Hafnium oxide interfaces were studied on two related group III rich semiconductor surfaces, InAs(0 0 1)−(4×2) and In0.53Ga0.47As(0 0 1)−(4×2), via two different methods: reactive oxidation of deposited Hf metal and electron beam deposition of HfO2. The interfaces were investigated with scanning tunneling microscopy and spectroscopy (STS). Single Hf atom chemisorption sites were identified that are resistant to oxidation by O2, but Hf islands are reactive to O2. After e− beam deposition of ∼1 ML of HfO2, single chemisorption sites were identified. At low coverage (≪1 ML), the n-type and p-type HfO2/InGaAs(0 0 1)−(4×2) interfaces show p-type character in STS, which is typical of clean InGaAs(0 0 1)−(4×2). After annealing below 200 °C, full coverage HfO2/InGaAs(0 0 1)−(4×2) (1–3 ML) has the surface Fermi level shifted toward the conduction band minimum for n-type InGaAs, but near the valence band maximum for p-type InGaAs. This is consistent with the HfO2/InGaAs(0 0 1)−(4×2) interface being at least partially unpinned, i.e., a low density of states in the band gap. The partially unpinned interface results from the modest strength of the bonding between HfO2 and InGaAs(0 0 1)−(4×2) that prevents substrate atom disruption. The fortuitous structure of HfO2 on InAs(0 0 1)−(4×2) and InGaAs(0 0 1)−(4×2) allows for the elimination of the partially filled dangling bonds on the surface, which are usually responsible for Fermi level pinning. © 2010 American Institute of Physics. [doi:10.1063/1.3427584]
elsewhere. The InAs(0 0 1)−(4×2) surface shows better long range order, has larger mean domain sizes, and has fewer defects. The InAs(0 0 1)−(4×2) surface is a better substrate than InGaAs samples. For the identification of specific bonding geometries of chemisorbates the STS technique since the accuracy is especially critical.

InGaAs samples are grown via MBE on commercially available InAs substrates described elsewhere. The InGaAs samples were grown via MBE by collaborators offsite on commercially available InP substrates. The MBE grown layers were 1.5 μm thick, and the doping concentration was 1.5 \times 10^{18} \text{cm}^{-2} for both p-type and n-type wafers, using Ge or Si as dopants, respectively. The samples were protected with an amorphous As₂ capping layer (60–100 nm thick) and shipped in rough vacuum. After transfer into the UHV analysis chamber, the samples were degassed at 200 °C for 3 h and heated to 380 °C for 2 h to desorb the As₂ capping layer. The InAs(0 0 1)−(4×2) reconstruction was formed by increasing the substrate temperature by ~0.2 °C s⁻¹ to 450 °C and holding for 10 min. The InGaAs samples were heating instead to a maximum temperature of 465 °C to obtain the (4×2) reconstruction. Surface periodicity was confirmed using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

Hafnium was evaporated from a 99.9% purity metal rod using an Oxford Applied Research HPEB4 electron beam evaporator. Hafnium oxide was evaporated from a 99.9% purity oxide tablet using an MDC e-vap 3000 electron beam evaporator. Both evaporators were located in a differentially pumped chamber at a base pressure of ~5 \times 10⁻⁶ Torr.

