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Reaction of aqueous ammonium sulfide on SiGe 25%

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SiGe 25% substrates were treated with aqueous solutions of ammonium sulfide with and without added acid to understand the adsorption of sulfur on the surface. X-ray photoelectron spectroscopy showed no sulfide layer was deposited from aqueous $(\text{NH}_4)_2\text{S}$ alone and instead both Si and Ge oxides formed during immersion in the sulfur solution. The addition of hydrofluoric and hydrochloric acids dropped the pH from 10 to 8 and deposited sulfides, yet increased the oxide coverage on the surface and preferentially formed Ge oxides. The sulfur coverage grew with increasing concentrations of acid in the aqueous $(\text{NH}_4)_2\text{S}$. The simultaneous deposition of O and S is suspected to be the result of oxidized sulfur species in solution. Metal-insulator-semiconductor capacitor (MISCAP) devices were fabricated to test the electrical consequences of aqueous ammonium sulfide wet chemistries on SiGe. MISCAPs treated with acidic ammonium sulfide solutions contained fewer interface defects in the valence band region. The defect density (D_{it}) was on the order of $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$. The flat band voltage shift was lower after the acidic ammonium sulfide treatment, despite the presence of surface oxides. Adsorption of S and potentially O improved the stability of the surface and made it less electrically active. © 2017 American Vacuum Society.

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I. INTRODUCTION

Germanium and silicon germanium are desirable alternatives to conventional silicon based devices due to the smaller bandgap and increased hole mobility of germanium.¹ The incorporation of Ge into SiGe films also allows for tuning the material properties. One problem with Ge and SiGe based devices is the formation of Ge oxides, such as GeO_2 , which are soluble in water and form a relatively high density of defects at the interface with Ge.^{2,3} These oxides are etched in halogen acids, but the freshly cleaned surfaces are susceptible to reoxidation in air.⁴

Forming a covalent bond between an atom or molecule, and the top most layer of atoms on SiGe that chemically passivates the surface could also electrically passivate the interface when a dielectric film is deposited. Passivation of Ge surfaces with sulfur has been studied using both gas and liquid phase processes. Weser *et al.* characterized the structure of sulfur-passivated Ge surfaces after exposure to S_2 in a vacuum. The surface was characterized using Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). A coverage of 0.3 monolayers (MLs) of sulfur was obtained, and the sulfur atoms were in two-fold bridging sites shared between two germanium atoms.^{5,6} Alternate sources of sulfur such as H_2S have also been investigated. Gas phase H_2S dissociatively adsorbs on the surface and reaches a saturation coverage of 0.25 ML at room temperature and up to 0.5 ML after heating to 553 K to desorb hydrogen from the surface.⁷

Deposition of sulfur from aqueous solutions, such as ammonium sulfide $(\text{NH}_4)_2\text{S}$, has also been studied. Anderson

et al. used AES to show that a single layer of sulfur was deposited from $(\text{NH}_4)_2\text{S}$ on a Ge(100) substrate. LEED patterns showed that the sulfur atoms formed a bridge bonded configuration similar to that achieved in gas phase studies.⁸ In contrast, Lyman *et al.* carried out a similar experiment on Ge(001) and achieved up to 2.5 ML consisting of a disordered sulfur layer above a thin layer of bridge bonded sulfur atoms.⁹ Disorder was also observed using scanning tunneling microscopy after short immersions in ammonium sulfide, which yielded 0.3 ML of sulfur.¹⁰ To better understand the mechanism of sulfur adsorption on Ge as well as the surface structure, Fleischmann *et al.* used x-ray absorption and molecular dynamics simulations to study sulfur on Ge. They found that S forms bridge bonds to Ge, as expected. The results also show that S interacts with other species on the surface, namely Ge oxides, which inhibit the formation of a complete sulfur layer.¹¹

