Self-Assembly of a 1-Eicosanethiolate Layer on InSb(100)

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Abstract

1-eicosanethiolate molecules form relatively weak bonds with the surface of InSb(100) limiting the order of the self-assembled monolayer despite the long length of the alkyl chain. Heating to only 225 °C in vacuum completely desorbed the eicosanethiolate layer from the surface based on x-ray photoelectron spectroscopy. Even after deposition times as long as 20 h in ethanol, the asymmetric methylene stretch was at 2925 cm⁻¹ in the attenuated total reflection Fourier transform infrared spectrum, which is indicative of alkane chains that are incompletely ordered. Atomic force microscopy images combined with ellipsometry showed that the eicosanethiolate layer conformed to the rough InSb(100) starting surface (2.3±0.2 nm RMS). The reoxidation kinetics in air of InSb(100) and InSb(111)B covered with eicosanethiolate layers was the same despite the lower surface roughness of the latter (0.64±0.14 nm). The bond that the S head group makes with the substrate is the primary factor that determines the cohesiveness of the molecules on the surface. Although interactions between the alkane chains in the layer are sufficient to form a self-assembled layer, the fluidity of the molecules in the layer compromised the chemical passivation of the surface resulting in reoxidation in air after 20 minutes.

Keywords: passivation, self-assembly, liquid phase, eicosanethiol, InSb(100)

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1. Introduction

InSb has the smallest bandgap (0.18 eV) of all the binary compound III-V semiconductors [1], and it can be grown in single crystal form by conventional techniques [2]. These properties lend themselves to applications that require
5 detection and emission in the infrared and in optical filters. The wavelength range and sensitivity of infrared detectors fabricated with narrow band gap semiconductors such as InSb are superior to those based on Pb, Si, and Ge [3]. Due to its high electron mobility and conductivity, InSb is a potential material for low power field effect transistors [4, 5]. InSb is known to rapidly
10 form a layer of complex and nonstoichiometric oxides when exposed to air [6]. Since the interface between InSb and its oxides is electrically defective [7], these oxides must be removed. A simple approach to cleaning semiconductor surfaces is the thermal desorption of contaminants. Heating InSb desorbs the Sb oxides, but the temperature required to remove the In native oxides is close to the
15 melting point of InSb ($\sim 527^\circ\text{C}$) [8]. Cleaning InSb(100) substrates with radio frequency-generated hydrogen radicals at 275°C removed the native oxides and left an In-rich surface while maintaining a root mean square (RMS) surface roughness of 0.5 nm [8]. Clean InSb(100) surfaces with roughness values of 0.15 nm [9] and 0.28 nm [10] were obtained when oxidized substrates were exposed
20 to atomic hydrogen at 250°C . Other approaches include gas phase removal of InSb oxides using TiCl_4 , which selectively removes In [11]. Gas phase mixtures of HF and water vapor partially removed the native oxides while maintaining a surface roughness of 0.45 nm without excessive Sb enrichment [12].

The presence of dangling bonds at the semiconductor-oxide interface creates
25 surface states, which affect the ability to precisely control the charge carriers in the near surface region and to obtain a small recombination velocity [13]. The surface state density of InSb is very large ($\sim 1 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ [14]) compared to that of silicon ($\sim 1 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ [15]). In order for InSb and other

III-V semiconductors to compete with Si in high volume manufacturing appli-
cations, a passivation layer that satisfies these dangling bonds is required [14].
The layer must prevent reactions when the semiconductor surface is exposed
to air or contaminants (chemical passivation) as well as eliminate and prevent
interfacial states from forming, while creating a barrier for the loss of electrons
(electrical passivation) [16]. For a device application, a protective layer that can
be removed without compromising the integrity of the substrate is desirable.

Liquid phase processes to chemically etch the native oxides and passivate
semiconductor surfaces are convenient because of their simplicity and low cost.
The use of chalcogenide (sulfur and selenium) atoms to modify the surface of
III-V semiconductors decreases the density of surface states in the band gap and
provides temporary protection against oxidation [17]. A thin S or Se overlayer
can also serve as a source of dopants [18, 19]. When InSb(001) and InSb(111)B
surfaces were cleaned with atomic hydrogen and modified with a sulfur layer in
an electrochemical cell for 30 min at $\sim 275^\circ\text{C}$, x-ray photoelectron spectroscopy
(XPS) revealed the formation of Sb-S and In-S bonds [19]. High resolution elec-
tron energy loss spectroscopy (HREELS) showed an increase in the surface
Fermi level for both crystal orientations with flat band conditions (passivation
of the electron depletion) in the case of InSb(001) and electron accumulation
in the case of InSb(111)B, with an estimated sulfur coverage of ~ 2 monolayers.
Sodium sulfite (Na_2S) was used to etch the native oxides leaving an In-S layer
[20]. The InSb(100) substrates were immersed in 1 M Na_2S at 45°C for 7 min,
and XPS spectra of the freshly treated samples showed the disappearance of
oxygen and oxide peaks and the appearance of an Sb sulfide peak in the Sb
 $3d_{5/2}$ core-level spectrum. There were no $3d_{5/2}$ high binding energy peaks due
to sulfide or oxide states after annealing the substrate at 150°C in ultra-high
vacuum. In another study, InSb(111)A substrates were immersed in ammonium
sulfide, $(\text{NH}_4)_2\text{S}$, solutions at room temperature [21]. Atomic force microscopy
(AFM) and XPS showed that a 1 min immersion in 10% $(\text{NH}_4)_2\text{S}$ yielded a
surface roughness of 0.56 nm (initially 0.51 nm) and oxygen levels below de-
tection limits immediately after sulfide deposition. The inert layer was almost

