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Indium diffusion through high-k dielectrics in high-k/InP stacks

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Evidence of indium diffusion through high-k dielectric (Al₂O₃ and HfO₂) films grown on InP (100) by atomic layer deposition is observed by angle resolved X-ray photoelectron spectroscopy and low energy ion scattering spectroscopy. The analysis establishes that In-out diffusion occurs and results in the formation of a PO_x rich interface. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4817932]

High mobility III-V channel materials are contenders to replace Si in semiconductor devices like metal oxide semiconductor filed effect transistors (MOSFETs) for the sub 22 nm technology node.¹ Extensive research is being carried out to determine the validity of these III-V materials for use as the channel, in a variety of structures ranging from planar to 3D Fin-FETs.^{2,3} However, the improvement of interfacial quality between a high-k dielectric and these III-V materials is still a hurdle to overcome in order to achieve suitable electrical performance.⁴ Efforts have been made recently using InP as a barrier layer between InGaAs and the high-k dielectrics, which show improved electrical performance relative to devices with the high-k dielectrics directly in contact with the channel.^{5,6} Recently, however, Gu *et al.* reported that the interface between this InP barrier layer and high-k dielectrics impact the sub-threshold swing of the devices.' The density of interface states (D_{it}) has been found to be strongly correlated to the In-P-oxides present at the interface based on a study investigating the impact of post deposition annealing (PDA) of HfO₂ on InP at different temperatures.⁸ An *et al.* and Kang et al. have reported diffusion of In atoms and P-oxides through a thick (>6 nm) HfO₂ layer on InP by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS).^{9–11} However, detailed analysis of this substrate elemental diffusion through other high-k dielectrics as well as interfacial chemistry upon annealing has not been reported.

In this study, the diffusion behavior of the substrate elements in the HfO₂/InP and Al₂O₃/InP systems is studied by angle resolved X-ray photoelectron spectroscopy (ARXPS) and low energy ion scattering spectroscopy (LEIS). In order to highlight the significance of In-diffusion and rule out the possibility of interfacial oxide regrowth due to air exposure,¹² thick HfO₂ (~5.6 nm) and Al₂O₃ (~5 nm) films on various of InP (100) samples are grown by atomic layer deposition (ALD).

Four n-type InP (100) samples, cleaved from the same 50 mm single crystal wafer obtained from IQE Ltd., are used in this study, and the treatments are listed in Table I. Samples A and C are native oxide InP (100) degreased using sequential

dips in acetone, methanol, and isopropyl alcohol for 1 min each, and samples B and D are initially degreased and then treated by 10% (NH₄)₂S at room temperature for 20 min.¹³ The (NH₄)₂S treatment is widely used to decrease the native oxide concentration and passivate the III-V semiconductor surfaces to reduce reoxidation prior to high-k dielectric deposition,^{7,13} and is used in this study to compare the relative thermal stability of native oxide and (NH₄)₂S treated surfaces.

Trimethylaluminum (TMA) and tetrakis(dimethylamido)-hafnium (TDMA-Hf) were used as the metal precursors for Al₂O₃ and HfO₂, respectively, and deionized water was used as the oxidant.^{8,14} Fifty cycles of Al₂O₃ was deposited on samples A and B at 300 °C, with the ALD cycle process consisting of a 0.1 s TMA/10 s N₂ purge/0.03 s water/10 s N₂ purge sequence, with a deposition rate of ~0.1 nm/cycle, for a thickness of 5 nm. Seventy cycles of HfO₂ was deposited on samples C and D at 250 °C consisting of a 0.5 s TDMA-Hf/20 s N₂ purge/0.03 s water/20 s N₂ purge sequence, for a thickness of 5.6 nm (0.08 nm/cycle). All ALD processes were carried out *ex situ* using a Cambridge Nanotech Savannah-100 ALD system, and the ALD growth rates were calibrated by transmission electron microscopy.

For XPS analysis, a monochromatic Al K α XPS source (h ν = 1486.7 eV) was used, along with a 7 channel hemispherical analyzer operating at a pass energy of 15 eV. The XPS is calibrated following the ASTM standard procedure.¹⁵ The ARXPS spectra were taken at angles of 35°, 45°, 60°, 70°, and 80° with respect to the sample surface after ALD and following *in situ* annealing in UHV at 400 °C in order to establish an elemental depth profile of material in the various samples. In order to compensate for surface charging or band bending, all XPS spectra were referenced to the InP bulk peak at 444.8 eV in the In $3d_{5/2}$ spectra, which is the same binding energy as the native oxide sample before ALD.^{16,17}

The LEIS scans were carried out *ex situ* in a Qtac¹⁰⁰ analyzer by IonTOF¹⁸ before anneal and after XPS scans of the 400 °C annealed surfaces. The detector enables extremely high efficiency in the detection of the scattered ions, so that a low dose of ions can be used during the measurement preventing significant modification of the surface due to sputtering. Both 3 keV He⁺ and 5 keV Ne⁺ ions were used to study

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TABLE I. The four samples employed in this study.

