Use of 3-aminopropyltriethoxysilane deposited from aqueous solution for surface modification of III-V materials

Daniel B. Knorr, Jr.^{a,}, Kristen S. Williams^a, Neil F. Baril^b, Conan Weiland^c, Jan W. Andzelm^a,
Joseph L. Lenhart^{a,*}, Joseph C. Woicik^c, Daniel A. Fischer^c, Meimei Z. Tidrow^b, Sumith V.
Bandara^b, Nathan C. Henry^{b,d}*

^a U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005

^b US Army, RDECOM, CERDEC, NVSED, Ft. Belvoir, VA 22060

^c National Institute of Standards and Technology, Gaithersburg, MD 20899

^d Corbin Company, Alexandria, VA 22314

Corresponding Authors

* joseph.l.lenhart.civ@mail.mil, Telephone: 410-306-1940, Fax: 410-306-0676

* daniel.knorr.civ@mail.mil, Telephone: 410-306-1593, Fax: 410-306-0829

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ABSTRACT Focal plane arrays of strained layer superlattices (SLSs) composed of InAs/GaSb are excellent candidates for infrared imaging, but one key factor limiting their utility is the lack of a surface passivation technique capable of protecting the mesa sidewall from degradation. Along these lines, we demonstrate the use of aqueous 3-aminopropyl triethoxysilane (APTES) deposited as a surface functionalizing agent for subsequent polymer passivation on InAs and GaSb surfaces following a HCl/citric acid procedure to remove the conductive oxide In_2O_3 . Using atomic force microscopy, variable angle spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), and modeling with density functional theory (DFT), we demonstrate that APTES films can successfully be deposited on III-V substrates by spin coating and directly compare these films to those deposited on silicon substrates. The HCl/citric acid surface preparation treatment is particularly effective at removing In_2O_3 without the surface segregation of In oxides observed from use of HCl alone. However, HCl/citric acid surface treatment method does result in heavy oxidation of both Ga and Sb, accompanied by segregation of Ga oxide to the surface. Deposited APTES layer thickness did not depend on the substrate choice, and thicknesses between 1 and 20nm were obtained for APTES solution concentrations ranging from 0.1 to 2.5 vol%. XPS results for the N1s band of APTES showed that the content of ionic nitrogen was high (~50%) for the thinnest films (~1nm), and decreased with increasing film thickness. These results indicate that APTES can indeed be used to form a silane surface layer to cover III-V materials substrates. Such APTES silane layers may prove useful in surface passivation of these materials alone, or as surface functionalizing agents for subsequent covalent binding with polymer overlayers like polyimide.

1. Introduction

Strained layer superlattices (SLSs) composed of InAs/GaSb have a variety of potential uses in meteorology, astronomy, gas detection, fundamental science, and military applications[1-3]. These materials are often employed as photodetectors operating in the long-wave infrared region (8-12 μ m). InAs/GaSb SLSs have a comparable absorption coefficient to conventionally used mercury-cadmium-telluride and have additional natural advantages in terms of strong suppression of Auger recombination rates, which reduces dark current [1, 4], and lower sensitivity to variations in composition[5].

Many photodetector applications of these superlattice materials require the formation of focal plane arrays for infrared imaging. Part of the fabrication process involves patterning and etching the superlattice to form the individual mesas comprising the focal plane array. During this process, defects arise due to dangling bonds, chemical segregation, and contaminant incorporation on the sidewall surfaces of the mesas, resulting in the formation of various surface states. These surface states are detrimental to device performance as they can fall within the band gap of the superlattice and/or cause band bending at the surface, leading to Fermi level pinning. Furthermore, some of the oxides that spontaneously form on the exposed surface are themselves conductive[4], leading to diminished device performance, and excess noise due to surface leakage current[6].

One key factor limiting the performance of these devices is the lack of a surface passivation technique capable of mitigating the surface defects and protecting the sidewall from further degradation[7]. Specifically, there is a lack of chemical and electronic control of the surface properties due to the complex oxides, which spontaneously form on the exposed surfaces[8]. A

variety of techniques have been employed to passivate the surfaces of III-V materials, and they can broadly be placed into three categories: (i) strategies employing an inorganic overlayer, (ii) strategies that attempt to bond sulfur directly to the III-V material, and (iii) organic strategies that involve coating surfaces with polymers.

Inorganic passivation strategies involve the deposition of some type of inorganic layer over the III-V material. For example, Rehm et al. reported that epitaxial overgrowth of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{Sb}_{1-y}$ was capable of suppressing leakage current in $\text{InAs}/(\text{GaIn})\text{Sb}$ superlattices[6]. Other inorganic strategies have involved deposition of silicon in the form of SiN_x [2, 4, 9, 10] and SiO_2 deposited by plasma-enhanced chemical vapor deposition[2-4, 7, 10-12]. Razeghi et al., however, showed that SiO_2 passivated devices required a graded doping profile and a shallow etch technique. Another strategy, highlighted by Szmulowicz and Brown, is the use of GaSb itself to passivate InAs/GaSb mesas[13]. While these techniques have met with varying degrees of success, many of them are expensive and require additional processing[7].

Sulfur based passivation techniques have also received a great deal of interest recently. Fundamentally, these techniques seek to exploit the ability of sulfur to covalently bond to atoms in III-V materials[14, 15]. Among these strategies it is most common to use a sulfiding agent such as ammonium sulfide[16], zinc sulfide[4], and sodium sulfide[17], generally dissolved in an organic alcohol. These techniques have been shown to reduce surface conductivity and improve device performance. Thiols, including alkane thiols[18, 19], have been deposited on InAs and have been shown to be stable against degradation in air and when exposed to various solutions. An amine functionalized thiol, cysteamine, has also been investigated for use on III-V surfaces[8, 20]. Thioacetamide has been suggested as an alternative sulfidizing agent to the commonly used ammonium sulfide[21] due to its ability to form bonds directly with III-V metals

(e.g., Ga-S), rather than bonds with an intermediate oxide (e.g., Ga-O-S) [5]. Electrochemical sulfur deposition from a Na₂S solution in ethylene glycol[5] also showed the potential to improve performance of InAs/GaSb SLS detectors. Again, while these techniques have proved promising, there is evidence that suggests they may not protect long-term against surface oxidation and that passivation chemistry may differ for different III-V elements [21].