completely removed by annealing in vacuum at 300 °C. Oxidized InSb(100) substrates were treated in $(\text{NH}_4)_2\text{S}$ solutions in water and isopropanol at room temperature [22]. After a 35 min treatment in a 1:10 solution of $\sim 20\%$ $(\text{NH}_4)_2\text{S}$ diluted in isopropanol, a smaller O 1s peak than that obtained with an equivalent concentration of $(\text{NH}_4)_2\text{S}$ in water was observed by inspection of the Sb 3d XPS region.

To address the issue of the short-term stability of sulfide layers and to better understand the mechanism of sulfur passivation of GaAs, organic approaches involving aromatic thiols, aliphatic thiols, and aliphatic dithiols were studied [23]. Carbonaceous layers are hydrophobic and can present a physical barrier to the diffusion of molecular oxygen and water in air. The sulfur head group tethers the organic tail group to the surface. An enhancement in the photoluminescence indicating a reduction of surface states was observed when GaAs(100) substrates were immersed in solutions containing ethanedithiol and 4-Cl-thiophenol. Since that early work there are several reports of the chemical passivation of GaAs using self-assembled monolayers (SAMs) of organic molecules with thiol head groups [24, 25, 26, 27, 28, 29, 30]. In one of these studies, eight linear alkanethiols with carbon chains lengths (n) between 12 and 19 were compared in the formation of SAMs on clean GaAs(001) in ethanol solutions [26]. The carbon coverage calculated from XPS analysis agreed with the theoretical prediction for constant monolayer coverage for $n \geq 15$. Furthermore, for $n \geq 17$ the percentage of As oxide in the As 3d XPS region after brief air exposures was below detection limits. The position of the $-\text{CH}_3$ antisymmetric stretch in the Fourier transform infrared (FTIR) spectrum reached a minimum of 2917 cm^{-1} indicative of a solid-like layer of thiol molecules. A solid layer that is densely packed and highly ordered can act as a diffusion barrier against molecular oxygen and water vapor. A peak position greater than 2919 cm^{-1} is associated with a disordered liquid-like state of adsorbed thiol molecules based on transmission measurements in the same work.

We reported that long deposition times were necessary to form an alkanethiolate layer on InSb(100) that protected the surface, but oxide regrowth was

prevented for only 3 min [31]. We suggested that the atomically rough starting surface introduced defects in the alkanethiolate layer and this contributed to the rapid reoxidation. To test this idea, we formed alkanethiolate layers in this study on both InSb(100) and an InSb(111)B surface that had less than half the
95 average roughness, and found that the reoxidation kinetics were the same. Despite optimizing the solvent, immersion time, and surface preparation steps to form the self-assembled layer based on ellipsometry, XPS, and attenuated total reflection (ATR) FTIR measurements, the bond that the alkanethiolate makes with InSb is weak, which compromises the protection of the surface.

100 2. Experimental

Semiconductor grade acetone, hydrofluoric acid (HF, 49%), hydrochloric acid (HCl, 37%), isopropyl alcohol (IPA, VLSI grade) and hydrogen peroxide (H_2O_2 , 30%), were obtained from Honeywell. Ethanol (anhydrous, 99.5%), toluene (anhydrous, 99.8%), and ammonium hydroxide (28.0-30%, NH_3 basis), were purchased from Sigma Aldrich, and chloroform (CHCl_3 , 99.8%) and 1-eicosanethiol
105 (ET, 98%), from Alfa-Aesar. Cyclohexane (99%) was obtained from Fisher Scientific. All the solvents and reagents were used as received. The deionized water (DIW) water had a resistivity of 18.2 $\text{M}\Omega\text{-cm}$.

InSb(100) (Xiamen) and InSb(111)B (Firebird Semiconductors) wafers (undoped, 51 mm diameter, 500 μm thickness) were cleaved into $14 \times 18 \text{ mm}^2$
110 pieces and degreased by sonication in acetone and DIW for 1 min each, followed by a DIW rinse and a nitrogen dry. The InSb substrates out of the box were covered in a cap layer that was etched using a sequential liquid phase process. Each sample was immersed for 1 min in 0.28 M HF with a 30 s rinse in DIW and nitrogen dry, followed by a 2 min immersion in 1.0 M H_2O_2 with DIW rinse
115 and nitrogen dry. This process was performed twice to produce a clean starting surface.

The samples were finished with halogen acid etches—1 min each in 0.28 M HF and 1.0 M HCl—and immersed in the solution containing eicosanethiol.