InP samples	Initial treatments	ALD conditions
А	Native oxide	Al ₂ O ₃ at 300 °C 50 cycles
В	10% (NH ₄) ₂ S 20 min	Al ₂ O ₃ at 300 °C 50 cycles
С	Native oxide	HfO2 at 250 °C 70 cycles
D	10% (NH ₄) ₂ S 20 min	HfO_2 at 250 °C 70 cycles

the Al₂O₃/InP and HfO₂/InP samples, respectively, as the He^+ ion source provides greater energy resolution for low Z elements (e.g., Al and P), and the Ne⁺ source is better able to resolve In and Hf peaks. The analysis areas for LEIS and XPS on the same sample were kept separate.

Figure 1 shows the In $3d_{5/2}$ spectra from the Al₂O₃/InP system at XPS scan angles of 45° and 80° for the (a) native oxide and (b) (NH₄)₂S treated samples, before and after annealing at 400 °C under ultrahigh vacuum (base pressure $\sim 5 \times 10^{-10}$ mbar) representative of the spectra taken at different scan angles. The peak with a binding energy separation of +0.54 eV to the InP bulk peak is assigned to In-O on sample A and In-S/O for sample B before annealing (the difference in binding energy separation due to S and O bonding is small and difficult to resolve). The peak with a binding energy separation of $1.6 \pm 0.05 \,\text{eV}$ and $1.8 \pm 0.05 \,\text{eV}$ to InP is assigned to In-O for samples A and B, respectively, after annealing.¹⁹ The decrease in intensity of both the In-P and In-O features for both samples A and B before annealing (due to the decreasing sampling depth as the analysis angle is changed from 80° to 45°) is consistent with equal attenuation of both features by the overlying HfO₂ film (with the In-O located at the interface). However, after annealing for both samples A and B, the lack of a similar change in the In-O feature (the In-O areas are approximately the same from scans at 45° and 80°) suggests that the In-O is distributed throughout the HfO₂, as well as possibly on the sample surface. The relatively smaller binding energy separation of In-O from In-P before annealing suggests the In-O state is in a



FIG. 1. In $3d_{5/2}$ core level spectra at XPS scan angles of 45° and 80° from the Al₂O₃/InP system, (a) the "native" oxide sample, before and after annealing at 400°C; (b) (NH₄)₂S treated ("S_InP") before and after at 400°C anneal.

different bonding environment from the diffused In-O after annealing.

Figure 2 shows the In $3d_{3/2}$ XPS spectra (the In $3d_{3/2}$ core level is used in this case for clarity as the In $3d_{5/2}$ partially overlaps with the Hf $4p_{1/2}$ peak) from the HfO₂/InP system before and after the annealing at 400 °C, again at scan angles of 45° and 80° . For sample C, the binding energy separation of InP to In-oxide is $0.9 \pm 0.05 \text{ eV}$ before and after annealing, which suggests that the In-oxide chemical state did not change. For sample D, the In-O component binding energy separation to InP bulk is 0.7 ± 0.05 eV before annealing, which is higher than that of the initial surface before ALD (0.54 eV, spectra not shown here) and less than that of after annealing $(0.9 \pm 0.05 \text{ eV})$, suggesting there is a change in chemical state at this interface. For both samples C and D before annealing, the decrease in intensity of both the In-P and In-O features due to the decreasing sampling depth as the analysis angle is changed from 80° to 45° is not consistent with the equal attenuation of both features by a HfO₂ overlayer suggesting instead that the In-oxide is distributed inside the HfO₂ layer before annealing for both samples C and D. After annealing, the In-O area remains approximately the same from the XPS scans at 45° and 80° , suggesting the In-O has diffused further into the HfO₂ and is closer to the surface for both samples C and D.

Figure 3 shows (a) the P 2p spectra for samples A and B, and (b) for samples C and D before and after annealing at XPS angles of 45° and 80°. The peak with a binding energy separation of +6.1 eV relative to InP is assigned to P₂O₅, and the binding energy separation of +5.1 eV to InP bulk peak is assigned to In(PO₃)₃.^{16,20} The actual assignment of these states is still a matter of debate, with the formation of AlPO₄ also possible, which would have a similar BE position to that of peak assigned here to P₂O₅.¹⁹ However, the interfacial oxide clearly becomes more phosphorous rich with respect to In with an increase of the binding energy for P-oxide. For sample A, both before and after annealing, the decrease in intensity of both the In-P and P-oxides features due to the decreasing sampling depth as the XPS angle



FIG. 2. In $3d_{3/2}$ core level spectra at XPS scan angles of 45° and 80° from HfO₂/InP system, (a) the "native" oxide sample, before and after annealing at 400 °C, (b) (NH₄)₂S treated ("S_InP") before and after annealing at 400 °C.