We report on the reaction of aqueous $(\text{NH}_4)_2\text{S}$ on clean $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.25$) (SiGe 25%) and characterize the bonding of both S and O on the surface and their impact on electrical performance. Previous work shows that $(\text{NH}_4)_2\text{S}$ solutions deposit 0.54 ML of S, but both Si and Ge oxides remain after treatment.¹² We investigated how the addition of acid to $(\text{NH}_4)_2\text{S}$ changes the S and O coverages. To complement the chemical characterization of the surface, we fabricated metal-insulator-semiconductor capacitor (MISCAP) devices to mimic the gate stack in a transistor. The electrical performance of these devices can be used to learn how to reduce the most electrically active defects and improve the performance of SiGe transistors which are in production. The problem of Ge oxides remaining on the SiGe surface has prompted studies on how to control the interface between SiGe and a dielectric. Nearly all steps in fabricating the

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MISCAPs have been studied as a means of figuring out how to control electrical defects. Recently, there have been studies on controlling the growth of both Si and Ge oxides at the SiGe/high-k (Al_2O_3) interface by manipulating the composition of the metal contact layer, plasma postnitridation, pre-atomic layer deposition (ALD) dosing, and wet chemical sulfur passivation.^{12–17} When sulfur chemistries were used before Al_2O_3 dielectric deposition in SiGe 30% MISCAPs, the density of interface defects reported was as low as $2.0 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$.¹²

II. EXPERIMENT

Hydrogen peroxide (H_2O_2 , 30%), hydrochloric acid (HCl, 37%), and VLSI grade hydrofluoric acid (HF, 49%) were purchased from Honeywell. Ammonium hydroxide (NH_4OH , 28%–30% NH_3 basis) was purchased from Sigma Aldrich. Ammonium sulfide [$(\text{NH}_4)_2\text{S}$, 20%–24%] was purchased from Alfa-Aesar. Ultrapure water (UPW, 18 $\text{M}\Omega\text{cm}$) was used to make solutions and for rinsing. All reagents and solvents were used as received.

$\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.25$) ($\sim 40 \text{ nm}$) on p-type Si(100) wafers were cut into $1.0 \times 1.8 \text{ cm}^2$ coupons. Organic contaminants were removed by immersion in SC-1 $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ with the ratio of 1:1:500 for 2 min followed by rinsing with UPW for 1 min and blown dry with N_2 . Oxides were removed by immersion in $\text{HF}:\text{HCl}:\text{H}_2\text{O}$ with the ratio of 1:3:300 for 5 min. The cleaned coupon was transferred directly, without rinsing or drying, either into an aqueous $(\text{NH}_4)_2\text{S}$ solution at room temperature for 20 min or into a water bath for 20 min, which served as a control. Acidic $(\text{NH}_4)_2\text{S}$ solutions were prepared by diluting $(\text{NH}_4)_2\text{S}$ and adding appropriate volumes of HF and HCl. Upon addition of acids, a precipitate formed. The coupon was removed, rinsed with UPW for 30 s, and blown dry with N_2 . Within 4 min, during which it was exposed to air, the coupon was loaded in a vacuum. Either the surface of the coupon was characterized immediately or a dielectric film was deposited on the coupon in the process of building a device. Electrical measurements were made on device coupons prior to any surface or film characterization.

The surface composition was measured using x-ray photoelectron spectroscopy (XPS, Physical Electronics, Model 549) equipped with a nonmonochromatic dual-anode Al/Mg x-ray source and a double-pass cylindrical mirror analyzer. The Al $K\alpha$ x-ray source (1486.6 eV) was used for all analyses, and high resolution spectra were obtained using a 0.1 eV resolution with a pass energy of 50 eV. The instrument was calibrated with the Au $4f_{7/2}$ peak at 84.0 eV (FWHM = 1.9 eV). The Ge 3d photoelectron line at 29.4 eV was used for charging correction. Peak analysis was carried out using Igor Pro (WaveMetrics, Inc., v.6.2). Shirley background subtraction was performed, and the peaks were fitted with Voigt line-shapes.¹⁸ Si/Ge peak area ratios were calculated using the Ge 2p and Si 2p peak areas and appropriate sensitivity factors.¹⁹