A final category of passivation techniques employs polymeric materials to provide a protective coating on the III-V surface to prevent further oxidation due to air exposure. Specifically, this has involved the use of SU-8 photoresist, which showed a one order of magnitude reduction in dark current [1]. Further, surface resistivity for the SU-8 passivated SLS detector was higher than an SiO₂ passivated device, but lower than that of a ZnS passivated device. Polyimide, a polymer commonly used for surface capping in conventional silicon based technologies, has also been employed for III-V materials[9, 22, 23]. Therein, polyimide was found to greatly reduce surface current leakage[22], and provide surface stability[23]. The advantages of using polyimide are that it is inexpensive, readily available, and often used in conventional technology.

While the use of polyimide is attractive, there is no evidence to suggest that polyimide itself would covalently bond with the III-V material. In addition, it is well established that water will adsorb at polyimide-silicon oxide surfaces. If similar water adsorption effects also occur with polyimide-III/V interfaces, then surface leakage current and device performance could gradually change with time due to slow oxidation and eventual polyimide delamination. Adhesion promoters like those commonly used in silicon-based electronic materials might therefore be useful for III/V materials. For example, 3-aminopropyl triethoxysilane (APTES), is commonly used to modify silicon surfaces[24] in preparation for the application of a polyimide coating. However, little is known about their structure on III/V surfaces.

In this paper, we explore the use of APTES on InAs and GaSb surfaces using atomic force microscopy (AFM), variable angle spectroscopic ellipsometry (VASE), X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS). We further employ density functional theory to explore adsorption energies of APTES on gallium oxide surfaces to elucidate the possible mechanisms of deposition. We particularly focus on the ability to process APTES from aqueous solutions, eliminating the need for organic solvents that are more commonly described in the literature[25]. We demonstrate that APTES films can successfully be deposited on III-V substrates and directly compare these films to those deposited on silicon substrates.

2. Materials and Methods

2.1. Materials

Citric acid ($\geq 99.5\%$, ACS reagent, Sigma Aldrich), hydrochloric acid (37%, Semiconductor Grade, Sigma Aldrich), hydrofluoric acid (49%, OmniTrace Ultra, EMD Millipore), 3-aminopropyltriethoxysilane ($>95\%$ APTES, VM651, HD Microsystems), acetone (Spectroscopy grade, Sigma Aldrich), and isopropanol (99.9%, Chromasolv, Sigma Aldrich) were used as received. Undoped, 3 μm thick, InAs and GaSb substrate layers used in this study were deposited on 3 inch diameter GaAs substrates with a (100) molecular orientation via molecular beam epitaxy by IQE, Inc. (Bethlehem, PA). The bulk InAs and GaSb layers were deposited immediately preceding SLS device growth in the same molecular beam epitaxy reactor to ensure they were representative of the InAs and GaSb found in SLS device layers.

2.2. Sample Preparation

2.2.1. Silicon wafer oxide preparation

The native oxide of the silicon wafer samples was removed and regrown using the procedure described herein. First, silicon wafers (Rogue Valley Microdevices, <100>, p-type, boron doped) were cleaned in a UV/ozone cleaner (Novascan PSD Pro) for 30 minutes. This was followed by sonication in fresh toluene and ethanol for 30 minutes each. After sonication, the wafers were rinsed with ultrapure DI water (18.1 M Ω ·cm) and were then blown dry with ultrapure nitrogen. To remove the native oxide, the wafers were then placed in a 1wt% solution of HF in ultrapure DI water for 2 minutes. Wafers were then removed and rinsed three times with ultrapure DI water before being blown dry with ultrapure nitrogen. To regrow the oxide layer, the wafers were placed in the UV/ozone cleaner for 2 minutes. Ellipsometry measurements showed that the regrown oxide had a thickness of 2.0nm.

2.2.2. Surface preparation

First, organic contaminants were removed from all substrate surfaces by rinsing with acetone followed by isopropanol for 5 seconds each. To remove oxides from the surfaces of III-V materials in preparation for APTES deposition, two treatment steps were used; first, exposure to 10% HCl[26] followed by exposure to 1M citric acid[27], both in ultrapure water. For HCl treatment, the substrates were gently swirled in 10% HCl for 30 seconds, then placed in ultrapure DI water for 60 seconds, and then rinsed again with ultrapure DI water. Then, samples were placed in 1M citric acid, swirled for 30 seconds, removed to ultrapure DI water for 60 seconds, followed again by a rinse with ultrapure DI water. The only exception to this was the GaSb samples, which were not allowed to sit in the DI water for 60 seconds during either process; rather, they were merely rinsed with DI water to remove residual acid due to rapid water etching

of these substrates. After all treatment steps, the substrates were blown dry with ultrapure nitrogen and were immediately coated with APTES.

Four control substrates were prepared for each substrate. The first control group included substrates that were only rinsed with organic solvents (acetone, isopropanol) as described above and were then stored. A second control group were exposed to both acid washes as described above, but were not coated with APTES. A third group was only exposed to the HCl wash described above, but not the citric acid wash. Finally, a fourth group was prepared that was exposed only to the citric acid wash and not to the HCl wash. All these control samples were stored in covered wafer holders with the APTES coated samples for subsequent characterization.

2.2.3. APTES coating

APTES solutions in ultrapure DI water were prepared at concentrations of 0.1%, 0.25%, 0.5%, 0.75%, 1.0%, and 2.5% by volume. These solutions were spun cast onto the substrates at 3000 rpm for 60 seconds by means of a spin coater (CEE, Brewer Science) with an attached hot plate. After spinning, the samples were immediately placed on the hot plate, maintained at $120 \pm 0.5^\circ\text{C}$ for 120 seconds to drive off excess water and cause the silanol groups in the system to condense, forming the APTES silane surface layer.

2.3. Characterization and modeling

2.3.1. Atomic Force Microscopy (AFM)

Images and root mean square (RMS) roughness measurements were obtained using a Bruker Dimension 3100 AFM operating in tapping mode. Images of representative surfaces were obtained for $1 \times 1 \mu\text{m}$ and $5 \times 5 \mu\text{m}$ size scales. RMS roughness measurements were obtained over a

5x5 μ m region, and at least three separate regions were scanned to obtain an average value and standard deviation.

2.3.2. Ellipsometry

Estimation of the thickness of the oxide layer and APTES layers was performed using variable angle spectroscopic ellipsometry (VASE, J.A. Woollam Co., USA). Measurements were obtained for wavelengths from 270 to 1000nm at 10nm steps for five incident angles; 60°, 65°, 70°, 75° and 80°. Model fitting was performed in the WVASE32 software (J.A. Woollam Co., USA). Model parameters for GaSb, InAs and their oxides were taken from the literature.[28, 29] A Cauchy model (where refractive index, n , is a function of wavelength, λ , as $n=A+B/\lambda^2+C/\lambda^4$) was used for APTES where $A=1.407$, $B=0.0054$ and $C=0.0005$. This model was based on fits obtained for APTES samples spun cast on silicon. First, data at all angles and a wavelength of 600nm was fit using the bulk refractive index of APTES, $n=1.424$, given in the literature[30]; then, the fit was expanded to the entire measured wavelength range to determine the refractive index as a function of wavelength.

