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***In situ* study of e-beam Al and Hf metal deposition on native oxide InP (100)**

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The interfacial chemistry of thin Al (~ 3 nm) and Hf (~ 2 nm) metal films deposited by electron beam (e-beam) evaporation on native oxide InP (100) samples at room temperature and after annealing has been studied by *in situ* angle resolved X-ray photoelectron spectroscopy and low energy ion scattering spectroscopy. The In-oxides are completely scavenged forming In-In/In-(Al/Hf) bonding after Al and Hf metal deposition. The P-oxide concentration is significantly decreased, and the P-oxide chemical states have been changed to more P-rich oxides upon metal deposition. Indium diffusion through these metals before and after annealing at 250 °C has also been characterized. First principles calculation shows that In has lower surface formation energy compared with Al and Hf metals, which is consistent with the observed indium diffusion behavior.

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INTRODUCTION

High mobility III-V semiconductors metal oxide semiconductor (MOS) devices attract considerable attention for their potential to replace Si devices beyond the 14 nm technology node.^{1,2} However, oxidation of the III-V/high-k dielectrics interface can lead to Fermi-level pinning and frequency dispersion,³ which can in turn strongly affect the electrical performance of III-V based devices.⁴ InP has been successfully used as a barrier layer between high-k oxides and III-V channel layers and has exhibited excellent electrical performance.^{5–7} The InP barrier layer and the high-k dielectrics are in direct contact, so it is critically important to understand the chemistry at the interface between InP and high-k dielectrics.⁸ Atomic layer deposition (ALD) “half cycle” studies of Al₂O₃ and HfO₂ on the native oxide InP (100) surfaces using *in situ* X-ray photoelectron spectroscopy (XPS) has been reported.^{9,10} The “clean up” effect, whereby the oxygen is seen to transfer from the native oxides to form Al₂O₃ and HfO₂, is observed for the In-oxides after the first pulse of metal precursors, but the “clean up” effect does not occur for the P-oxides, leaving a P-rich oxide.⁹ Recently, indium out-diffusion through high-k dielectrics upon annealing has been reported,^{11,12} resulting in a P-rich interface, which have been correlated to the interface trap density (D_{it}) from electrical analysis.^{13,14} It is, therefore, critical to control this P-rich oxide concentration at the interface for InP/high-k stack.

In order to further remove the interfacial oxides from the InP surface, the deposition of Al and Hf metals are examined in this study in an attempt to scavenge the In and P-oxides that are present in the native oxide and thus without the reaction with ligands associated with metal ALD precursors. The interfacial chemistry and the elemental diffusion are studied through a sequence of thin layer metal

depositions on a native oxide InP (100) sample at room temperature (RT), which are characterized by *in situ* angle resolved XPS (ARXPS) and low energy ion scattering spectroscopy (LEIS).

EXPERIMENTAL AND MODELING METHODS

Two *n-type* InP (100) native oxide samples (supplied by AXT) cleaved from one wafer were used. The substrates were degreased by using acetone, methanol, and isopropanol for 1 min each at RT. Al and Hf were deposited on separate samples by electron beam evaporation (e-beam). The experiments are carried out in an *in situ* multi-deposition cluster tool described elsewhere.¹⁵ A four pocket e-beam deposition hearth is utilized in a physical vapor deposition (PVD) chamber (base pressure $\sim 5 \times 10^{-10}$ mbar), which is connected to the analysis chamber by a sample transport tube maintained at 10^{-10} mbar, allowing the samples to be transferred between the different chambers without exposure to the atmosphere. XPS spectra were acquired using a monochromatic Al K α ($h\nu = 1486.7$ eV) X-ray source with a seven channel hemispherical electron energy analyzer operating at a pass energy of 15 eV, at different take off angles of 45 and 80° (with respect to the sample surface) after each successive deposition and annealing step. The XPS and LEIS scan areas were displaced on the surface to avoid any spurious ion beam damage effects. XPS spectra of the In 3d_{5/2}, P 2p, O 1s, C 1s, Al 2p, and Hf 4d regions were measured to study the surface and interfacial chemistry of the metal films and the InP native oxide. XPS spectra were deconvoluted using AANALYZER peak fitting software.¹⁰ The LEIS was carried out using the same 7 channel analyzer as used for the XPS measurements with biasing conditions suitable for ion detection, and He⁺ ions excited by an ISE 100 fine focus ion gun using 1 kV bias and 10 mA emission current.