MISCAP devices were fabricated by depositing an alumina dielectric film on coupons prepared by one of the following three methods: (1) cleaning and drying only (control), (2)

cleaning and immersion in aqueous ammonium sulfide ($(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ 1:100, or (3) cleaning and immersion in aqueous ammonium sulfide with added acid $\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ in the ratio of 0.15:0.15:1:100. The alumina, Al_2O_3 , was deposited at 170 °C by ALD using trimethylaluminum [$\text{Al}(\text{CH}_3)_3$, Hi-K grade, Rohm and Haas] and water vapor with ultrapure nitrogen as a purge and carrier gas. The approximate Al_2O_3 film thickness deposited in each cycle was 1.3 Å, and the nominal film thickness was 10 nm measured using an ellipsometer (J.A. Woollam Company M-2000). See Fig. 3 in the supplementary material.³⁴ The dielectric film thickness was purposefully chosen to be thick enough to avoid oxide leakage. After ALD, the three coupons were fitted to a shadow mask for metal contact deposition. The shadow mask contained both a runway and four gate contacts for each coupon. Each gate contact had an area of $12.6 \mu\text{m}^2$, effectively creating three MISCAP devices per coupon. Ni and Au (50 nm/25 nm) layers were deposited through the mask using an e-beam evaporator (BOC Edwards Auto 306). To complete the fabrication of the MISCAP devices, all three coupons were annealed together in a glass tube furnace for 30 min at 400 °C in 1 slm of forming gas.

MISCAP devices were tested using an Agilent 4284a LCR meter at room temperature. Capacitance–voltage measurements from -2 to 2 V were taken for three MISCAP devices on a single coupon and averaged. Capacitance and conductance data from a single MISCAP device per coupon were used to calculate the density of interface defects (D_{it}) according to the conductance method developed by Nicollian *et al.*²⁰ Conductance was measured with a DC bias spanning accumulation to deep depletion and over a frequency range of 100 Hz–1 MHz. The applied AC signal was 10 mV. An upper limit of 1 MHz was used because D_{it} is known to be less accurate above this frequency.²⁰ All D_{it} values were corrected for series resistance if frequency dispersion in accumulation was observed. Frequency dispersion data are shown in Figs. 6 and 7 of the supplementary material.³⁴

III. RESULTS

The surface composition was monitored using XPS after treatment with $(\text{NH}_4)_2\text{S}$. Figure 1(a) shows the high resolution XPS spectra of the Si 2p, Ge 2p, O 1s, and S 2p regions of the SiGe native oxide surface with no solvent cleaning. In the Si 2p region, peaks at 99.4 and 103.3 eV correspond to bulk Si and SiO_x , respectively.²¹ Bulk Ge and GeO_2 are assigned at 1217.4 and 1221.3 eV in the Ge 2p region, and the O 1s region shows a single, broad peak at 532.7 eV (FWHM = 2.4 eV) corresponding to a mixture of Si and Ge oxides.^{21,22} The broad peak at approximately 168 eV is assigned to a satellite peak from the Si 2s photoelectron line.

Figure 1(b) shows a 2 min immersion in SC-1 solution and 4 min of air exposure as with all the other coupons. Si and Si oxides are detected in the Si 2p region. The area ratio shows that the intensity of the Ge 2p peaks is reduced by a factor of 1.8 compared to a native oxide surface due to the selective removal of Ge from the film. The bulk peak shifts slightly to higher binding energy at 1217.6 eV, and a broad

FIG. 1. XPS spectra of SiGe coupons after immersion in increasing concentrations of $(\text{NH}_4)_2\text{S}$. All coupons were previously cleaned with SC-1 and HF/HCl comixed solutions before immersion in $(\text{NH}_4)_2\text{S}$. Coupons were transferred to ultrahigh vacuum for analysis within 4 min of ambient air exposure. (a) Native oxides, (b) 2 min of immersion in $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ with the ratio of 1:1:500 followed by 1 min DIW rinse, (c) 5 min of immersion in HF:HCl: H_2O with the ratio of 1:3:300, (d) 20 min of immersion in UPW alone, and $(\text{NH}_4)_2\text{S}$ at dilutions v/v of (e) 1:1000, (f) 1:100, and (g) 1:10 and (h) undiluted. Solid lines correspond to the fitted peaks, and circle markers correspond to data.

peak at 1220.5 eV is attributed to a mixture of Ge suboxides on the surface. GeO_2 does not appear because it is soluble in water. The broad peak in the O 1s region shifts slightly (+0.2 eV) due to the selective removal of Ge atoms from the film and oxidation of the remaining Si. In the S 2p region, only the Si 2s satellite peak is detected at 168 eV.