2.3.3. X-ray photoelectron spectroscopy (XPS)

XPS was performed at the National Synchrotron Light Source Brookhaven National Laboratory on the NIST X24A beamline using a nominal beam energy of 2155-2165eV. The beamline employs a double Si (111) crystal monochromator, and a 400mm diameter detector. Survey scans were performed with a pass energy of 500eV, a step size of 200meV, and an integration time of 0.067s over 2 iterations. Individual element scans were performed with a pass energy of 200eV, a step size between 50 and 70meV and an integration time of 0.067s. At a

pass energy of 200eV, the resolution is dominated by the X-ray line width. Individual element scans were recorded over 10 iterations except for C1s, Si1s and Si2p, which were recorded over 15 iterations. All XPS spectra were obtained at an incident angle of 85°. Spectra were baseline corrected using the method suggested by Tougaard [31]. XPS spectra were deconvoluted using a Gaussian-Lorentzian product function [32], where, within data processing for a single species, the full-width at half-maximum and the Gaussian-Lorentzian ratio were the same for all peaks. Samples on Si wafers were corrected to the Si2p_{3/2} peak of elemental silicon at 99.4eV, while samples on InAs were corrected to the In3d_{5/2} peak for InAs, which is known to be 444.5eV (see Table 1). GaSb samples were corrected to the Ga4d_{5/2} peak of GaSb, which is known to be 31.9eV[33].

2.3.4. Near edge X-ray absorption fine structure (NEXAFS)

NEXAFS measurements were conducted at the NIST U7A beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. All the spectra were recorded at room temperature in the NIST material characterization chamber at 10⁻⁶ Pa. The spectra were normalized to the incident beam intensity, I₀, by collecting the total electron yield intensity from a gold coated 90% transmitting grid placed in the incoming X-ray beam path. A monochromator, with a 600 line/mm grating, provided ~0.10 eV resolution. The monochromator energy scale was calibrated by the carbon K-edge π* transition of graphite at 285.1 eV. Surface sensitive partial electron yield measurements were made (probe depth of approximately 5-6 nm) by applying a negative bias (in our case -150V) on the entrance grid of the channeltron electron detector. Spectra were collected at the magic angle (54.8°) relative to the film surface to avoid orientation effects. For the NEXAFS spectra in this paper the experimental standard uncertainty in the peak

position is similar to the grating resolution of ~ 0.15 eV. Further information on NEXAFS can be found in the Supplemental Information.

2.3.5. Density Functional Theory Modeling

Geometries and adsorption energies for several oxide/APTES silane interfaces were calculated with density functional theory (DFT) using the Perdew-Burke-Ernzerhof (PBE) functional [34]. A (100) surface model of gallium oxide was constructed from the β polymorph of Ga_2O_3 , which has a monoclinic crystal structure [35]. The atomic coordinates were optimized using 3D periodic boundary conditions and delocalized internal coordinates [36, 37]. A gallium oxide surface model was built by cleaving the β - Ga_2O_3 crystal along the [100] direction to create a 5-layer slab with 20 Å of vacuum separating periodic images. The (100) surface has two possible terminations, and we chose the $\text{Ga}_2\text{O}_3(100)\text{B}$ termination because it has been shown to be the lowest-energy surface of β - Ga_2O_3 [38] and has been used in several recent adsorption studies [39-43]. This termination leaves tetrahedral Ga atoms on the surface fully coordinated and octahedral Ga atoms with one dangling bond. OH groups were added to the unsaturated Ga atoms to both passivate the dangling bonds and represent hydroxylation of the surface. The silane coupling agent used in experiments was modeled with the hydrolyzed version of APTES, namely, aminopropylsilanetriol (APST), which tends to be the form of APTES in aqueous solutions at low concentration [44]. The APST molecule was placed on the $\text{Ga}_2\text{O}_3(100)\text{B}$ surface in different orientations, and the oxide/silane interfaces were re-optimized, holding the bottom two layers fixed in their bulk positions. All calculations were performed with DMol3, as implemented in the Materials Studio suite of modeling programs [45-47]. Partial charges on each atom were defined by the Hirshfeld charge partitioning scheme [48].

3. Results and Discussion

3.1. Atomic force microscopy

AFM topography images were obtained for the substrates at various preparation stages, shown in Figure S1 in the Supplemental Information. As shown, the InAs substrate does not change much between preparation steps, at least in terms of topography; similarly, the silicon wafer substrate shows little difference for different surface preparations. Solvent rinsed and citric acid treated GaSb samples also look very similar, however, after HCl treatment, the samples develop obvious small scale texturing that is likely due to removal of the native oxide layer and subsequent reoxidation of the surface in ultrapure DI water. This texture persists even after exposure to citric acid, as shown in the last row of Fig. S1. The combined acid treatment of HCl followed by citric acid was used prior to spin coating APTES on the substrates.

Topography images of the various substrates spun cast with various concentrations of APTES in ultrapure DI water are provided in Fig. S2 of the Supplemental Information. For InAs substrates, concentrations of 0.1% and 0.25% appear very similar to their uncoated counterpart in Fig. S1. However, once the concentration reached 0.5%, some light texturing due to silane deposition was observed. This trend continued until a concentration of 2.5%, wherein the mottled topography expected of APTES silane deposition was observed. In this series, it is important to note that the 1.0% sample shows large scale topography due to a large degree of what may be dust particles. This may have been due to dust associated with cleaving the sample during substrate preparation. For the GaSb series, again, the surface topography gradually changes from one similar to the uncoated acid treated samples in Fig. S1 to a clear silane coating

at a concentration of 2.5%. However, it is difficult to distinguish a transition from an uncoated to a coated substrate. In the case of the silicon wafers, the substrate coating process clearly begins right away at a concentration of 0.1%, albeit with non-uniform deposition occurring at this concentration. Concentrations as low as 0.5% seem to show fairly uniform coverage, and the image at 2.5% is very similar to those observed for the other substrates, indicating that a fairly thick silane layer is expected for this concentration, whatever the substrate.