A. Reactive Oxidation of Hf on InAs(0 0 1)−(4×2)

Figure 1(a) shows STM results for room temperature deposition of Hf metal on InAs(0 0 1)−(4×2) at low coverage. Single chemisorption sites are identified for Hf atoms (green arrows), although larger clusters are also apparent. High resolution STM images reveal two nearly equivalent Hf addition sites that both occupy locations on the side of the rows, and are identified as the row-edge [Fig. 1(b)] and...
As-bridge sites [Fig. 1(c)]. The row-edge site involves the Hf atom bonding adjacent to the row and protruding over the In–In dimer in the trough region, centered between the In atoms of the trough dimer. The As bridge site is distinguished from the row-edge site by the position of the Hf atom with respect to the In dimers in the trough. In the case of the As-bridge site, the Hf atom is between the In dimers rather than over one dimer and this position would cause it to bridge the neighboring row-edge As atoms. Proposed bonding geometries for the row-edge and As-bridge sites are shown in the ball and stick diagrams in the lower portions of Figs. 1(b) and 1(c). Nearly all other Hf sites on the surface are either simple combinations of these two sites or are high coverage sites with an unresolved structure. The single sites are studied for their oxidation properties since their structures are more readily identified.

Molecular oxygen was introduced into the STM chamber to observe the oxidation of the single Hf addition sites on InAs(0 0 1)−(4×2) in situ. A single Hf atom chemisorption site was considered to be oxidized when its appearance changed in the STM image. The unoxidized Hf sites are readily distinguished from the oxidized single HfO\(_2\) sites (not shown); the unoxidized single Hf sites are circular in filled state STM images with a height of ~0.3 Å above the row structure while the HfO\(_2\) sites change in shape and apparent height above the row structure.

The single Hf atoms were shown to have very low reactivity to O\(_2\) when chemisorbed to the InAs surface; only 20% ± 10% of the single Hf atoms were oxidized after a total O\(_2\) dose of 700 L, as obtained from one in situ oxidation experiment that tracked 26 Hf addition sites. The large uncertainty is due to the difficulty in counting and tracking reaction sites in STM data throughout the 35 consecutive images. Furthermore, reaction of O\(_2\) with the clean InAs substrate was observed, consistent with the previously observed mechanism.

The low reactivity for O\(_2\) on isolated Hf atoms (sticking probability of 1–4×10\(^{-4}\)) is probably due to Hf having a lower electronegativity than the In and As atoms of the substrate; therefore, it is likely that Hf has donated electron density when bonding to the surface. On other semiconductor surfaces, O\(_2\) dissociatively chemisorbs via charge addition to its π* antibonding orbital. The low reaction probability of O\(_2\) on Hf atoms is consistent with isolated Hf atoms providing little weakly bound electron density available for transfer to the incoming O\(_2\) molecule to accept into its π* orbital. The sticking probability for O\(_2\) on clean InAs(0 0 1)−(4×2) is ~10\(^{-4}\). The O\(_2\) reaction on clean InAs(0 0 1)−(4×2) involves the displacement of As atoms to form In–O–In bonds; it is likely that these displacement reactions will pin the Fermi level so it is imperative to find a method of increasing the Hf reactivity relative to the substrate.

After annealing the unoxidized low coverage Hf/InAs(0 0 1)−(4×2) surface to 400 °C, the single Hf atoms coalesce into islands [Fig. 2(a)]. The smallest islands consist of six Hf atoms, or Hf hexamers and one is shown in the inset of Fig. 2(a). Larger Hf islands exist on the surface, however, no smaller Hf islands appear after annealing, which indicates that the hexamers are the smallest stable islands for the conditions. A proposed ball and stick model for the Hf hexamer on InAs(0 0 1)−(4×2) is shown in Fig. 2(d). The standard allotrope of Hf forms a hexagonal close packed (hcp) crystal structure; as the Hf islands increase in size beyond six atoms, they begin to lack atomic corrugation in STM and appear as bright featureless regions. The difficulty in resolving atomic corrugation of the islands in STM is consistent with the Hf bonding closely together, as in the hcp structure.