In Fig. 1(c), the SiGe surface was etched in an aqueous mixture of HF and HCl. The peak due to Si oxides was removed below detection limits. A peak at 1219.2 eV was resolved and assigned to GeO. The intensity of the O 1s peak is reduced by a factor of 14 compared to the native oxide surface after etching, and a small peak at 532.4 eV was fitted. The Si 2s satellite peak in the S 2p region increases in intensity due to the removal of the oxide layer. Figure 1(d) shows a control experiment in which a cleaned SiGe surface was immersed in UPW alone for 20 min. Si oxides are not detected in the Si 2p region. In the Ge 2p region, bulk Ge is fitted at 1217.5 eV, while a peak at 1218.5 eV is assigned to a mixture of Ge suboxides. A peak was fitted at 532.7 eV in the O 1s region.

Figures 1(e)–1(h) show the SiGe surface after a 20 min immersion in increasing concentrations of $(\text{NH}_4)_2\text{S}$. Spectrum e corresponds to $(\text{NH}_4)_2\text{S}$ with the ratio of 1:1000 v/v. The Si 2p region shows only a bulk peak at 99.4 eV, while the Ge 2p region shows a small peak corresponding to the Ge^{+2} state. A single broad peak in the O 1s region at 532.4 eV again demonstrates that both the Si and Ge oxides were present. Sulfides, which are indicative of covalent bond

formation with the surface, are not detected in the S 2p region at 162 eV. Increasing the concentration to 1:100 v/v (spectrum f) shows similar results where only the presence of bulk Si is detected. Bulk Ge and Ge^{+2} are observed in the Ge 2p region. The O 1s region shows a mixture of both Si and Ge oxides at 531.9 eV. Increasing the $(\text{NH}_4)_2\text{S}$ concentration further to 1:10 v/v causes oxides to appear in the Si 2p region at 102 eV (spectrum g). Oxide growth is also detected in the Ge 2p region with the peak at 1219.3 eV attributed to the Ge^{+2} state. The intensity of the O 1s signal grows while the peak shifts slightly toward higher binding energy at 532.3 eV. Spectrum h is observed after a 20 min immersion in undiluted $(\text{NH}_4)_2\text{S}$. Both the Si and Ge peaks are attenuated because of oxide growth. The intensity of the peak at 102.9 eV attributed to Si oxides grew sharply. A broad peak (FWHM = 3.5) at 1219.6 eV corresponds to a mixture of Ge oxides on the surface. Bulk Ge is detected at 1217.5 eV, and a broad peak (FWHM = 3.6) at 1220.4 eV is assigned to Ge oxides. The area of the O 1s peak at 532.6 eV doubled. The Si 2s satellite peak at 168 eV in the S 2p region was attenuated due to the growth of the oxides on the surface, and there was no evidence of sulfide adsorption at 162 eV despite the high concentration of ammonium sulfide in solution.

The film stoichiometry after control and $(\text{NH}_4)_2\text{S}$ treatments is shown in Fig. 2. The ratio of oxidized Si and Ge with respect to bulk Si and Ge peaks was used to separately follow the oxidation of each surface atom. The overall oxide was tracked using the O 1s peak area compared to each

FIG. 2. (Color online) Peak area ratios calculated for coupons treated with varying concentrations of $(\text{NH}_4)_2\text{S}$. (a) Native oxide SiGe, (b) $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ in the ratio of 1:1:500 with 1 min of DIW rinsing, (c) $\text{HF}:\text{HCl}:\text{H}_2\text{O}$ in the ratio of 1:3:300, (d) UPW 20 min, and $(\text{NH}_4)_2\text{S}$ at dilutions v/v of (e) 1:1000, (f) 1:100, and (g) 1:10 and (h) undiluted.

substrate atom by summing all peaks in that region. Native oxide samples show the highest levels of oxidation [Fig. 2(a)]. SC-1 treatments show similar levels of Si oxides (Si^+/Si) while the relative amount of oxidized Ge atoms (Ge^+/Ge) drops due to etching of Ge by the solution [Fig. 2(b)]. Acid etched samples show no Si oxides and the lowest Ge oxide [Fig. 2(c)]. A small increase in oxides is observed in the UPW control [Fig. 2(d)]. Immersing the samples in aqueous $(\text{NH}_4)_2\text{S}$

increased the coverage of oxide without depositing sulfur, and ultimately, the oxide coverage was comparable to a native oxide covered surface [Figs. 2(e)–2(h)].