120 These steps were completed without intermediate rinsing or drying, and a thin liquid layer was carried over between steps to try and keep the surface free of oxides. Samples were placed vertically in stirred solutions of 0.1 mM eicosanethiol dissolved in ethanol for 20 min, 20 h, or 48 h. To compare deposition on the (100) and the (111)B crystal planes an eicosanethiol concentration of 0.4 mM
125 was used. During the immersion, the beakers containing the thiol solution were covered and less than 10% of the solution evaporated during the longest processes. IPA, toluene, chloroform, and cyclohexane were also investigated as solvents for eicosanethiol. After the thiol step, the samples were swished for 20-30 s in the corresponding solvent to remove physisorbed molecules and dried
130 with nitrogen. The shortest time that samples were exposed to air was 3 min between drying and loading into a vacuum chamber for analysis.

The thickness of the overlayer on the InSb surface after passivation was measured using a J.A. Woollam M-2000 spectroscopic ellipsometer at an incident angle of 75° . A two-slab model was used consisting of an InSb substrate covered
135 by InSb oxide even though an ET layer may also have been present alone or in combination. The measured thickness is approximate as the refractive index of alkanes (~ 1.5 , [32]) is not equal to that of Sb oxide (2.80 for Sb_2O_3 , [33]). All errors are reported with 95% confidence.

X-ray photoelectron spectroscopy (XPS) was performed on a Physical Elec-
140 tronics system equipped with a non-monochromatic dual-anode Al/Mg $K\alpha$ source and a double-pass cylindrical mirror analyzer (Model 549). High-resolution spectra were obtained using the Al $K\alpha$ source (1486.6 eV) with 0.1 eV steps and a pass energy of 50 eV. Sample charging was compensated by referencing to the Sb-In photoelectron line in the Sb $3d_{3/2}$ region at 537 eV. A Shirley
145 background was subtracted from each peak envelope and the result fit with a Voigt lineshape using custom algorithms and built-in packages in Igor Pro (Wavemetrics, Inc.). To obtain XPS data on the reoxidation kinetics of InSb after different treatments, a single sample was analyzed repeatedly after multiple ambient exposures.

150 Attenuated total reflection (ATR) FTIR spectra were recorded for InSb

coupons 50×10 mm in size with a single beam spectrometer (Nicolet Nexus 670) equipped with a nitrogen-cooled MCT detector. Spectra were collected within the first 10 min of exposure of the passivated sample to atmosphere, and a background was subtracted consisting of the atmosphere in the analysis chamber after purging with nitrogen for 10 min. Each spectrum consisted of
155 co-adding 200 scans at a resolution of 4 cm^{-1} . A trapezoidal Ge element ($50 \times 10 \times 3$ mm with 45° bevels) was used as the internal reflection element. The angle of incidence of the beam was 60° . ATR correction of the collected spectra was performed with the analysis software OMNIC (v.6.2).

160 Surface topography was imaged by atomic force microscopy (AFM) using a Multimode V station (Bruker) in tapping mode. Root mean square (RMS) roughness values were calculated over $500 \times 500 \text{ nm}^2$ areas with a scan rate of 1 Hz and a resolution of 512 pixels/line. The aluminum coated tips (TESPA Bruker AFM probes) had a nominal force constant of 42 N/m; first-order plane-fitting compensated for tilt.
165

Heating of the sample was done in vacuum and the temperature measured using a type-K thermocouple spot-welded to a 0.26 cm^2 piece of Ta foil pressed to the sample using a linear motion feedthrough.

3. Results and Discussion

170 Eicosanethiol contains a chain of 20 carbon atoms, which is the longest that is available commercially. The presence of a hydrophobic chain and the hydrophilic thiol head group suggest that the polarity of the solvent plays an important role in film deposition. In a study of the formation of a hexadecanethiolate layer, which contains a shorter chain, on the surface of GaAs(001),
175 Huang *et al.* concluded that a 1:1 mixture of ethanol and water promoted interactions among the thiol molecules, which increased the quality of the SAM based on FTIR and slowed down surface reoxidation as shown by XPS [24]. Using chloroform as the solvent weakened the interactions between alkane chains producing a poor quality layer and forming Ga_2O_3 , yet the concentration of sur-

face defects responsible for non-radiative recombination was reduced based on photoluminescence. We investigated whether the ET layer thickness depended on the polarity of the solvent used to deliver the molecule to the InSb surface. The relative permittivities (dielectric constants) of the solvents chosen for study are shown in Table 1. Cyclohexane and toluene are the least polar with dielectric constants near 2, and IPA and ethanol are the most polar with dielectric constants of about 20.

Solvent	Dielectric constant
Cyclohexane	2.02
Toluene	2.38
Chloroform	4.81
Isopropanol	20.2
Ethanol	25.3

Table 1: Dielectric constants of the solvents used to deposit ET [33].

The initial thickness of the overlayers shown in Figure 1 was measured after exposure to air for 3 min, which was the shortest time possible after the final liquid step. The thickness varied from 19.4 ± 0.6 Å for chloroform to 46 ± 3 Å for cyclohexane. The initial thickness in chloroform was approximately the same as that for a control experiment in pure ethanol without the thiol. We conclude that the thiol coverage was low or nonexistent using CHCl_3 and the thickness change is due only to reoxidation of the surface. A control experiment consisting of a 20 min immersion in pure ethanol after surface cleaning shows that InSb oxidizes rapidly. An oxide that is 24 Å thick forms in 3 min in air.