AFM was also used to obtain surface roughness measurements for 5 μm images (not shown) of the silane coated samples, and the RMS values are provided in Fig. 1. Samples denoted as '0' for the APTES concentration are those which have undergone solvent rinse followed by both HCl and citric acid washes. As shown for InAs, the surface is fairly rough, at around 2.2nm, even from the beginning of the treatment process. Furthermore, the roughness seems largely unaffected by silane deposition to a concentration of 2.5%, where the value falls to about 1.1nm. The latter data point implies that, at 2.5%, the silane surface is thick enough to dictate surface roughness. Qualitatively similar behavior is obtained for the GaSb substrate, which has a lower initial surface roughness of about 1.2nm for low silane concentration. This roughness steadily declines with increasing concentration to a value of about 0.5nm, which is similar to that obtained for the silicon wafer, again implying that a complete silane layer covers the surface at this concentration. Roughness on the silicon wafer is initially very low, about 0.15nm before APTES deposition, and steadily increases to a plateau value of about 0.25nm for a concentration of 0.25%, which is maintained up to 2.5%.

Fig. 1. Root mean square (RMS) roughness of samples as a function of APTES spin casting solution concentration. Lines are drawn as guides to the eye.

3.2. Ellipsometry

Variable angle spectroscopic ellipsometry was performed for all the samples to determine the thickness of the oxide layer, as well as the thickness of the silane layer, after deposition. Details regarding fitting of the ellipsometry data are provided in the Supplemental Information. A plot of the APTES generated silane thickness on the various substrates obtained via ellipsometry is presented in Fig. 2. The total silane thickness was taken to be the thickness of the APTES layer plus half of the thickness of the EMA layer for InAs and GaSb samples. As shown, the APTES thickness is very consistent between the different samples. Furthermore, as expected,[49] the thickness shows a linear trend in concentration given that the spin speed was held constant. These data suggest that the nature of the substrate does not heavily influence the thickness of the resulting silane layer.

Fig. 2. APTES silane thicknesses obtained from VASE data for all substrates studied. Dashed line is linear fit of all the data through the origin, providing a slope of 8.2.

3.3. XPS

3.3.1. Survey scans

X-ray photoelectron spectroscopy (XPS) was conducted on all the samples to gain insight into how the silane formed from APTES grows on the surface. Survey scans of the solvent rinsed and the combined HCl and citric acid treated control samples are shown in Fig. 3, along with the substrates coated with the silane. As shown, peaks specific to the substrate (e.g., As2p, In3p, In3d, Ga2p, Sb3p) decrease with increasing APTES solution concentration due to attenuation as APTES thickness increases. At silane concentrations of 2.5%, the substrate peaks are almost completely attenuated, which is consistent with the VASE thickness of 20nm, and the approximate effective XPS probing depth of <20nm. Furthermore, peaks associated with the silane (e.g., C1s, Si2p, N1s) increase with increasing APTES solution concentration. Peaks associated with oxygen (O1s) show various behaviors since the substrates themselves are oxidized prior to silane coating; also, the O1s peak occurs in the same region as Sb3d for the

GaSb substrate. The performance of each individual substrate will be discussed in more detail below, focusing on selected peaks that provide more insight.

Fig. 3. XPS survey plots for (a) InAs, (b) GaSb, and (c) Si for as-received (bare) substrates, substrates treated with HCl and citric acid (HCl/CA), and treated substrates spin coated with 0.1%, 0.25%, 0.5%, 0.75%, 1.0%, and 2.5% APTES in ultrapure water.

3.3.2. XPS for InAs

In3d and In4d. Figure 4(a) provides XPS data with fits for the In3d band of the InAs samples exposed to various acid treatments prior to APTES deposition. As shown, the data are well fit by a combination of three peaks: a peak at 444.5eV corresponding to In-As, a peak at 445.1eV corresponding to In^{+1} (In_2O or InO_x), and a peak at about 445.6eV, corresponding to In^{+3} (In_2O_3). All of these values are in reasonable agreement with those observed previously, as shown in Table S1 in the Supplemental Information. The initial oxide content in the sample that was only solvent rinsed was about 20%, as estimated by taking the area of the two oxide peaks compared to the total area. Both HCl and citric acid treatments successfully remove oxide and bring the total oxide content down to around 10% of the total peak area. Washing by HCl followed by citric acid did not further improve oxide removal beyond a single HCl or citric acid treatment. These same conclusions hold for the In4d band, shown in Fig. 4(b). Therein, the $\text{In}4d_{5/2}$ and $\text{In}4d_{3/2}$ spin orbit doublet associated with InAs were observed at 17.5 and 18.4eV, respectively (Table S1). Due to spin orbital splitting, it was difficult to parse the oxide peaks into specific components. However, the oxide peaks, fit only with singlets, observed at 18.9 and 19.4eV, can be tentatively assigned to In_2O and In_2O_3 . Again, the latter decreases dramatically after HCl treatment. In3d and In4d spectra of the samples coated with APTES (shown in the Supplemental Information Fig. S4) were largely the same as the sample washed with the combined HCl and citric acid treatment except that they became attenuated as the APTES thickness increased, as expected.

As2p and As3d. XPS spectra for As2p are found in Fig. 4(c), and, again, literature data for the peak positions are found in Table S1. For the present data, a peak position of 1322.7eV

was found for InAs, which is in agreement with the literature, Table S1. The portion of the spectrum showing the oxide (i.e., 1325-1328eV) was fit with two peaks, one for As^{3+} and one for As^{5+} at 1325.9 and 1327.0eV, respectively. These shift values are in good agreement with literature values shown in Table S1.

Fig. 4. XPS plots for (a) In 3d, (b) In 4d, (c) As 2p, and (d) As 3d, for solvent treated samples and samples with solvent treatment followed by HCl acid wash, citric acid wash (CA), and combined HCl and citric acid wash (HCl/CA). Dashed lines indicate approximate peak positions used for fitting the data.

Several observations can be made regarding the acid treatment based on the data. First, the solvent treated sample contained both As_2O_3 and As_2O_5 , but the latter was more prevalent by a factor of 2-3 based on the ratio of peak areas. HCl treatment was effective in removing some of the oxide, however, citric acid was more effective, resulting in nearly a three-fold greater reduction in total oxide peak area. The combined HCl and citric acid treatment showed oxide removal similar to that of citric acid. The same conclusions can be reached for the As3d band, shown in Fig. 4(d). Here, $\text{As}3d_{5/2}$ and $\text{As}3d_{3/2}$ peaks associated with InAs were observed at 41.0 and 41.7eV, respectively, and a broad oxide peak was observed in the range of 44-46eV. Other than the expected peak attenuation due to silane thickness, the APTES coated substrates do not show any remarkable behavior in the As2p or As3d spectra (see Supplemental Information Fig. S5).