The hexamers and larger Hf islands are more reactive toward O\(_2\) than the single Hf atoms, consistent with their having a metallic character. After an equivalent 700 L dose of O\(_2\), 64% ± 7% of the 14 hexamer islands observed reacted with O\(_2\), and 60% of the reaction occurred within the first 100 L of O\(_2\) exposure. Similar criteria employed for oxidation of the single Hf addition sites were used to determine whether a Hf hexamer was oxidized. The unoxidized Hf hexamer islands have a length of ~24 Å and a height of ~0.5 Å above the row structure, while the oxidized islands have an irregular shape and appear much higher in STM images. Figure 2(b) shows a group of Hf hexamers (green arrows) on the InAs(0 0 1)−(4×2) surface before O\(_2\) is introduced into the UHV chamber. Figure 2(c) is the same area of the surface after 350 L O\(_2\) exposure, showing the resulting oxidation. The oxidized hexamers in Fig. 2(c) showed an increase in apparent STM height of about 1.5 Å
from Fig. 2(b). The uniform oxidation of the Hf hexamers contrasts with the oxidation of the single Hf atoms, which showed only sporadic single oxidation events throughout the O$_2$ exposure time.

The annealed Hf-deposited surface shows high selectivity for oxidation of the Hf over the III–V substrate. After oxidation of the Hf islands, the surface was annealed at 400 °C to attempt to form a more ordered overlayer of HfO$_x$ on the InAs surface. Some local order is observed, but the majority of the regrowth shows amorphous island formation (Fig. 3). Although the exact structure cannot be determined since the island is amorphous, it is identified as an oxide based on the height increase during oxidation as explained above. The amorphous island formation is consistent with a preferential bonding of the HfO$_x$ to itself, rather than the InAs(0 0 1) substrate. The mobility of the HfO$_x$ on the surface at 400 °C is also consistent with relatively weak bonding between the HfO$_x$ and the substrate.

**B. Direct deposition of HfO$_2$ on InAs(0 0 1)−(4×2) and InGaAs(0 0 1)−(4×2)**

On InAs(0 0 1)−(4×2) at 200 °C, low coverage of HfO$_2$ deposited via e$^-$ beam evaporation is shown in the STM data in Fig. 4(a). This image contains only the lowest-coverage sites, whose bonding structure is more readily identified than for larger sites. The HfO$_2$ bonds to itself in a variety of structures, making identification of specific molecular structures for the larger sites more challenging. The smallest sites (~8 Å in diameter) are attributed to HfO$_2$ molecules bonding on the side of the rows and over the trough regions, observed either singly or in pairs of bridging sites.

In the low coverage regime, HfO$_2$ is often observed in STM as double, row “bridge” sites as shown in the blue box of Fig. 4(a). These specific chemisorption sites have been modeled using density functional theory (DFT), and those results are published in a companion paper. In that paper, DFT results reveal that the double HfO$_2$ bridge site is slightly more stable than the single HfO$_2$ half-bridge “row edge” site by about 0.4 eV/HfO$_2$ molecule. This is consistent with the STM results, showing the population of bridge sites is larger than one would expect by a random distribution of single sites. In STM images, single HfO$_2$ sites appear different than the single Hf atom sites—the HfO$_2$ sites are slightly larger in diameter and higher above the row. The DFT calculations of Bishop et al. show that the lowest energy bonding structure for a HfO$_2$ molecule is for it to be oriented over the trough region, along the side of the row via O–In bonds and Hf–As bonds. This bonding configuration is illustrated in the ball and stick diagram of the half-bridge row-edge site in Fig. 4(b). On the clean surface, the substrate atoms for these sites all have dangling bonds that result from their tricoordinated configuration. The proposed HfO$_2$ site shown in Fig. 4(b) would eliminate these dangling bonds on the row-edge As atoms and trough-dimer In atoms.

At higher coverages, a Volmer–Weber growth mode is observed with small HfO$_2$ islands forming on the InAs(0 0 1)−(4×2) surface for substrate temperatures of 200 °C during e$^-$ beam HfO$_2$ deposition. This is represented in the STM data in Fig. 4(c) and the corresponding histogram of the pixel heights. For the coverage in Fig. 4(c), 14% of the surface area is first layer growth and 11% is second layer growth or higher, typical for Volmer–Weber growth. The
first layer growth shows small regions of order, indicated by the green arrows in Fig. 4(c). This ordered reconstruction was observed to be more prevalent at higher deposition or annealing temperatures (≥300 °C). Deposition of HfO₂ via e⁻ beam is known to produce polycrystalline films for elevated temperatures of >250 °C and smooth, amorphous films at lower temperatures. This study is consistent with those results.