The results in ethanol, IPA, and toluene are clustered together at an initial thickness of 32-35 Å. Since the length of an ET molecule is 26.9 Å (calculated using ChemDraw), the difference is due to physisorbed ET molecules, reoxidation of the surface, or inaccuracies in the ellipsometry model. If the first ET layer is bound S end down with the chains extending outward from the surface at an angle with respect to the surface normal, then chains may be physisorbed

to the hydrophobic methyl groups exposed to the solution. The angle between the ET molecules and the substrate could not be obtained from ellipsometry because the measured thickness was greater than the length of the molecule.

205 The ellipsometry model that we used did not distinguish between the thiol layer and surface oxide since there is not enough contrast in the refractive indexes. Moreover, different scenarios are possible for the relative position and surface coverages of the oxide and the thiol layer. Since the initial thickness in cyclohexane is 46 Å or almost twice the length of ET, either a bilayer or patches of

210 multilayers and regrown oxides contribute. Over time in air up to 60 min the thickness increases to about 55 Å. Ethanol, IPA, and toluene yielded a starting thickness closer to the length of ET and provided better control of the thickness over time, increasing to 36-38 Å over the course of one hour in air.

XPS was used to differentiate between oxide regrowth and thiol deposition.

215 Figure 2 shows the XPS spectra after immersion in the thiol solution for 60 min using chloroform as the solvent and the standard 20 min in toluene, ethanol, and IPA. The spin-orbit coupled bulk Sb 3d_{5/2} state is at 527.7 eV (in comparison, previous works report 528.0 eV [20],[21]) and the Sb 3d_{3/2} state was fixed at 537.0 eV (reported at 537.3 eV [21]). The bulk In 3d_{5/2} state was assigned at

220 444.0 eV (444.0 eV for a native oxide surface and 444.4 eV for a sulfur-treated surface have been reported [20]) and the In 3d_{3/2} state is at 451.5 eV. The states at 530.5 eV and 540.0 eV to higher binding energies are due to Sb oxide and sulfide. The O 1s state overlaps the Sb-O and Sb-S states, and the peak around 530.5 eV contains contributions from all three states. The presence

225 of Sb oxide in the 3d_{5/2} state has been reported at 530.8 eV and ~530.3 eV [20] and, specifically, Sb³⁺ contributions were resolved at 530.5 eV and Sb⁵⁺ at 531.4 eV [21]. O 1s contributions have been found at ~531 eV [19] and ~532 eV [21], and Sb-sulfide bonding has been reported at 530.4 eV [20] and ~530 eV. No additional oxidation states were resolved for In due to the small

230 binding energy difference between the bulk and the In₂O₃ states. Furthermore, the bulk In peaks did not shift to higher binding energy, suggesting that the surface was terminated with Sb atoms. Since the 530.5 eV peak is larger than

the bulk peak at 527.7 eV when either chloroform or toluene was used as the solvent (Figure 2a and b) and S was not detected on the surface, oxide must have regrown. The presence of the O Auger state at 975 eV supports this conclusion. The origin of the slightly thicker oxide when toluene was used compared to chloroform is not clear from these data because sulfur was not detected in either experiment and the carbon XPS peaks are similar. Although ellipsometry shows that the overlayer thickness is the same in toluene and the alcohols, the composition of the layer made using toluene must be primarily Sb oxide. The substrates immersed in toluene solutions have more oxide than those treated in CHCl_3 from comparison of the O Auger state. Since XPS shows that CHCl_3 does not promote bonding of ET to InSb, but still slows down the oxidation compared to the toluene solution and the control experiment, CHCl_3 itself could be chemisorbed on the surface. A Cl 2p peak was detected only after immersion in CHCl_3 (data not shown). Control experiments showed that surfaces finished in HCl and immersed for 20 min in pure toluene, chloroform, and ethanol had Auger peak areas after 4 min of air exposure that were a factor of two or more higher than when the alkanethiolate was present (data not shown). Less oxide was formed when pure ethanol was used in the control experiments than the other solvents.

Using IPA or ethanol to dissolve the thiol reduced the size of the higher binding energy 3d peaks due to oxidized Sb, and produced both a detectable S peak at 162-163 eV and a larger C peak at 284.5 eV. The C states are much stronger in the case of the two alcohols because of the presence of the long C chain attached to the thiol. The C peak observed when using toluene is likely to be due to background contamination or ET deposition at submonolayer coverage. The Sb $3d_{5/2}$ state in Figure 2c and d is shifted slightly lower in binding energy to 530 eV because the state is due primarily to S. The state at 162 eV was assigned to sulfide. The O Auger state can just be distinguished above the background noise. Based on these results the two alcohols yielded similar results as on GaAs [24], and we chose ethanol as the solvent for all of the following thiol experiments.