As mentioned in the literature, As oxides are water soluble[50], which may lead to an increased concentration of indium at the surface during processing in aqueous solutions. To determine whether or not this occurred, we plotted ratios of total In to total As XPS signals, as shown in Fig. 5. Two ratios were selected based on the data in Fig. 4, i.e., $\text{In}3d/\text{As}2p$ and $\text{In}4d/\text{As}3d$. While the absolute number of the ratio is not of particular importance, the relative change between surface treatments is of value. As shown, surface treatment by HCl alone lowers the In/As ratio in both cases, indicating that HCl may selectively strip In oxides rather than As oxides. However, citric acid treatment alone and the HCl and citric acid (HCl/CA) treatments are very similar to the as-received wafer, indicating that these combined treatments do not result in changes in surface composition relative to the as-received sample.

Fig. 5. Ratio of Group III to Group V total XPS signals including oxide.

3.3.3. XPS for GaSb

Ga2p and Ga3d. Figure 6(a) provides XPS data with fits for the Ga2p_{3/2} band of the GaSb samples exposed to various acid treatments prior to APTES deposition. As shown, the data are well fit by a combination of two peaks, a peak at 1117.1eV, which corresponds to Ga in GaSb, and a second peak at about 1118.2, which corresponds to Ga-O bonds (Table S1). As shown, treatment with acids resulted in increased oxide peaks relative to the solvent treated samples. Specifically, the area of the GaSb (Ga-O) peak in the Ga2p was found to be 56.3% (43.7%), 49.6% (50.3%), 56.7% (43.3%), 14.5% (85.5%) of the total area for solvent treated, HCl treated, citric acid treated, and combined HCl and citric acid treated samples, respectively. Previous work with GaAs substrates showed that formation of gallium chlorides is possible when treating with an HCl solution[50]. However, in our case, the survey scans (Fig. 3) did not show any Cl where the 2p band would be expected (about 200eV binding energy); this may be due to the fact that our treatment time was significantly less than that in the previous study (10 minutes)[50]. Furthermore, some studies in the literature on GaAs[50-52] suggest that oxidation

of Ga in the presence of water results in the formation of surface Ga-OH groups that result from water adsorption. The presence of Ga-OH should be indicated by a Ga2p peak around 1119.4eV (Table S1), and this may be included in the large, broad oxide peak observed after the combined HCl and citric acid treatment in Fig. 6(a); however, there does not seem to be substantial justification for fitting the large oxide peak with multiple, smaller peaks based on the quality of the fit with a single oxide peak. The shift in the oxide peak in Fig. 6(a) and Fig. 6(b) may reflect increased -OH content on the surface after a combination of treatments. This observation is particularly important because, as we will show from DFT modeling, the presence of surface hydroxyl groups contributes to both covalent and hydrogen-bonding interactions between the oxide surface and the deposited silane molecules.

Similar results were obtained for the Ga3d band, shown in Fig. 6(b). Here, peaks at 19.0 and 19.4eV represent a doublet due to spin orbital splitting and are associated with Ga in GaSb. The oxide in the Ga3b band was modeled as a single, wide peak, whose center was in the 20.3-20.7eV range, depending on the surface treatment. Again, after the combined HCl/citric acid treatment, the oxide itself increased dramatically. APTES coated substrates do not show any remarkable behavior in the Ga2p or Ga3d spectra (see Supplemental Information Fig. S6) other than peak attenuation due to the APTES silane layer.

Sb3d and Sb4d. Figure 6(c) provides XPS data with fits for the Sb3d_{3/2} band of the GaSb samples exposed to various acid treatments prior to APTES deposition. As shown, the data are well fit by a combination of three peaks, the Sb-Ga bond in GaSb at about 537.3eV and two oxide peaks at about 539.6 and 540.1eV, which correspond to Sb₂O₃ and Sb₂O₅, respectively. As shown in Fig. 6(c), the oxide content does not change much from the solvent-only treatment for either the HCl or citric acid treatment. However, the combination of the two treatments results in

a substantial increase in oxide layer and a reduction in the Sb-Ga peak observed. Similar results are observed for the Sb4d band, Fig. 6(d), where the Sb4d_{5/2} and Sb4d_{3/2} band peaks associated with InAs were observed at 31.9 and 33.2, respectively. Further, two oxide peaks were observed at about 34.3eV and 35.7eV, again showing a substantial increase in oxide after HCl/citric acid treatment. XPS results for APTES coated substrates in the Sb4d spectra (see Supplemental Information, Fig. S7) again show peak attenuation due to the silane layer.

As shown in Fig. 5, the ratio of Ga/Sb for various bands was investigated to again determine if surface segregation occurred. As shown, there is little difference in the Ga/Sb ratio, except for the sample that underwent HCl/citric acid treatment, where it is clear that the surface becomes relatively more Ga-rich than the as-received sample. This segregation of the Ga oxide layer to the surface has been observed previously[53-55], and is usually in conjunction with a layer of elemental Sb beneath the Ga oxide layer. Generally, the justification for this has been the presence of multiple peaks beyond the expected spin orbital peak splitting in the Sb4d band. However, in our case, there seems to be no reason to add multiple fitting peaks beyond those associated with GaSb in Fig. 6(d). The same can be said of the Sb3d band in Fig. 6(c), which would require an additional peak as well near 537.5eV. Given these data, neither the HCl treatment alone nor the citric acid treatment alone resulted in the surface segregation of Ga oxide. Rather, either the HCl treatment seems to have resulted in some significant initial Ga oxidation that paved the way for surface segregation during citric acid treatment, or the additional time in acidic conditions simply contributed to the final state of the heavily oxidized and Ga oxide segregated substrate. XPS was also performed on the bare silicon wafer before and after acid treatments (not shown); as expected, no changes in the Si2p band were observed after HCl/citric acid combined treatment.

Fig. 6. XPS plots for (a) Ga2p, (b) Ga3d, (c) Sb3d, and (d) Sb4d for solvent treated samples and samples with solvent treatment followed by HCl acid wash, citric acid wash (CA), and combined HCl and citric acid wash (HCl/CA). Dashed lines indicate approximate peak positions used for fitting the data.

3.3.4. XPS for APTES Silane Layers

XPS was performed on the APTES silane layers to gain insight into how silane formation occurs on the surface of the various substrates. XPS data were obtained for C1s, O1s, N1s and Si1s bands for APTES concentrations in ultrapure water of 0.1%, 0.25%, 0.5%, 0.75%, 1.0%,

and 2.5% by volume. Here, the control samples (HCl/CA) correspond to substrates that were solvent rinsed followed sequentially by HCl and citric acid washing as explained above.