Aluminum metal was deposited on the InP sample surface at room temperature for 1 min, and then an additional 10 min (resulting in a ~ 3 nm overlayer based on the

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attenuation of the underlying P 2*p* XPS signal) under the same deposition conditions (e-beam power = 2430 W) and subsequent annealing at 250 °C in ultrahigh vacuum (UHV). A separate InP sample was also covered with a 2 nm Hf layer (e-beam power = 1800 W) and subsequently annealed at 250 °C for comparison. *Ex situ* atomic force microscopy (AFM) measurements were carried out to characterize the surface morphology before and after annealing on a companion sample under the same deposition conditions in each case.

The total energies of Hf, Al, In, P, Al₂O₃, HfO₂, AlPO₄, InPO₄, In(PO₃)₃, P₂O₅, Hf₃P, InP, AlP, and the Hf, Al and In metal (100) surface formation energies have been calculated using density functional theory (DFT) with projector augmented wave (PAW) pseudopotentials implemented in the Vienna *ab initio* simulation package (VASP). The exchange correlation interactions are incorporated as a functional of the generalized gradient approximation (GGA). The total energies of the various compounds are calculated using their crystal structures from various crystal databases^{16,17} and relaxing the atomic positions and keeping the volume constant. The surface formation energies are calculated as follows:

$$E_{\text{form}}^{\text{slab}}(T, p) = \frac{G_{\text{slab}}(T, p, \{N_i\}) - \sum_i N_i \mu_i(T, p)}{A}, \quad (1)$$

where $E_{\text{form}}^{\text{slab}}$ is the surface formation energy, G_{slab} is the total Gibbs free energy of surface (with vacuum), A is the total surface area of the slab, and μ_i are the chemical potentials for the respective elements with N_i the numbers of species. The energy and force convergence criteria used were 10⁻⁴ eV and 0.01 eV/Å, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the (a) In 3*d*_{5/2}, (b) P 2*p*, (c) Al 2*p*, and (d) O 1*s* spectra before e-beam Al deposition, after 1 min of Al deposition, after 11 min (total) of Al deposition, and after

annealing at 250 °C under UHV, respectively. For In 3*d*_{5/2}, the peak with a binding energy separation of -0.51 eV (-0.6 eV after anneal) from the InP bulk peak is assigned to In-In/Al bonding.¹⁸ The peak with a binding energy (BE) separation of +0.54 eV to the InP bulk peak is assigned to In-O bonding (likely In₂O).¹⁰ The peak with a BE separation of +1.08 eV to the InP bulk peak is assigned to InPO₄/In(PO₃)₃,¹⁹ and the peak with a binding energy separation of +1.7 eV to the InP bulk peak is assigned to InPO_x.²⁰

A significant decrease in the In-oxide concentration occurs upon Al deposition and with the emergence of the In-In peak, suggests that the Al metal scavenges the In-oxide to form In-In bonds and Al-oxide after the initial 1 min of Al metal deposition. No In-Al bond formation is assigned, due to the lack of the detection of a corresponding Al-In BE feature from the Al 2*p* spectra after the initial 1 min of Al metal deposition. The In-oxide concentration is below the XPS detection limit after the 11 min of Al metal deposition process, and after annealing at 250 °C. In-Al bond formation is detected after the 11 min of Al deposition, and after the UHV annealing at 250 °C, from both the Al 2*p* and In 3*d*_{5/2} spectra.