The thin liquid layer of aqueous HCl carried over into the solution of ET and
 265 ethanol protects the surface during the brief air exposure since InSb oxidizes so
 readily when exposed to air. The impact of the carryover layer on the thiol
 solution was investigated by varying the acid concentration of the last HCl
 step. Based on pKa, thiols are much more acidic than alcohols [34]. ET should
 deprotonate in ethanol to form the sulfide head group, S^- . Lowering the pH
 270 can reverse this step and protonate the sulfide, S^- , to thiol, SH . The HCl
 concentration in the last acid step was varied, and XPS spectra (not shown)
 were collected after immersing the samples in the ET solution. The ratio of
 the Sb 3d metal to oxide (Sb-O, Sb-S, and O 1s for 3d_{5/2} only) states was
 calculated for each HCl concentration. Figure 3a-d shows the ratios for both
 275 the Sb 3d_{3/2} (no O 1s peak) and 3d_{5/2} (includes O 1s peak) states for 1 min
 immersions in 0.1 M, 0.5 M, 1.0 M and 2.0 M HCl. In Figure 3e, the sample was
 finished in 1.0 M HCl and an HCl amount equivalent to that carried over by the
 liquid film on the sample was added to the thiol solution, effectively doubling
 the HCl concentration in solution. Similar ratios were obtained in Figure 3d
 280 when the HCl last concentration was doubled. Since Sb oxide regrows quickly
 in the first few minutes of air exposure if the surface is not protected and the
 thiol layer that forms in ethanol is approximately one molecule thick based on
 ellipsometry, the ratio of the Sb 3d metal peaks to the oxidized peaks (assuming
 that S bonds mainly to Sb) is a measure of how free the surface is of oxide when
 285 the thiol layer formed. A higher ratio corresponds to a lower amount of oxide,
 but the ratio saturates when the thiol layer is complete because Sb-S contributes
 to the denominator. The largest peak area ratios—2.6 for the 3d_{5/2} state and
 0.7 for the 3d_{3/2}—were obtained at an HCl concentration of 1.0 M in the last
 oxide etching step (Figure 3c). Repeated measurements showed that there was
 290 no statistical difference among the HCl concentrations studied, and an HCl
 concentration of 1.0 M was chosen for the last cleaning step in the rest of the
 experiments in the study.

The same criterion was used to investigate the impact of lengthening the time
 of immersion in the thiol solution. Figure 3f and g show the ratios calculated for

295 samples cleaned using 1.0 M HCl last and immersed for 20 h and 48 h in 0.1 mM
 ET dissolved in ethanol. The ratio of the $3d_{5/2}$ bulk to oxide peak areas rose to
 3.7 at 20 h but fell to 2.7 after 48 h. Also there was a visible film on the surface
 after immersion for 48 h. Although the statistical variation was high, these
 results were used to define our best performing process on InSb(100), namely a
 300 1.0 M HCl last for 1 min followed by immersion of the sample in 0.1 mM ET
 dissolved in ethanol for 20 h. XPS spectra are shown in Figure 4 comparing
 this process (Figure 4b) to the 20 min process (Figure 4a) and to a 20 h process
 but after 4 h of air exposure (Figure 4c). The peaks that appear in the C 1s
 and S 2p region are similar for the two immersion times, and there is no shift
 305 to higher binding energies of the In 3d peaks. The amount of oxygen in the O
 Auger state is close to background noise in both cases. The difference appears in
 the Sb 3d region, where the high binding energy peaks are shifted towards 530
 eV due to the lower coverages of Sb oxides. The smallest high binding energy
 peaks in the region correspond to the 20 h process, as already shown in Figure
 310 3f. Exposing this film to air for four hours alters the elemental states due to
 surface oxidation. There is less sulfide in the S 2p region, and an additional
 state appeared between sulfide and where sulfate is expected. The C 1s state is
 smaller and shifted to a higher binding energy due to oxidation. These changes
 are the result of the desorption and degradation of the thiol layer. A distinct
 315 peak appeared in the O Auger region. The In 3d peaks shifted to higher binding
 energy due to the formation of In_2O_3 , and the high binding energy Sb 3d peaks
 dominate those of bulk Sb. The high binding energy peak in the $3d_{5/2}$ region
 has shifted back to 530.5 eV. The thiol layer blocked oxygen and water vapor
 from diffusing to the InSb surface for 3 min, but after 4 h most of the passivation
 320 layer desorbed and the surface was almost completely reoxidized.

To better understand the structure of the thiol layer deposited by a long
 immersion time, the density of the ET layer on the InSb(100) surface after
 the 20 h process was probed with FTIR. Attenuated total reflection was used
 because InSb absorbs strongly in the infrared. Figure 5 compares the ATR
 325 spectrum of an InSb sample after surface cleaning and reoxidation to that of