C1s. XPS spectra for the C1s band of APTES silane on the various substrates are provided in Fig. 7. As shown, the spectra for a given concentration of APTES are very similar in terms of peak positions and relative peak areas. Three peaks were sufficient to deconvolute the spectra. The first peak, which corresponds to C-C bonding, occurs in the 285-286eV range, while a second peak, associated with C-N or C-O bonding, was found in the range of 286.5-287eV. A final peak, from 289.0-289.5, corresponds to oxidation of APTES layers, known to occur in the form of ketone formation on the carbon adjacent to the primary amine, which can also explain the presence of C-O bonding [24, 56]. These values are in reasonable agreement with those found in the literature, listed in Table S2 in the Supplemental Information. One interesting feature of the data is that the primary C-C peak shifts from a value close to the expected 285eV for aliphatic carbon to values closer to 286eV with increasing APTES concentration (i.e., thicker APTES layers). Previous studies[56, 57] did not see this shift in binding energy largely because they corrected to the C1s aliphatic peak at 285.0eV for either calibration or static charging, which is common, but can also lead to some problems interpreting spectra[58]. Our corrections for static charging were performed for signals specific to the substrate, which shows this subtle (<1 eV) change, which is most prominent moving from the control sample to samples at a concentration of about 0.5% APTES. This shift could be attributed to slight charging of the surface as the APTES layer thickness increases, or could reflect a change from XPS detection of the adventitious carbon that is native to the substrate to the silane generated carbon from APTES.

Fig. 7. XPS plots for the C1s band of APTES silane layers deposited on (a) InAs, (b) GaSb, and (c) silicon wafer. APTES concentrations (vol% in ultrapure water) are indicated on the graphs.

O1s. XPS spectra for O1s from silicon and InAs are shown in Fig. 8. The O1s peak in GaSb overlaps with the $\text{Sb}3d_{5/2}$ peak (see Table S1)[59], making deconvolution of oxygen specific species difficult. As such, it is excluded from the discussion here. As shown in Fig. 8, the spectra for 2.5% APTES silanes are very similar. Given that the thickness of these films is on the order of 20nm or so (see Fig. 2), the majority of the signal should be coming from oxygen within the silane layer itself. As such, we can assign the large peak at 533.5eV to Si-O bonding within the silane layer itself (Table S2). The small peak at 535.0eV to the left of the main peak can be assigned to C=O bonding due to the oxidation of carbon discussed above (Table S2). The peak to the right of the main peak, at 532.0-532.4eV might be due to unhydrolyzed ethoxy groups; these tend not to exist in aqueous solutions at low concentration[44] and are more likely O-C bonds due to oxidation of carbon described above. Moving lower in concentration from 2.5%, the spectra look similar and the peak assignments are the same until about 0.5%, where influences of oxygen from the substrate are readily apparent in the InAs data. At this point,

oxygen associated with O-In and O-As bonds (see HCl/CA control sample) likely are superimposed with O-Si bonds, making determination of specific peaks difficult. For the HCl/CA O1s spectrum of InAs, the more prominent peak is attributed primarily to O-In bonding, while the smaller peak likely relates to O-As bonding (Table S2). For the HCl/CA O1s spectrum of Si, only a single peak, reflecting the oxide on the surface, SiO_x , is observed.

Fig. 8. XPS plots for the O1s band of APTES silane layers deposited on (a) InAs and (b) silicon wafer. APTES concentrations (vol% in ultrapure water) are indicated on the graphs.

N1s. XPS data for the N1s band for InAs, GaSb and Si with deposited APTES silane are presented in Fig. 9. In this figure, the peak in the range of 399.7-400.3eV corresponds to $-\text{NH}_2$ character, as found in the literature, although this peak may also contain the expected C-N character as well (see Table S2). The peak at higher binding energies (i.e., 401.5-402.0eV) is associated with ionic $-\text{NH}_3^+$ character or hydrogen bonded NH_2 , as has been extensively discussed in the literature (Table S2). An interesting observation from Fig. 9 is that, for thin

layers (i.e., <2.5nm, low APTES concentrations of 0.1-0.25%), the quantity of ionic N is approximately equivalent to that of free NH_2 . However, with increasing thickness (increasing APTES concentration) the free amine content becomes dominant at thicknesses at and above about 5nm ($\sim 0.5\%$ APTES).

Fig. 9. XPS plots for the N1s band of APTES silane layers deposited on (a) InAs, (b) GaSb, and (c) silicon wafer. APTES concentrations (vol% in ultrapure water) are indicated on the graphs.

These observations imply that the APTES layers, when thin, likely form ionic or hydrogen bonding interactions with the substrate surface, or possibly with Si-OH moieties remaining in the system that did not undergo condensation during the heating step. The possibility of hydrogen-bonding interactions between the silane layer and the oxide surface, as well as charge transfer leading to ionic NH_3^+ species, will be discussed in the section on DFT modeling. As shown in Fig. 9, for the thinnest film ($\sim 1\text{nm}$, i.e., 0.1%) the quantity of ionic nitrogen is approximately the same as non-ionic nitrogen; this is in agreement with previous observations for APTES

monolayers deposited out of an aqueous solution[60], but in contrast to an APTMS (trimethoxy rather than triethoxy) solution deposited in anhydrous toluene, which only showed NH_2 character, though 12 layers deposited using the same method showed some ionic character[61].

In addition to taking spectra at an incident angle of 85° with respect to surface normal, several N1s scans for APTES on InAs and Si were also obtained at an incident angle of 45° to provide more surface sensitivity in an attempt to determine if the ionic nitrogen was segregated more toward the surface or the bulk. These spectra at 45° (not shown) were fitted in the same manner as those in Fig. 9, and the resulting peak area ratio of free amine to ionic NH_3^+ are shown as a function of APTES film thickness (from ellipsometry) for all the obtained data in Fig. 10. As shown, the trend is very consistent across all of the substrates and shows that the quantity of non-ionic amine nitrogen detected increases with increasing film thickness. Ionic species account for roughly half of all nitrogen for the thinnest films ($\sim 1\text{nm}$), which is quite high. Further, the data obtained at 45° fall within the same trend as the 85° data for film thicknesses less than about 5nm . This is likely because the entirety of the film is being probed by both incident angles for these thicknesses. Interestingly, for the thickest films ($\sim 20\text{nm}$), the 45° data show a significantly lower ratio (~ 6) than the data at 85° (~ 8), indicating that more ionic nitrogen is present at the surface of the thicker films than in the bulk.

Fig. 10. Plot of the ratio of the area of NH_2 to NH_3^+ peaks from N1s spectra.