Hydrofluoric and hydrochloric acids were added to lower the pH, with the intent of etching oxides that form when coupons are immersed in aqueous $(\text{NH}_4)_2\text{S}$ solutions. Figure 3 shows the XPS spectra of SiGe surfaces treated with acidic $(\text{NH}_4)_2\text{S}$. The pH of both aqueous and acidic $(\text{NH}_4)_2\text{S}$ solutions was measured using pH paper. Aqueous $(\text{NH}_4)_2\text{S}$ solutions had a pH of approximately 10, and the addition of HF and HCl to the solution dropped the pH to 8. Figures 3(a)–3(c) are used for reference and show the surface with the native oxide, after oxide removal, and after immersion in aqueous $(\text{NH}_4)_2\text{S}$ (1:100 v/v) without acid. Note that the $(\text{NH}_4)_2\text{S}$ (1:100 v/v) solution contained a small volume (20–100 μl) of acid introduced by the carryover layer on the coupon when it was transferred from the etching solution to the ammonium sulfide bath. Surfaces treated with the acidic $(\text{NH}_4)_2\text{S}$ solutions are shown in Figs. 3(d)–3(f). Figure 3(d) was obtained after immersion in a solution of $\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ with a volumetric ratio of 0.05:0.05:1:100. The Si 2p region shows bulk Si detected at 99.4 eV and Si oxides at 101.8 eV. Bulk Ge is shifted slightly to 1217.6 eV, and the peak corresponding to a mixture of Ge suboxides was fitted at 1219.7 eV. The mixture of Si and Ge oxides could not be separated in the O 1s region, and a peak was fitted at 532.2 eV. The S 2p region shows the Si 2s satellite peak, and sulfides are still not detected. The spectra after increasing the concentration of HF and HCl in the $(\text{NH}_4)_2\text{S}$ solution to 0.1:0.1:1:100 ($\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$) are shown

FIG. 3. XPS spectra of SiGe coupons after immersion in acidic $(\text{NH}_4)_2\text{S}$ solutions. (a) Native oxide SiGe, (b) $\text{HF}:\text{HCl}:\text{H}_2\text{O}$ in the ratio of 1:3:300, and $(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ (1:100 v/v) with $\text{HF}:\text{HCl}$ in the ratios of (c) 0:0, (d) 0.05:0.05, (e) 0.1:0.1, and (f) 0.15:0.15. Solid lines correspond to fitted peaks, and circle markers correspond to data.

in Fig. 3(e). The presence of Ge^{+2} is detected at 1219.1 eV. A peak at 532.3 eV was fitted in the O 1s region. A small shoulder is observed near 162 eV in the S 2p region corresponding to the formation of sulfide bonds. This shoulder became more pronounced when increasing the volume of acid added to the aqueous $(\text{NH}_4)_2\text{S}$. In Fig. 3(f), the surface treated with $\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ v/v in the ratio of 0.15:0.15:1:100 for 20 min is shown. A small peak was fitted at 102.4 eV corresponding to Si oxides. Additionally, Ge oxides were detected at 1219.7 eV. A peak was fitted at 532.2 eV in the O 1s region despite the addition of more acid. A strong sulfide peak was detected at 162 eV in the S 2p region.

Peak area ratios for acidic $(\text{NH}_4)_2\text{S}$ processes were calculated and are plotted in Fig. 4. The peak areas were taken from the spectra in Fig. 3 and corrected for the XPS peak sensitivity. Ratios of sulfides to substrate peaks were also included. Experiments (a)–(c) are for reference corresponding to the surface with native oxide, after acid etching, and after treatment with $(\text{NH}_4)_2\text{S}$ (1:100 v/v) without acid. Adding acid to $(\text{NH}_4)_2\text{S}$ deposits sulfur, and the coverage increases (S/Ge) as the acidity of the solution is increased. Despite the addition of HF and HCl to the solution, the formation of oxides is still observed. The relative amount of oxides increases as a function of increasing HF and HCl concentration despite the presence of sulfur on the surface. These results suggest the simultaneous deposition of oxygen and sulfur species, such as a sulfate, on the surface.