the 20 h process. Peaks characteristic of the alkane chain of ET are present at 2963 cm^{-1} (asymmetric stretch of methyl), 2925 cm^{-1} (asymmetric stretch of methylene), 2877 cm^{-1} (symmetric stretch of methyl), and 2847 cm^{-1} (symmetric stretch of methylene). The weak absorbances observed, in comparison
330 to those reported for 1-octadecanethiol (ODT) layers adsorbed on GaAs(100) [27], indicate that the ET layer on InSb is only partially ordered. There are contributions at 2963 cm^{-1} and 2925 cm^{-1} due to intrinsic absorption from the clean InSb substrate. When layers of 1-nonadecanethiol were deposited on GaAs(001) surfaces, vibrational modes were found at 2967 cm^{-1} (asymmetric
335 stretch of methyl), 2917 cm^{-1} (asymmetric stretch of methylene), 2877 cm^{-1} (symmetric stretch of methyl), and 2850 cm^{-1} (symmetric stretch of methylene) [26]. Furthermore, a transition of the phase of the alkane chains from liquid to solid is associated with a shift of the asymmetric methylene peak from 2928 cm^{-1} to 2917 cm^{-1} [35]. The peak at 2925 cm^{-1} in Figure 5 shows that the
340 alkane chains are still in a liquid like phase and not well-ordered as in a solid. The thickness of an eicosanethiolate layer deposited for 20 h on InSb measured with ellipsometry was 41.6 ± 2.8 Å after 4 min of air exposure. The measured layer thickness 4 min after the 20 min process was 34.6 ± 0.6 Å (Figure 1). Since XPS analysis indicates that InSb surfaces treated for 20 h have a lower oxide
345 coverage than those treated only for 20 min, the difference of ~ 7 Å in the measured thickness must be due to the physisorption of ET at the longer deposition time. A portion of this increase could be due to a denser eicosanethiolate layer but molecules physisorbed to this layer also contribute. Incubation times of at least 20 h were necessary to form highly ordered and dense octadecanethiolate
350 layers on GaAs(001) [36].

Self-assembled monolayers of thiols have been used to modify III-V surfaces, primarily GaAs. After the first studies that showed photoluminescence enhancement of GaAs(100) with short chain thiols [23], SAMs prepared with longer alkanethiols have been analyzed with XPS ([24, 26, 27, 29, 30, 36, 37]),
355 FTIR ([24, 27, 29, 30, 36, 38]), photoluminescence ([24, 29, 37]), contact angle ([30, 36, 37]), and other techniques. In one of these studies, the effect of

the deposition solvent on the SAM quality was studied [30]. A mixture of water and ethanol in a proportion of 1:1 instead of pure ethanol improved the conformational order of 16-mercaptohexadecanoic acid on GaAs(001) by FTIR analysis (the asymmetric methylene stretch shifted from 2922.7 cm^{-1} to 2918.5 cm^{-1}). Less oxide states were found by XPS in the Ga 3d and As 3d regions when using the water and ethanol mixture. Adsorbate packing-induced stress due to intermolecular forces was found to play a critical role in the ordering of ODT layers on GaAs(111), (110), and (100) [27]. GaAs(111)A substrates, which are believed to be less prone to surface rearrangement, yielded methylene stretches at higher wavenumbers in the FTIR and weaker absorbances than the other studied surfaces. Vapor deposition of ODT layers on GaAs(100) surfaces showed superior structural properties compared to those of layers deposited in dilute ODT solutions in ethanol (lower Ga 3d and As 3d oxide levels and a larger contact angle that changed less than 10% after 4 months of exposure to air) [37].

One possibility for the relatively poor ordering of the ET layer on InSb(100) is surface roughness. The topography of the surfaces after cleaning (sequential oxide etching) and reoxidation and after the 20 h ET deposition process was measured using AFM (Figure 6). The surface roughness was $2.3\pm0.2\text{ nm}$ for the wafer out of the box, $3.8\pm1.2\text{ nm}$ after cleaning and reoxidation only, and 2.8 (single measurement) nm after the adsorption of an ET monolayer and 20 min of air exposure. Even before processing, the surface of InSb is rough on an atomic scale. The sequential cleaning processes introduce more variability in the surface topography, which could be the result of selective etching in the H_2O_2 and HCl cleaning steps. This could explain the islands in the AFM image observed after cleaning and reoxidation only (Figure 6b). The surface roughness previously reported for InSb cleaning is $\sim0.7\text{ nm}$ after liquid phase HF etching and as low as $\sim0.5\text{ nm}$ for gas phase HF/ H_2O etching ($\sim0.5\text{ nm}$ for the untreated surface) [11].

The topography after cleaning is representative of the surface that is immersed into the thiol solution. The ET layer does not increase the roughness

but instead appears to smooth out the islands (Figure 6c). The variable topography could cause small islands of well-ordered ET to be mixed with less
 390 ordered patches, which is consistent with the ATR-FTIR data. An atomically rough InSb surface is consistent with the relatively poor quality thiol monolayer that formed. A model to explain the shift to higher wavenumbers of the symmetric and asymmetric methylene stretch in FTIR for dodecanethiol on roughened Si(100) surfaces suggests that annealing and gap filling occur when depositing
 395 layers on smooth surfaces at high temperature (200 °C), but on rough surfaces (RMS=7.3 μ m) the steps and defects limit the ordering and the overlap of alkane chains at the steps (the position of the asymmetric methylene stretch was independent of the deposition temperature on the rough surface) [39]. If a surface is atomically rough, then more binding sites are exposed per unit area and the
 400 number of sites not covered by thiol increases yielding partial passivation [40]. Roughness could also contribute to the thickness of 41.6 ± 2.8 Å measured by ellipsometry after the 20 h process and explain why the eicosanethiolate layer is thicker than one molecule.