For the P 2*p* spectra in Figure 1(b), the peaks with a binding energy separation of 4.0 eV, 4.5 eV, 5.1 eV, and 6 eV are assigned to P-OH bond, InPO₄, In(PO₃)₃, and P₂O₅ states, respectively.^{9,20,21} A contribution from an asymmetrical Al 2*s* plasmon peak is incorporated at 134.5 eV from the Al 2*s* spectra of the Al-metal peak, which overlaps with the P-oxide feature. The P 2*s* spectra are thus also taken to avoid this overlap, as shown in Figure 2(b). Only the P₂O₅ state is detected after the 11 min of Al deposition and after the subsequent annealing. A decrease in the concentration for this P₂O₅ state is also detected after a total 11 min of Al deposition and subsequent annealing in UHV, which is concomitant with the increase in the concentration of Al oxides and attributed to the transfer of oxygen from the P₂O₅. From the Al 2*p* spectra, the Al is only in an Al-oxide chemical state, which

FIG. 1. The XPS core level spectra of (a) In 3*d*_{5/2}, (b) P 2*p*, (c) Al 2*p*, and (d) O 1*s* spectra prior to Al deposition, after the initial Al deposition, after 3 nm deposition, and after annealing at 250 °C under UHV condition.

FIG. 2. The XPS core level spectra for (a) In 3*d*_{5/2} and (b) P 2*p*, after 3 nm Al deposition and after annealing at 250 °C under UHV condition at XPS scans angles of 45 and 80°.

explains why no Al plasmon peak is detected after the initial Al deposition. The BE of the Al 2s feature is located at 117.7 eV.

The P-oxide chemical states are seen to change during Al depositions and the subsequent annealing process. The InPO₄ and P-OH states are seen to change to the In(PO₃)₃ predominant state with the emergence of P₂O₅ after the 1 min Al deposition step, and with only the P₂O₅ state detected after the 11 min total Al-deposition. The P₂O₅ concentration is observed to decrease after annealing at 250 °C and may be attributed to desorption.

The remaining P-oxides after the Al metal deposition on the InP native oxide sample are in contrast with the complete scavenging of In, Ga, and As-oxides from an oxidized InGaAs sample surface by Al metal deposition in a previous study.²² Therefore, a less effective clean up effect occurs on InP compared with InGaAs.

The total energy calculated by DFT is used instead of the Gibb's free energy for the chemical reaction energies in this study, because the contribution to the Gibb's free energy by the change of entropy and enthalpy due to finite temperature are minimal compared to the total energy.²³ The calculated total energies of the compounds and elements involved in this study are summarized in Table I. The total energies of Al₂O₃, P₂O₅, AlPO₄, and HfO₂ in this study are consistent with the values calculated by Hautier *et al.*,²⁴ which are also included in Table I as a comparison, where consistent reaction energies are derived compared with the experimental database. The possible exothermal chemical reactions are identified as follows:

TABLE I. The total energy of all the elements and compounds present in the chemical reactions in this study, as well as the total energy derived from Ref. 24.

Chemical formula	Total energy ΔU (kcal/mol) calculated in this work	Total energy ΔU (kcal/mol) derived from Ref. 24
Al ₂ O ₃	-869.17	-862.5796
InPO ₄	-919.31	
In(PO ₃) ₃	-2079.2	
P ₂ O ₅	-1130.45	-1131.742
AlPO ₄	-1039.34	-1034.4
HfO ₂	-716.45	-704.8916
Hf	-227.24	
Al	-78.43	
In	-58.42	
P	-116.15	
Hf ₃ P	-853.53	
InP	-192.97	

After the initial 1 min Al deposition, the InPO₄ interacts with the Al metal and forms In-In bonds and In(PO₃)₃ as shown in Eq. (2). The P₂O₅ is formed from interaction between In(PO₃)₃ and the Al metal after the 3 nm Al metal deposition process as shown in Eq. (3). The subsequent UHV annealing stage causes O to be scavenged from P₂O₅ by Al metal, forming volatile P, and reduces the P₂O₅ concentration, as indicated in Eq. (4). A contribution of desorption/decomposition of P₂O₅ in UHV is also possible to account for the decrease in the concentration of the P₂O₅ state.²⁵

The Al 2p spectra in Figure 1(c) show an Al-oxide state after the initial 1 min of deposition. After the 11 min of Al deposition, a strong Al metal (Al-Al and/or Al-In) peak is detected while the oxide peak intensity is not seen to increase significantly because of the attenuation of the Al metal film. After annealing, the Al metal peak decreases significantly because of oxidation through scavenging of the native oxides and aggregation of Al metal (see Figure 6), and the Al oxide peak (75.5 eV) intensity increases significantly.