Si1s. XPS data for the Si1s band in APTES coated InAs and GaSb substrates are provided in Fig. S8 in the Supplemental Information. As shown, Si is clearly present, with increasing intensity for increasing vol% APTES. These plots confirm the presence of Si-O bonds related to a condensed silane layer indicating successful deposition of APTES even at the lowest (0.1 vol%) concentration.

3.4 NEXAFS

To provide further insight into the behavior of APTES layers on the various substrates, NEXAFS was performed, and the results are presented in Fig. 11. Looking at the C-edge plots (a through c), there is excellent agreement in the shape of the curves for concentrations of about 0.5% and above. Concentrations below 0.5% (~5nm thick) show a transition to a curve resembling that of adventitious carbon, shown in the HCl/CA control samples (0%). Key features in the C-edge spectra include the carbon π^* peaks, located at about 285.5eV, which are relatively small for all the samples here. Some of this character will still exist, however, due to

either aging or radiation induced damage during the measurement [56, 57, 62]. The peak at about 289eV is associated with C-H* character, while the broad peak at about 292.5 is associated with σ^* C-C and C-N bonding.[57] Figure 11(d) shows that the C-edge jump height, a qualitative indication of the quantity of carbon on the surface, is essentially the same regardless of substrate. This observation supports the ellipsometry data in Fig. 2 that show that film thickness is largely independent of substrate. A similar argument can be made for the N-edge jump height data, shown in Fig. 11(h).

N-edge NEXAFS plots are provided in Fig. 11(e-g) for the various substrates. As shown, the control samples essentially show no N present on the surface, and the N content increases with increasing thickness (ATPES concentration) until a concentration of about 0.5% APTES (film thickness of about 5nm). At this point, the general shape of the curve is established and persists for concentrations up to 2.5%. The general shape of the N-edge NEXAFS data and observed energy values are in good agreement with previous work on APTES [56, 57, 62]. Based on previous work[56, 57, 62], the peaks at about 399eV in the N-edge spectra are related to N π^* species that occur as a result of X-ray exposure, while the shoulder at 402eV is due to amine (N-H σ^*) character. The large peak at about 407eV is associated with C-N σ^* transitions riding on top of the N K-edge at 406.4eV.

Fig. 11. C-edge NEXAFS results for (a) InAs, (b) GaSb, (c) and Si substrates along with (d) C-edge jump values as a function of APTES solution concentration. N-edge NEXAFS results for (e) InAs, (f) GaSb, (g) and Si substrates along with (h) N-edge jump values as a function of APTES solution concentration.

3.5. Density Functional Theory Modeling

One major unanswered question is how the APTES specifically binds to the surface of III/V materials. On silicon wafers, APTES first undergoes hydrolysis of the ethoxy groups to hydroxyl groups, which then participate in a condensation reaction with surface hydroxyl groups present on the silicon oxide surface to form Si-O-Si bonds to the surface. A similar mechanism may occur with InAs and GaSb, but would require the presence of surface hydroxyl groups. This is a possibility, as previous computational studies have shown that OH adsorption from water dissociation on gallium and indium oxides is favorable [41, 63, 64]. Unfortunately, XPS cannot provide information about the presence of adsorbed OH groups on the oxide surface, which would imply that 3-aminopropyltriethoxysilane could form covalent bonds with the oxide. Furthermore, XPS results indicate the presence of ionic $[\text{NH}_3]^+$ head groups in the thinnest silane layers. We therefore hypothesized that depositing the silane coupling agent from an aqueous solution may allow non-bonded silane molecules to interact with hydroxyl groups on the oxide surface or on adjacent molecules. Such an interaction may induce local charge transfer, which could explain the effective $[\text{NH}_3]^+$ signal observed in the silane layer. This hypothesis was explored for the gallium oxide surface using DFT, where hydrolyzed APTES, i.e., aminopropyltrisilanol (APST), was used as a probe molecule.

Condensation reactions involving a single APST molecule on $\text{Ga}_2\text{O}_3(100)\text{B}$ are defined as shown in Fig. 12(a). This reaction can be written as

where x is the number of displaced H_2O molecules. These reactions create covalent Si-O-Ga bonds between APST and the $\text{Ga}_2\text{O}_3(100)\text{B}$ surface while simultaneously displacing an equivalent number of H_2O molecules. A molecular illustration of the result of this reaction—condensation to create one Si-O-Ga bond and eliminate one H_2O molecule—is shown in Fig. 12(b). Adsorption energies, E_{ads} , for condensation reactions involving one, two, or three silanols were calculated, and the results are given in Table 1.

Adsorption models were constructed for the $\text{Ga}_2\text{O}_3(100)\text{B}$ surface terminated with and without hydroxyl groups for comparison. Negative values of E_{ads} correspond to favorable binding, and the modeling results show that condensation is energetically favorable and that the APST molecule will bind covalently to the hydroxylated $\text{Ga}_2\text{O}_3(100)\text{B}$ surface. The trends in E_{ads} show that formation of three Si-O covalent bonds on the hydroxyl terminated surface is energetically preferred over only one or two bonds, and the energy of a single Si-O bond on the Ga_2O_3 surface is $\sim 15\text{-}20$ kcal/mol on average. In contrast, covalent bonding is not very favorable on oxide surfaces without OH groups, indicating that covalent bonding of APST to the Ga_2O_3 surface depends on the presence of surface hydroxyl groups that can condense with OH moieties on the silane molecule.

Figure 12. (a) Schematic of proposed condensation reaction occurring between silane coupling molecule (APST) and hydroxyl groups on $\text{Ga}_2\text{O}_3(100)\text{B}$ surface. (b) Atomistic model of a single APST molecule binding to the $\text{Ga}_2\text{O}_3(100)\text{B}$ surface via one Si—O bond. The $\text{Ga}_2\text{O}_3(100)\text{B}$ surface is drawn as solid tetrahedra, while the APST molecule is represented with a ball-and-stick model. Color legend: tan = Ga, red = O, white = H, grey = C, yellow = Si, blue = N.