To test how the thiol layer forms on a smoother surface, the reoxidation
 405 kinetics of InSb(100) and InSb(111)B covered with ET layers were studied by exposing the substrates to air for different lengths of time. The (111)B surface was chosen because this crystal plane is terminated by Sb atoms [41]. Based on the XPS, the (100) surface is terminated by Sb after the etch in the halogen acids. The Sb to In ratio after the last HCl step and water rinse was 2.75. The
 410 roughness of the InSb(111)B surface was 0.64 ± 0.14 nm, which is lower than the InSb(100) that we used. After cleaning, samples were immersed in 0.4 mM ET for 20 min followed by ambient exposure for increasing periods of time. The results are shown in Figure 7. Based on the Sb 3d_{5/2} region, which contains the contribution from the O 1s peak, the two surfaces oxidized at the same rate
 415 (slope of the unfilled points in Figure 7a). The ET layers slowed the initial rate of reoxidation compared to control experiments in which InSb(100) and InSb(111)B were finished with HCl and rinsed in ethanol before being exposed to air (filled points at 3.5 min). An alternative control experiment in which

InSb(100) was finished with HCl but not rinsed appeared to slow the oxidation
420 rate (filled circles in Figure 7a). Chlorine was detected by XPS (data not shown)
and could passivate the surface.

In Figure 7b, the area under the corresponding O Auger peaks is plotted for
different air exposure times. Although less sensitive than the corresponding XPS
states, the O Auger peak contains contributions from all oxygen species and is
425 not affected by the presence of the sulfide. Reoxidation was slowest for InSb
treated with ET and the rate of oxidation was the same for the (100) and the
(111)B surfaces. In comparison, the Auger data show that the surface reoxidized
faster after the HCl last without a rinse. This trend is masked in the XPS data in
Figure 7a by the higher background due to the presence of S on the thiol-treated
430 surfaces. Care has to be exercised when comparing the Auger peak areas because
this state is attenuated only on the samples containing the alkanethiolate layer.
However, the 20 h ET process produced both the smallest Sb $3d_{5/2}$ peak area
ratios and the smallest O Auger peak areas. The alkanethiolate layer formed
by the 20 h process was the most effective at slowing reoxidation of the surface
435 even after 4 h of air exposure (point marked by arrow). Moreover, based on the
Auger peak area, the alkanethiolate layer prevented oxide regrowth for 20 min.

The identical reoxidation rates measured for the (100) and (111)B planes
shows that surface roughness can not explain the short protection times of only
about 20 min. The forces driving molecular self-assembly are the result of
440 the interaction of the S head group with the substrate and the interactions
between molecules within the layer. Both surfaces are terminated by Sb after
cleaning, hence the bond between the thiol and these planes should be similar.
The strength of the bond between the S atom in thiols and metal atoms varies
widely depending on the structure of the thiol [42]. The S-Sb bond strength
445 is consistently reported at ~ 379 kJ/mol [33, 43]. For comparison, the S-As
bond is stronger with values of ~ 380 kJ/mol [33], ~ 478 kJ/mol [43], and a
theoretical estimate of 588 kJ/mol [44] reported. The stronger sulfur-metal
bond is consistent with the longer time of about 2 weeks to reoxidize GaAs(001)
covered with an octadecanethiol layer (determined by the absence of As and Ga

oxide peaks in the XPS 3d regions) [36].

Another aspect to consider is the cohesive energy of the alkanethiolate molecules on the surface. The lattice parameter of InSb is 6.48 Å and that of GaAs is 5.65 Å [33]. The substrate surface atom densities computed from these values are $6.0 \times 10^{14}/\text{cm}^2$ for InSb and $7.9 \times 10^{14}/\text{cm}^2$ for GaAs. The surface of InSb is more open than GaAs exposing the underlying layer of atoms. Alkanethiolate molecules tethered to the surface by S may be farther apart on InSb than on GaAs depending on how the surface restructures. The alkanethiolate molecules that fit between the tethered moieties defined by S–Sb bonds interact with the second layer of substrate atoms, which on the (100) plane are In atoms. Sulfur makes a weaker bond to In than to Sb [33, 43]. The weaker bonding and longer interaction length—since the In atoms are, in principle, in the second layer—lowers the average bond energy of the alkanethiolate molecules with the surface. The weaker average bonding between the S head group and the substrate makes the alkanethiolate layer more fluid, which is supported by the FTIR data. Moreover, the van der Waals attraction between alkane chains is insufficient to compensate for the weak bonding between S and the substrate.

Another measure of cohesion of the self-assembled layer is the energy required to separate or desorb molecules from the surface. To test the removal of the protective layer in vacuum and obtain an estimate of the bond strength, InSb(100) covered with an ET layer using the 20 h process was heated and analyzed afterward with XPS. Comparison of Figure 8a and b shows peaks consistent with the formation of a thiol monolayer that protects the surface from a short (3-5 min) exposure to air as we described previously. The presence of S in the 2p region and the small peaks at high binding energy in the Sb 3d state that are shifted lower in energy compared to oxides are characteristic of the thiol layer. Notice the attenuation of the Sb and In signal intensities due to the presence of the ET layer. After heating to approximately 225 °C, there are no peaks indicative of either oxide or sulfide in the Sb spectrum and only the bulk metal peaks are present at 527.5 eV and 537 eV (Figure 8c). Furthermore there is no O 1s peak at 532 eV, and the C 1s peak is at background levels. A new peak

appears at about 541 eV near the Sb 3d peaks due to a surface plasmon loss that is characteristic of a clean surface [12]. The ET layer desorbed at a moderate temperature leaving a clean surface. Assuming the desorption process is first order, an estimate of 60-70 kJ/mole is obtained for the activation energy to remove the thiol from the surface [45]. Although we do not have data on GaAs for comparison, this relatively low activation energy demonstrates the importance of the strength of attachment between the alkanethiolate and the substrate, and ultimately the performance of the self-assembled layer to chemically passivate the surface and serve as a diffusion barrier.