Figure 5 shows the averaged C-V profiles for three different surface treatments, with the average calculated from three MISCAP devices on each coupon. The MISCAP devices on coupons that were cleaned had an average flat band voltage of 0.88 ± 0.01 V and an average calculated oxide thickness of 16 ± 0.44 nm. For MISCAP devices on coupons that were cleaned and treated with aqueous $(\text{NH}_4)_2\text{S}$ (1:100 v/v), the average flat band voltage was 0.78 ± 0.07 V and the averaged calculated oxide thickness was 16 ± 0.07 nm. On the devices cleaned and treated with the $\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ solution in

Fig. 5. (Color online) Averaged C-V profiles measured at 1 MHz for $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.25$) MISCAP devices with the following surface treatments: (a) cleaned and dried, (b) cleaned and immersed in aqueous ammonium sulfide $[(\text{NH}_4)_2\text{S}$ (1:100 v/v)], and (c) cleaned and immersed in aqueous ammonium sulfide with added acid $[\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ in the ratio of 0.15:0.15:1:100].

the ratio of 0.15:0.15:1:100, which yielded the highest S coverage, the average flat band voltage was 0.40 ± 0.20 V and the average calculated oxide thickness was 18 ± 1.5 nm.

Midband gap voltages were calculated with depletion capacitance data. D_{it} values at the midgap and around the $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.25$) band gap are shown in Fig. 6. At a midgap voltage of 0.57 V, the D_{it} without an ammonium sulfide surface treatment was $6.4 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$. Likewise, for the two ammonium sulfide surface treatments, the D_{it} values are $4.4 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ at $V_{\text{mid}} = 0.48$ V for the $(\text{NH}_4)_2\text{S}$ (1:100 v/v) solution and $1.4 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ at $V_{\text{mid}} = 0.15$ V for the $\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ solution with the ratio of 0.15:0.15:1:100.

IV. DISCUSSION

After etching in halogen acids, the (100) faces of both pure Si and Ge surfaces are hydrogen terminated.^{23,24} XPS of the Cl 2p region (supplementary material, Fig. 4) shows no Cl bound to the surface after etching in HF/HCl .³⁴ The SiGe 25% surface contains an equal number of Si–Si and Si–Ge dimers, on average. On SiGe 25%, the hydrogen termination must be incomplete because there are small Ge^{+2} oxide and O 1s peaks in the XPS [Fig. 1(c)]. In pure water, slightly more oxides formed. The O 1s peak area was 1.4 times larger for coupons with a 20 min UPW immersion compared to freshly cleaned coupons and Ge surface atoms oxidized preferentially to Si. We expected the aqueous ammonium sulfide solutions to deposit sulfur on the freshly cleaned SiGe surface. Instead, sulfur was not detected, and the surface was reoxidized after etching in the HF and HCl acid mixture. In the least concentrated 1:1000 v/v $(\text{NH}_4)_2\text{S}$ solution, the oxide coverage doubled compared to the water control. As the $(\text{NH}_4)_2\text{S}$ became more concentrated, the

Fig. 4. (Color online) Peak area ratios for coupons treated with varying concentrations of $(\text{NH}_4)_2\text{S}$. (a) Native oxide SiGe, (b) $\text{HF}:\text{HCl}:\text{H}_2\text{O}$ in the ratio of 1:3:300 and $(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}$ (1:100 v/v) with $\text{HF}:\text{HCl}$ in the ratios of (c) 0:0, (d) 0.05:0.05, (e) 0.1:0.1, and (f) 0.15:0.15.

FIG. 6. (Color online) D_{it} for MISCAP devices with the following surface treatments: (a) cleaned and dried, (b) cleaned and immersed in aqueous ammonium sulfide $[(\text{NH}_4)_2\text{S}]$ (1:100 v/v), and (c) cleaned and immersed in aqueous ammonium sulfide with added acid $[\text{HF}:\text{HCl}:(\text{NH}_4)_2\text{S}:\text{H}_2\text{O}]$ in the ratio of 0.15:0.15:1:100.

oxide coverage increased. Ge atoms oxidized preferentially, and at the highest ammonium sulfide concentrations, Si oxides formed (Fig. 1). Ultimately, treatment with the highest concentration of $(\text{NH}_4)_2\text{S}$ resulted in 6.4 times more oxygen on the surface compared to the water control. The oxides that form must be the result of the solution chemistry because no sulfur was detected on the surface and the dissolved oxygen concentration, although not controlled, was presumably the same for all the experiments. Moreover, the time of air exposure of the coupons between liquid solution processing and loading into the vacuum chamber for analysis was controlled and fixed in each experiment.