The O 1s spectra in Figure 1(d) shows that the chemical state at the lower binding energy converted to that at higher binding energy state during the successive Al deposition, and the Al-O state is seen to be predominant after annealing under UHV. Sferco *et al.* reported the atomic structure of the InP-oxides; the InPO₄ has all non-bridging bonds, In(PO₃)₃ has two non-bridging bonds and two bridging bonds (one bridging bond on average), and P₂O₅ has one non-bridging and three bridging bonds (1.5 bridging bonds on average).²⁶ Therefore, the P-oxide is expected to lose oxygen to form Al-O and more P-rich oxides concurrent with more Al deposition and following annealing. A change in the P-oxidation states is also observed during the ALD process, where more P-rich oxide states such as In(PO₃)₃ and P₂O₅ are formed.⁹ For both the metal deposition and high-k oxide ALD processes, the formation of an Al-O-PO_x bond is also possible because Al and Al-oxides contact to P-oxides directly.

Figures 2(a) and 2(b) show the In 3d_{5/2} and P 2s core level spectra at takeoff angles of 45° and 80° (as measured between the detector and sample surface) before and after annealing at 250 °C under UHV conditions, respectively. For the In 3d_{5/2} spectra before annealing, the decrease in the In-In and In-P peak intensities because of the decreasing sampling depth from 80 to 45° is consistent with equal attenuation by the Al/Al-oxide overlayer, suggesting the metal In (i.e., In-In bonding) and InP are in close contact. However, for the In 3d_{5/2} spectra after the annealing process, the decrease of In-In and InP peak intensity caused by the decreasing sample depth from 80° to 45° is not consistent with equal attenuation due to the Al/Al oxide overlayer. The lack of any obvious intensity change in the In-In bond intensity with the different scan angles suggests that the In-In bond is actually closer to the top layer of the sample after annealing. This suggests indium diffusion through the Al/Al-oxide overlayer.¹²

For the P 2s spectra, the bulk peak at 186.8 eV is assigned to InP, and the peak with a binding energy separation of +6 eV from the InP bulk peak is assigned to P₂O₅, which is consistent with the deconvolution of the P 2p

spectra. In contrast to the In-In bond, both before and after annealing, the decrease in intensity for both the In-P and the P-oxide peaks is consistent with equal attenuation by the Al/Al-oxide overlayer, suggesting that no P-oxide diffusion is detected by ARXPS. These results are also consistent with indium out-diffusion^{11,27} and no detectable P-oxide diffusion through the high-k dielectrics from the high-k/InP stacks.¹²

Figures 3(a)–3(d) show the In $3d_{5/2}$, P $2p$, In $4d$ /Hf $4f$, and O $1s$ spectra, respectively, from the initial InP surface, after 2 nm e-beam Hf deposition (based on the attenuation of In $3d_{5/2}$ spectra) and following UHV annealing at 250 °C. For the In $3d_{5/2}$ spectra, the peak with a binding energy separation to the InP bulk (at 444.8 eV) of -1.09 eV is assigned to the In-Hf peak, and the peak with a binding energy separation of -0.67 eV is assigned to the In-In peak. For the In-In bonding, the slight change in binding energy separation compared to the Al deposition process is likely because of the band bending difference, and/or due to error involved during the fitting process using symmetric line shape for In-In peak. However, this possible slight uncertainty of the InP bulk peak does not affect the qualitative analysis of the results in this study. In-oxides are scavenged to concentrations below the XPS detection limit, and concurrently the emergence of an In-Hf bond is also seen after the Hf metal deposition. However, after the UHV annealing, the In-O signal is slightly above the detection limit, and In-Hf is seen to decrease below the XPS detection limit, which is concurrent with the emergence of In-In bonding.