In contrast to the chemisorbed silanols that experienced the condensation reaction, several physisorbed configurations of the APST molecule on the relaxed $\text{Ga}_2\text{O}_3(100)\text{B}$ hydroxyl terminated surface were also modeled. We considered 15 starting structures, and optimized geometries with the lowest energies are shown in Figure 13. The adsorption energies and Hirshfeld partial charges for these models are listed in Table 3. Models having the $\text{Si}-(\text{OH})_3$ moiety down or the full chain parallel to the surface have energies ~ 20 kcal/mol, while the adsorption energy for the NH_2 moiety down is only ~ 7 kcal/mol. This indicates that the APST molecule prefers to orient with the $\text{Si}-(\text{OH})_3$ moiety down, likely because multiple OH groups are available to hydrogen bond with hydroxyl groups on the surface. These favorable hydrogen bonding interactions between APST and the oxide surface are not present in the models without OH groups. So, adsorption mechanisms having the $\text{Si}-(\text{OH})_3$ moiety down or the full chain parallel to the surface are much weaker on the hydroxyl-free surface, having energies of only ~ 2 - 5 kcal/mol.

Figure 13. Optimized geometries of several physisorbed configurations of a single APST molecule on the Ga₂O₃(100)B surface: (a) Si—(OH)₃ moiety down, (b) NH₂ moiety down, (c) chain parallel to surface, (d) [NH₃]⁺ moiety down, (e) magnification of (d). Coloring same as Figure 12.

The least favorable adsorption mechanism on the hydroxylated surface is that with the NH₂ moiety down; this is due to weak interactions between NH₂ groups on the APST chain ends and hydroxyl groups on the Ga₂O₃(100)B surface. However, in several models, we observe that geometry optimization can force a single H atom to be abstracted from a surface OH group, forming a [NH₃]⁺ end group on the silane molecule. This substantially increases the partial charge on the amine end group. In contrast, geometry optimization of models with the [NH₃]⁺ end group near a Ga₂O₃ surface with *no* OH groups is unstable. Such models always donate one H atom back to the surface, forming a single OH group on the surface and leaving an NH₂ end group on the silane molecule. This reveals another mechanism (other than water adsorption [41,

65] or H₂ dissociation [40, 65, 66]) by which OH groups can form on the gallium oxide surface. To our knowledge, this mechanism has never been reported for silane deposition on metal oxides.

Table 1. Adsorption energies and summed Hirshfeld partial charges on NH₂ and SiO₃ end groups of an optimized APST molecule on the relaxed Ga₂O₃(100)B surface.

		<i>Surface models with OH groups</i>			<i>Surface models without OH groups</i>		
adsorption mechanism	# of displaced H₂O molecules	<i>E</i>_{ads} (kcal/mol)	<i>q</i>(NH₂)	<i>q</i>(SiO₃)	<i>E</i>_{ads} (kcal/mol)	<i>q</i>(NH₂)	<i>q</i>(SiO₃)
1 Si—O surface bond	1	-17.41	0.05	-0.40	-3.50	0.03	-0.45
2 Si—O surface bonds	2	-31.62	0.01	-0.60	-2.88	0.04	-0.55
3 Si—O surface bonds	3	-54.35	0.06	-0.55	11.08	0.03	-0.57
Si—(OH) ₃ moiety down	0	-22.40	0.05	-0.39	-2.14	0.05	-0.45
NH ₂ moiety down	0	-7.09	0.10	-0.40	-10.91	0.11	-0.39
[NH ₃] ⁺ moiety down	0	-28.18	0.27	-0.39	unstable*		
Chain parallel to surface	0	-20.68	0.01	-0.32	-4.48	-0.02	-0.25

Data is included for surface models both with and without OH groups. The four physisorption mechanisms (those with zero displaced water molecules) are shown in Figure 13. *This adsorption mechanism is unstable against geometry optimization.

First principles modeling thus shows that a number of different adsorption mechanisms are favorable for APST on the Ga_2O_3 surface. On an oxide surface with no OH groups, adhesion of the silane molecules through either Si—O covalent bonds or physisorption is weaker than on the hydroxyl-terminated surface. This is because the presence of adsorbed OH groups helps to stabilize physisorbed configurations through hydrogen bonding at the oxide/silane interface and facilitates the condensation reaction that eliminates OH groups in the form of displaced water. We therefore expect that a thin silane layer deposited from aqueous solution will most likely contain a mixture of these different adsorbed states, depending on the surface coverage of hydroxyl groups in the deposition region. Our models also show that $\text{N}\cdots\text{HO}$ charge transfer can occur between the physisorbed silane molecules and hydroxyl groups on the oxide surface, which could explain one source of experimental signals of $[\text{NH}_3]^+$ on the surface. Although we did not expressly model silane adhesion on the indium oxide surface, condensation to form covalent Si—O bonds should occur if the In_2O_3 surface is hydroxyl-terminated. This should be the case, given that the dissociation of water and subsequent formation of adsorbed hydroxyl groups on indium oxide is even more energetically favorable than on gallium oxide [63, 64].

4. Conclusions

Based on the reported results, the combined HCl/citric acid surface preparation treatment is particularly effective at removing oxide from InAs, including the conductive In_2O_3 oxide that is detrimental for photodetector device operation. Specifically, HCl alone removes oxide but results in segregation of In to the surface while citric acid is very effective at removing As oxide, and the combination of HCl and citric acid prevents In surface segregation. The HCl/citric acid

surface treatment method does, however, result in heavy oxidation of both Ga and Sb accompanied by segregation of Ga oxide to the surface.

The deposition of APTES from aqueous solution and subsequent formation of a silane layer was successfully conducted on InAs, GaSb and silicon wafers. Remarkably, the deposited layer thickness did not depend on the substrate choice, and thicknesses between 1 and 20nm could be obtained for APTES concentrations ranging from 0.1 to 2.5 vol%. AFM measurements showed that these silane layers were of high quality and that for InAs and GaSb substrates the roughness of the film decreased with increasing APTES thickness. NEXAFS spectra showed that the carbon in these layers resembled adventitious carbon for layers below 5nm (~0.5vol%) in thickness, before showing spectra characteristic of APTES silane layers. XPS results for the N1s band showed that the content of ionic nitrogen was high (~50%) for the thinnest films (~1nm) and decreased with increasing film thickness. DFT calculations showed that covalent binding with surface hydroxyl groups via a condensation reaction was a possible mechanism of film formation. Furthermore, $N\cdots HO$ charge transfer between physisorbed silane molecules and surface hydroxyl groups is favorable, which could explain the ionic character of the nitrogen XPS results.

These results indicate that APTES can indeed be used to form a silane surface layer to cover III-V materials substrates via covalent bonding or physisorption between APTES and the surface. Such silane layers may prove useful in surface passivation of these materials alone or as surface functionalizing agents for subsequent covalent binding with polymer overlayers like polyimide. [Future testing in devices is necessary to determine the efficacy of such a passivation strategy.](#)

Supporting Information. Further information on NEXAFS, AFM images, details related to ellipsometry measurement, previously measured binding energies, and additional XPS measurements is available online.

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