In order to rationalize these results, we consider the solution chemistry. Ammonium sulfide dissociates completely in water into ammonium and sulfide ions

The ammonium ion dissociates into ammonia and a proton

and the sulfide ion is reduced by protons ultimately forming hydrogen sulfide

The extent of these reactions depends on the pH of the solution. When treated with $(\text{NH}_4)_2\text{S}$ alone, which had a pH of about 10, more oxides formed. Previous studies have reported the use of Lewis bases such as NH_3 and pyridine as catalysts for low temperature growth of SiO_2 .^{25,26} While these studies were done using gas phase reactants, it is possible that a similar mechanism is responsible for the growth of

oxides on the SiGe surface in $(\text{NH}_4)_2\text{S}$ solutions which contain both NH_4^+ and NH_3 even though nitrogen species were not detected in the XPS (supplementary material, Fig. 1).³⁴

The sulfide and hydrosulfide ions can react with oxygen forming sulfites and sulfates

Reactions (5) and (6) have large equilibrium constants and are effectively irreversible as written forming sulfite SO_3^{2-} and thiosulfate $\text{S}_2\text{O}_3^{2-}$. However, there is no direct evidence for the adsorption of either of these anions on the surface. Sulfites are expected at binding energies of 167 eV, while adsorption of thiosulfate species would yield two peaks at 162 and 168.5 eV due to the different oxidation states of the sulfur atoms.^{27,28} Both of these overlap the Si 2s satellite peak, and the FWHM of the Si 2s satellite peak does not change with the ammonium sulfide concentration with or without acid compared to the clean surface control. In Fig. 1, the Si 2p, Ge 2p, and Si 2s satellite peaks are all attenuated after immersing in ammonium sulfide, and the O 1s state increases sharply. The Ge oxide to Ge ratio varies, but higher concentrations of ammonium sulfide yield a higher ratio. One interpretation of these data is that the sulfite and thiosulfate adsorb on the SiGe surface and oxidize it. Monolayer adsorption of sulfate ions on SiO_2 has been observed from very low concentrations (0.05 M) of K_2SO_4 and Na_2SO_4 .²⁹ It is possible that the reaction of Ge atoms has a lower barrier and these react first, and ultimately, Si atoms oxidize as the ammonium sulfide concentration is increased. The Si to Ge peak area ratio increases sharply for the most concentrated $(\text{NH}_4)_2\text{S}$ solution, which shows that Ge etched because GeO_2 formed and dissolved in water (supplementary material, Fig. 5).³⁴

Adding acid to the ammonium sulfide solution deposited sulfides on the surface. Figure 4 shows peak area ratios of oxides to bulk for both substrate peaks for various processes. Comparison of the $(\text{NH}_4)_2\text{S}$ 1:100 aqueous treatment [Fig. 4(c)] with acidic ammonium sulfide processes [Figs. 4(d)–4(f)] shows that the deposition of sulfur also results in more oxygen. As the amount of acid in solution is increased, the peak attributed to sulfides grows, but oxides continue to grow. The highest sulfur coverage achieved [Fig. 3(f)] resulted in an increase in oxides by a factor of 2.8 compared to aqueous $(\text{NH}_4)_2\text{S}$. To quantify these coverages, thicknesses of the sulfur and oxide layers were calculated from XPS peak areas using the sulfide peak at 162 eV and peaks attributed to oxides at 102 eV in the Si 2p region. A simple model of Si/ SiO_2 /S was assumed. The sulfur layer was calculated to be approximately 0.4 Å thick for spectra d and e in Fig. 3. The SiO_2 layer from spectra d and f ranged from 0.3 to 0.4 Å in thickness. The maximum sulfur thickness achieved, shown in Fig. 3(f), was 0.7 Å. These thickness values correspond to submonolayer coverages.