The P $2p$ spectra in Figure 3(b) show that the initial InPO_4 state changed to $\text{In}(\text{PO}_3)_3$ and P_2O_5 states upon Hf metal deposition. The concentration of the P-oxides is significantly lowered upon Hf metal deposition and decreased below the XPS detection limit after UHV annealing at 250 °C. A significant increase of the broadening in the P $2p$ spectra after annealing suggests the formation of Hf-P, and the increase in the intensity of the P $2p$ spectra also indicates the diffusion of P to the sample surface, so less attenuation due to the Hf/Hf-oxide film. This hypothesis is consistent

with the slightly decrease in In $3d$ peak of the InP bulk peak after annealing, which ruled out the possibility of P $2p$ peak intensity increase due to the Hf removal.

The Hf $4f$ /In $4d$ peak in Figure 3(c) primarily indicates the presence of Hf metal (Hf-Hf/In) after e-beam deposition. After UHV annealing, most of the Hf metal signal decreases below the XPS detection limit and forms Hf-O and Hf-P bonding by the reaction of Hf and native oxides and InP substrate. This decrease of Hf metal peak is consistent with the decrease of the In-Hf peak with an emergence of the significantly increased In-In peak after annealing. The O $1s$ peak in Figure 3(d) is shown to be strongly attenuated by the Hf metal film before annealing, but a higher intensity is observed after annealing, which consists mostly of Hf-O bonding.

Figure 4 shows the angle resolved In $3d_{5/2}$ and P $2p$ spectra before and after UHV annealing (with XPS scan takeoff angles of 45 and 80°). The decrease in intensity of the In-P from the take off angle at 80°–45° both before and after annealing is consistent with the equal attenuation of the Hf/Hf-oxide overlayer. However, the lack of a change in the intensity of the In-Hf/In peaks with respect to different XPS take off angles suggests that indium diffusion occurs both before and after the annealing process.¹² For the P-oxides, however, the decrease in intensity is consistent with equal attenuation by the Hf/Hf-oxide overlayer, suggesting that there is no P-oxide diffusion within the XPS detection limits. However, as stated previously, P diffusion to the sample surface in a form of Hf-P bonding after annealing is possible.

Figure 5 shows the LEIS results for (a) Al/InP and (b) Hf/InP before and after UHV annealing. LEIS is used to determine the surface atomic layer elemental composition.²⁸ For the Al/InP sample, Al and In features are both detected before and after annealing, but the relative In intensity is seen to increase significantly after annealing. This indicates that In/Al intermixing has already occurred before annealing, and is more pronounced after annealing. This is also consistent with the ARXPS results for In-diffusion after annealing. The absence of P features before and after annealing suggests there is no detectable P-diffusion to the surface.

FIG. 3. The XPS core level spectra of (a) In $3d_{5/2}$, (b) P $2p$, (c) Hf $4d$ /In $4d$, and (d) O $1s$ spectra prior to Hf deposition, after 2 nm Hf deposition and after annealing at 250 °C under UHV condition.

FIG. 4. The XPS core level spectra for (a) In $3d_{5/2}$ and (b) P $2p$, after 2 nm Hf deposition and after annealing at 250 °C under UHV condition at XPS scans angles of 45 and 80°.

FIG. 5. LEIS spectra of (a) after 3 nm of Al deposition prior to annealing, and after annealing at 250 °C in UHV, (b) after 2 nm of Hf deposition prior to annealing, and after annealing at 250 °C in UHV.

For the Hf/InP sample, similar intensities are seen for the In and Hf features in the LEIS spectra both before and after annealing, suggesting that indium out-diffusion significantly begins before annealing, and this is consistent with the ARXPS results. Therefore, the indium atoms behave like surfactants during Hf metal deposition, *viz.* diffusing to the surface. The absence of any P features before annealing suggests that no detectable P-diffusion occurs. However, a P peak is detected after UHV annealing, suggesting that diffusion of elemental P possibly occurs. This is consistent with the previously discussions based on the XPS results.