At higher coverage of HfO₂ on the group III rich InAs(0 0 1) or InGaAs(0 0 1) surfaces, the growth is amorphous at substrate temperatures up to ~200 °C. Since the growth mode is Volmer–Weber-like, full coverage only occurs after the equivalent of several monolayers of oxide has been deposited. For an annealing temperature of 100 °C, full coverage of HfO₂ on the InGaAs(0 0 1)–(4×2) surface [Fig. 5(a)] shows smooth, amorphous growth with an rms roughness of 0.8 Å. Similar results are seen for the InAs(0 0 1)–(4×2) surface (not shown).

At annealing or deposition temperatures of 300 °C, the HfO₂ on InGaAs(0 0 1)–(4×2) shows small regions of ordered structures that are only in the first layer and also disordered, multilayer island growth [Fig. 5(b)]. These first layer ordered regions are similar to the ordered regions formed by oxidation of the annealed Hf atoms on the InAs(0 0 1)–(4×2) surface (Fig. 3, green arrows). However e⁻ beam deposited HfO₂ may also induce substrate roughening, as evidenced by the dark pits in the STM image of the HfO₂/InGaAs(0 0 1)–(4×2) surface [Fig. 5(b), green arrows].

While amorphous gate oxides are usually preferable for MOSFETs, an ordered first layer of gate oxide is usually desired. An ordered first layer is often optimal since it will allow further oxide growth to have uniform thickness without pinholes and because ordered structures are more likely to leave the surface unpinned. The first-layer order seen in Fig. 5(b) suggests that the HfO₂ bonds to the III-V substrate are relatively weak; the diffusion of HfO₂ on the surface to form these ordered regions would not be likely to occur for this refractory oxide if the bonds to the substrate were strong. DFT calculations by Bishop et al. show that the chemisorption energy of the HfO₂ molecule to the III-V surface is...
STS experiments were only performed on InGaAs since the HfO$_2$ makes three bonds to the surface.

The p-type character of both InGaAs surfaces is reproducible in STS experiments since the small band gap of InAs inhibits precise determination of the Fermi level energy shift with respect to the band edges on InAs(0 0 1), especially for surfaces with the rough topology induced by oxide deposition.

For the clean surface, both n-type and p-type InGaAs(0 0 1)−(4×2) show dI/dV curves that indicate that the surface Fermi level ($E_F$) is located near the VBM, as shown in Figs. 6(a) and 6(b) (red lines). In each case, $E_F$ = VBM+0.2 eV. This apparent p-type character for n-type InGaAs(0 0 1)−(4×2) is likely due to pinning induced by defect states on the clean surface. The p-type character of both InGaAs surfaces is reproducible in STS experiments and is described as being “pinned p-type.”

After full-coverage deposition of HfO$_2$ (substrate temperature of 25 °C followed by a 100 °C anneal and a growth rate of ~0.2 ML s$^{-1}$), the STS results show at least a partial unpinning of the surface. The blue dashed line in Fig. 6(a) (p-type InGaAs) is the STS data after oxide deposition; the results show that the CBM position remains nearly the same with respect to $E_F$, but the valence band-edge density decreases. The origin of this decrease in valence band-edge density on the p-type material is unknown and does not occur with the n-type material, but the difference could be due to irregularities in the thickness of the oxide layer. In Fig. 6(b) (n-type InGaAs), the Fermi level position shifts with respect to both the CBM and VBM, consistent with a partially unpinned surface Fermi level (blue dashed line). The overall shift is only about 0.2 eV. It appears that the band gap was reduced in this case by 0.1 eV. However, the band gap is still close to the expected value (0.73 eV) and the Fermi level position clearly moves toward the CBM and away from the VBM.