Surfaces treated with aqueous $(\text{NH}_4)_2\text{S}$ showed no Ge–S bond formation. The addition of HF and HCl to the solution

drives the reaction equilibria toward the formation of H_2S which reacts on the surface. Sulfides are not expected to bond to the Si atoms, primarily due to the much shorter Si–S bond length (2.24 Å) compared to an ideally reconstructed Si(100) surface (2.34 Å) as well as a much larger bond angle for Si–S (118.4° compared to 109.4°).³⁰ Another possibility for the deposition of sulfur under acidic conditions is the formation of sulfate species in solution. Sulfates cannot be resolved in the S 2p region due to the Si 2s satellite peak; however, sulfate species in solution could explain the simultaneous deposition of sulfur and oxygen on the surface. Under acidic conditions, the reduction of the sulfate species produces elemental sulfur and hydrogen sulfide that adsorb and react on the surface.

The surfaces treated with aqueous ammonium sulfide with and without acid result in MISCAP devices with less interface defects at the valence band edge than a control. Both sulfides and oxides appear to reduce interface defects with energies near the valence band. Sulfur was detected on the surface after immersion in an acidic ammonium sulfide solution and before ALD [Fig. 3(f)]. Sulfur was not detected by XPS without acid, but D_{it} is still less compared to the control MISCAP device (Fig. 6). This may mean that sulfur bonds are present but not enough to be detected using XPS. Based on the chemical and electrical data we cannot distinguish whether it is the sulfides and/or oxides that reduce D_{it} [Figs. 3(c) and 3(f)].

For these MISCAPs, the flat band voltages are nearly equal for the control and the aqueous ammonium sulfide solution surface treatment at 0.90 and 0.87 V. These flat band voltages are shifted from literature reported flat band voltages for similar devices, but our MISCAPs have a dielectric layer that is thicker by a factor of three or more.¹² The positive voltage shift could be due to the increase in fixed oxide and/or interface charge, and the shift scales linearly with the thickness of the dielectric layer. According to theory, a thicker dielectric layer will increase the absolute magnitude of the fixed oxide charge contribution to the flat band voltage.^{31,32} Interface charge should be minimized with the 400 °C postmetallization forming gas anneal though.²⁰ The MISCAP treated with acidic ammonium sulfide produces a flat band shifted by -0.64 V with respect to the MISCAP treated with ammonium sulfide and no acid (Fig. 5). The acidic ammonium sulfide could yield a thicker dielectric stack, less interface charge, and less fixed oxide charge.

A similar trend is observed for the calculated Al_2O_3 thickness for the three types of MISCAP devices, with the acidic ammonium sulfide treated MISCAP being 26% thicker. (All the thickness values reported were found by assuming that the dielectric layer is only Al_2O_3 .) The calculated oxide thickness is inversely proportional to capacitance in accumulation and proportional to the dielectric constant. If there were an interfacial layer or the effective dielectric constant were lower (due to a different quality alumina) in this MISCAP, the electric field across this oxide and thus the capacitance in accumulation would be lower. Such an interfacial layer would be composed of oxides resulting from either of the ammonium sulfide surface treatments before

ALD [Figs. 4(b), 4(c), and 4(f)]. For example, if a layer of GeO_2 were present, it would result in a slightly lower capacitance in accumulation because its dielectric constant is 4.5 compared to approximately 9 for alumina.³³ It is also possible that these surface treatments result in bulk Al_2O_3 layers that differ in the amount of defects even though the physical thicknesses of the Al_2O_3 layer on each of these surfaces measured by ellipsometry were nearly equal at approximately 10 nm (supplementary material, Fig. 3).³⁴

V. CONCLUSIONS

SiGe surfaces were treated with aqueous ammonium sulfide at increasing concentrations. Sulfides did not bond to the surface atoms, but instead the surface oxidized at a faster rate compared to the control. At high concentrations of ammonium sulfide, the surface became enriched with Si, possibly due to the etching of Ge by NH_4OH in solution. Adding halogen acids to the solution facilitates the deposition of a thin layer of sulfur, but oxides also grow, likely due to sulfate species formed in solution, which adsorb to the surface. Even though Si and Ge oxides were present before ALD, the MISCAP with the most sulfur bonds to SiGe has a lower interface defect density and a smaller flat band voltage shift.

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