The possible chemical reactions during the Hf deposition and after the following UHV anneal are as follows:

FIG. 6. The AFM images (a) after 3 nm of Al deposition, (c) after annealing at 250 °C under UHV condition; (b) after 2 nm of Hf deposition, and (d) after annealing at 250 °C under UHV condition.

During the Hf metal deposition, In metal bond formation, transformation of P-oxides to more P-rich oxides, and a decrease of the P-oxide concentration are all observed from the In 3d_{5/2} and P 2p spectra. These observations are consistent with Eqs. (5) and (6). The detection of Hf-P bonding from the P 2p spectra and the diffusion of P to the sample surface from LEIS spectra are consistent with Eq. (7).

The surface formation energies of Al, Hf, and In are calculated to be 0.055 eV/Å², 0.105 eV/Å², and -0.059 eV/Å², respectively, on InP (100) surfaces. From minimizing the surface energy perspective, In atoms tend to distribute on the surface instead of Al or Hf. This is consistent with the experimental observation of In diffusion, which is likely one of the reasons why indium out-diffusion is detected after room temperature deposition of Hf. However, in contrast, significant indium out-diffusion only occurs after UHV annealing at 250 °C in the Al/InP system. Another reason for the different diffusion behavior is that Al₂O₃ is expected to be a better diffusion barrier for indium according to previous studies.^{12,29}

Figures 6(a) and 6(c) show the AFM images of the Al/InP surfaces before and after annealing. An agglomeration of Al metal occurs on the sample surface after annealing at 250 °C. This is also consistent with decreases in the peak areas of the Al metal, and the increases in the In 3d_{5/2}, P 2p, and O 1s peaks. Another contribution to this Al metal peak area decrease is the reaction of Al metal to the InP native oxide, but this does not introduce less attenuation to the In 3d_{5/2}, P 2p, and O 1s spectra, Figures 6(b) and 6(d) show the AFM images of the Hf/InP surface before and after annealing. A more uniform surface is obtained after annealing under UHV, which is likely due to the reaction of Hf metal and the InP substrate and the InP native oxide, consistent with the Hf 4f and P 2p spectra behavior as discussed in previous paragraph.

The diffusion of In through both Al and Hf films, the agglomeration of Al metal, and the chemical reaction of Hf metal with the InP substrate suggest that it is not optimal to grow Al₂O₃ or HfO₂ by oxidation of e-beam deposited Al and Hf metals. Both In and P-oxides have been correlated with interface defect density previously,¹⁴ but In-oxides are easy to remove during the high-k ALD process while persistent P-oxides are difficult to remove not only by ALD process but by metal scavenging as well.^{9,10} Therefore, reducing the P-oxide concentration for the high-k/InP system remains a challenge.

CONCLUSIONS

In summary, Al metal e-beam deposition and Hf e-beam deposition processes were performed on native oxide InP (100) surfaces at room temperature, and the surfaces were characterized by *in situ* XPS and LEIS. Both the Al and Hf metals scavenge most of the In-oxides and transform them to In-In/Al and In-In/Hf bonds, respectively, as well as Al and Hf oxides. For the Al/InP sample, the P-oxide chemical states are found to change initially from InPO₄ to In(PO₃)₃ and P₂O₅ after the initial Al deposition, then change completely to P₂O₅ after 3 nm of Al deposition, forming volatile species (P and/or P₂O₅) under UHV after annealing at

250 °C. For the Hf/InP sample, the P-oxide chemical states are seen to change from InPO_4 to P_2O_5 and $\text{In}(\text{PO}_3)_3$ after Hf deposition and are decreased below the XPS detection limit, resulting in Hf-P bond formation after UHV annealing. Indium atom out-diffusion is detected upon both the Al and Hf deposition and is pronounced after the annealing process. The diffusion of P is also detected from the Hf/InP sample after annealing. The persistence of P-oxides highlights the need for a surface passivation prior to the high-k deposition process to minimize the concentration of the P-oxides in order to improve the electrical performance.

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