td>LHFAoxNH$_3$M</td>
<td>29.2 ± 11.2</td>
<td>9.6 ± 7.4</td>
<td>26.0 ± 10.1</td>
<td>67.4 ± 28.5</td>
</tr>
</tbody>
</table>

$^c$ The abbreviations are Nox (native oxide), LHF (liquid phase HF), Aox (ALD Al$_2$O$_3$), FGA (forming gas annealing in hydrogen), NH$_3$ (ammonia annealing), M (metal deposition), $\omega_{1,2,3}$ (LSC frequency peak of correlated traps) $N_{tr1,2,3}$ (effective correlated traps density), $\sigma_{tr1,2,3}$ (effective correlated traps capture cross-section), and $S_{tr1,2,3}$ (surface recombination velocity of correlated traps). Error bars are 95% confidence interval of the mean value, obtained over 10 gates on each MISCAP device, except for the NoxAoxM and LHFAoxM devices where averaging extended over four MISCAP devices for each rather than one device. The $N_{tr1,2,3} = D_{tr1,2,3}E_g$, where $D_{tr1,2,3}$ is defect density per eV and it is obtained from LSC signal peaks$^{12}$, and band gap energy of $E_g \approx 0.74eV$ is used for Ga$_{0.47}$In$_{0.53}$As.
References