4. Conclusions

The effect of solvent polarity, immersion time, and acid concentration in the last surface preparation step were studied in the formation of a 1-eicosanethiolate self-assembled monolayer on InSb(100). XPS showed that the layers formed in polar solvents such as ethanol and isopropanol slowed reoxidation of the surface after cleaning, while chloroform and toluene produced poor quality layers that oxidized immediately when exposed to air. Finishing the surface with a dip in 1 M HCl and carrying over a thin liquid layer into the thiol solution reduced oxide regrowth as did extending immersion time from 20 min to 20 h in the thiol. The eicosanethiolate layer was partially ordered based on ATR-FTIR. Although the InSb(100) substrate was rough on an atomic scale, ordering of the thiol and the cohesiveness of the layer were not improved on the smoother InSb(111)B surface based on the kinetics of reoxidation when the surfaces were exposed to air. Support for weaker bonding is shown by the complete desorption of the layer when the surface was heated to about 225 °C in vacuum. The lower atomic density of the InSb surface that provides points of attachment for a protective layer and the highly reactive substrate due to the narrow bandgap suggest that molecules that interact more strongly than alkanethiolates or that make more than one bond to the surface or to each other may be needed to chemically passivate the surface of InSb.

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Figure 1: Thickness of the overlayer (ET, InSb oxides, or both) on InSb(100) measured by ellipsometry after oxide etching finishing in HCl and 20 min immersions in 0.1 mM ET dissolved in the solvents shown. The control sample was cleaned and immersed in ethanol without ET.

Figure 2: Sb 3d, In 3d, O Auger, C 1s, and S 2p XPS regions for InSb(100) cleaned and immersed for 20 min in 0.1 mM ET dissolved in a) chloroform, b) toluene, c) ethanol, and d) IPA. All samples were exposed to air for 4 min. Circle markers correspond to data and solid lines to fitting curves. Vertical dashed lines show the position for bulk, oxide, and sulfide states.

Figure 3: Ratio of the XPS peak areas in the Sb 3d region after an HCl finishing step at concentrations of a) 0.1 M, b) 0.5 M, c) 1.0 M, d) 2.0 M followed by a 20 min thiol deposition; e) 1.0 M HCl last and acid added to the thiol solution followed by a 20 min thiol deposition; 1.0 M HCl last step followed by a f) 20 h and a g) 48 h thiol deposition. All samples were exposed to atmosphere for 3 min before analysis.

Figure 4: Sb 3d, In 3d, O Auger, C 1s, and S 2p XPS regions of InSb(100) cleaned using 1.0 M HCl last and immersed in 0.1 mM ET dissolved in ethanol for a) 20 min and 3 min of air exposure, b) 20 h and 3 min of air exposure, and c) 20 h and 4 h of air exposure. Circle markers correspond to data and solid lines to fitting curves. Vertical dashed lines show the position for bulk, oxide and sulfide states.

Figure 5: Attenuated total reflection FTIR spectra of InSb(100) that was sequentially cleaned and finished in HCl: clean control surface on which an oxide was regrown and after the 20 h alkanethiolate layer deposition process. Both samples were exposed to atmosphere for approximately 10 min after the last liquid phase steps.

Figure 6: AFM images of InSb(100) a) as received (2.3 ± 0.2 nm RMS), b) after sequential cleaning finishing in HCl and reoxidation in atmosphere (3.8 ± 1.2 nm), and c) after sequential cleaning, immersion for 20 h in 0.1 mM ET, and exposed to air for 20 min (2.8 nm, single measurement).

Figure 7: Comparison of the reoxidation process of InSb(100) and InSb(111)B surfaces after various treatments. In a) the ratio of the oxide to bulk Sb peak area of the Sb 3d_{5/2} state was calculated for clean surfaces finished in HCl and rinsed with ethanol (■ InSb(100), and ▲ InSb(111)B), immersed in ET in ethanol for 20 min after acid cleaning finishing in HCl (□ InSb(100), and ▷ InSb(111)B), cleaned in acid finishing in HCl without any rinse (● InSb(100)), and treated with ET for 20 h after the acid cleaning (◇ InSb(100)). The oxide peak contains contributions from Sb oxides, Sb sulfides, and the O 1s state. In b) the area under the O Auger peak was compared for the same set of experiments. Each data series corresponds to a single sample analyzed repeatedly with XPS after various ambient exposure times. The arrows mark points after a 4 h air exposure, which were moved to make comparison easier.

Figure 8: Sb 3d, In 3d, O Auger, C 1s, and S 2p XPS regions for InSb(100) cleaned finishing in HCl and immersed for 20 min in 0.1 mM ET dissolved in ethanol. a) Control (no ET), b) 20 h immersion in ET and exposed to atmosphere for 4 min, c) same as b) after heating to 225 °C. Circle markers correspond to data and solid lines to fitting curves. Vertical dashed lines show the position for bulk, oxide and sulfide states.