Consistent with a partially unpinned interface, the STS results for HfO$_2$ on p-type InGaAs(0 0 1)−(4×2) show no change for the Fermi level position with respect to the CBM ($E_F$=CBM−0.5 eV), while the STS results for HfO$_2$ on n-type InGaAs(0 0 1)−(4×2) show that the Fermi level moves from 0.5 eV below the CBM to 0.2 eV below the CBM. Additionally, for HfO$_2$ on n-type InGaAs(0 0 1)−(4×2), the Fermi level position moves from VBM to CBM+0.4 eV. These results suggest that a partially unpinned interface is formed between HfO$_2$ and InGaAs(0 0 1)−(4×2) for the conditions of low annealing temperature ($\approx$200 °C). At higher annealing temperatures ($\approx$300 °C), the Fermi level position on n-type material is not as close to the CBM and appears more p-type. This is likely related to the substrate roughening seen for 300 °C annealed HfO$_2$/InGaAs(0 0 1)−(4×2). For p-type material and higher annealing temperatures, the Fermi level position remains near the VBM. For low annealing and deposition temperature (<200 °C), the unpinning may not be complete due to oxidation of the III-V substrate during deposition. The background pressure during e− beam deposition reaches the range of 10$^{-6}$ Torr in the differentially pumped evaporation chamber, indicating that the HfO$_2$ evaporates incongruently. Adventitious oxygen species could chemisorb onto the InGaAs surface and create pinning states.

Oxygen-induced pinning has been seen for other III-V surfaces. Investigation is warranted of other deposition methods (atomic layer deposition) since the reactions may involve less adventitious O$_2$ and the undesired arsenic oxide “clean up” effect has been observed for other high-k oxide metal precursors such as trimethylaluminum.

The partial unpinning of InGaAs(0 0 1)−(4×2) is very instructive for identifying other possible oxide-semiconductor unpinned interfaces. The only other STM study that showed the atomic positions for an unpinned interface was Ga$_2$O$_3$/GaAs(0 0 1)−(2×4) where the Ga$_2$O$_3$ made simple Ga−As bonds to the surface; the surface was unpinned by just forming a bulklike transition to the oxide. For HfO$_2$/InGaAs(1 0 0)−(4×2), the interfacial bonds are not bulklike; instead they are Hf−As bonds and O−In/Ga bonds. Strong highly ionic bonds are expected to create midgap states which pin the interface, but this does not occur for HfO$_2$/InGaAs(0 0 1)−(4×2). Instead the bonds are relatively weak, as shown by the formation of some locally ordered regions at medium coverage. This relatively weak bonding to the surface occurs because the HfO$_2$ formula units already have cationic-anionic charge exchange. Furthermore, the fortuitous structure of HfO$_2$ allows elimination of the partially filled dangling bonds on the surface which are thought to be responsible for Fermi level pinning of InGaAs(0 0 1)−(4×2) even on the defect free surface.
IV. CONCLUSION

In this study, deposition methods for HfO₂ on two different III-V substrates were examined and their combined results reveal complementary aspects of the oxide/semdiconductor interface formation. This approach takes advantage of the low defect density of InAs(0 0 1)−(4×2) for atomic structure identification and the larger band gap of In₀.₅₃Ga₀.₄₇As(0 0 1)−(4×2) for electronic structure determination.

Oxidation of Hf metal on the InAs(0 0 1)−(4×2) surface was observed in situ via STM. Two different single atom Hf chemisorption sites were identified on the InAs(0 0 1)−(4×2) surface, but these single atom addition sites had low reactivity to O₂. Annealing the results reveals complementary aspects of the oxide/fernet III-V substrates were examined and their combined

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