FIG. 3. P 2p core level spectra at XPS scan angles of 45° and 80° from (a) Al₂O₃/InP system, (b) HfO₂/InP system before and after annealing at 400 °C.

changed from 80° to 45° is consistent with the equal attenuation of both features by the overlying HfO₂ film, suggesting that no P-diffusion is detected from an ARXPS perspective. However, for sample A, the concentration of P-oxide (mainly P₂O₅) is detected to slightly increase after annealing, which is likely due to the oxidation of P at the interface. Therefore, the In-diffusion from sample A is accompanied by a more P-O rich interface. In contrast, the signal from the P-oxide for sample B is close to the detection limit of XPS before and after annealing, suggesting that there is no P-diffusion taking place within the XPS detection limits.

From samples C and D, P 2p features from the In-P peak at the bulk sensitive 80° scan angle were detected, but no P-oxide is detected at the surface sensitive 45° scan angle, suggesting that there is no P-oxide diffusing to the sample surface within the XPS detection limit. The weak signals are due to the attenuation by the thick films used, and this is more pronounced for HfO₂/InP samples, because the electron effective attenuation length is shorter in the higher density HfO₂ film compared to Al₂O₃. The relatively higher intensity in In $3d_{5/2}$ spectra compared with P 2p is related to the difference in photon ionization cross sections.^{21,22} For both HfO₂/InP and Al₂O₃/InP systems, P-diffusion upon annealing is below the detection limit of ARXPS. It is also notable that the P-oxide concentrations are close to detection limit from the S-passivated interfaces before and after annealing, consistent with a decreased initial surface oxide due to S-passivation.²⁰ However, the (NH₄)₂S treatment does not prevent the In-diffusion due to annealing at 400 °C.

LEIS is an extremely surface sensitive surface analysis technique, and is used for determination of the chemical species in the first atomic layer of a material.²³ The LEIS results in Figure 4 show the top-most layer atomic composition from samples A–D before and after annealing. Initially, the indium signal is below the LEIS detection limit on samples A, B, and D before annealing; however, an indium feature is detected on all samples after annealing. For sample C, In atoms are detected on top of the HfO₂ layer even before annealing, with the In concentration observed to increase significantly after annealing. This indicates that In diffusion



FIG. 4. LEIS spectra from (a) Al_2O_3 on native oxide InP (sample A), (b) Al_2O_3 on $(NH_4)_2S$ treated InP (sample B), (c) HfO₂ on native oxide InP (sample C), and (d) HfO₂ on $(NH_4)_2S$ treated InP (sample D) before and after annealing at 400 °C.

occurs even during the ALD HfO_2 process on the native oxide InP at a substrate temperature of 250 °C.

From detailed ALD "half cycle" studies using *in situ* XPS, In-oxides are consumed by the first pulse of TMA.²⁰ However, incomplete consumption of In-oxides by TDMA-Hf is observed during the initial ALD HfO₂ process.²⁴ The incomplete removal of In-oxides from the HfO₂/InP interface during ALD may cause the In-diffusion before annealing at 400 °C for sample C.

The P signal is below the detection limit of LEIS for sample A and B before and after annealing. For the Ne⁺ source used to examine the HfO2/InP surface, it is difficult to determine the presence of P atoms because of an elevated background signal, so in this case, the He⁺ source was also used on the HfO₂/InP stack as well to determine the presence of detectable P on the surface. The P signal is also below the LEIS detection for both samples C and D before and after annealing (not shown). The detection of In-diffusion through high-k dielectrics with no observable concurrent diffusion of P by both ARXPS and LEIS reported here is consistent. The P-oxide at the interface is in a form of PO₄ tetragonal complex $(InPO_4/In(PO_3)_3/P_2O_5)$,²⁵ which has a strong affinity to O, with a P-O bond energy of 191 kcal/mol, much stronger than that of In-O $(82.8 \pm 0.8 \text{ kcal/mol})$.^{25,26} The size of a PO₄ tetragonal complex (P-O bond length is 1.5 Å) is greater than that of an In atom (radius is 0.7 Å),²⁵ suggesting a lower energy barrier for In elemental diffusion. The defects and vacancies in the high-k oxides likely provide a diffusion path with a lower energy barrier in the high-k film.²⁷ The In outdiffusion is possibly exacerbated from the low energy barrier to break the In-P bond ($47.3 \pm 2 \text{ kcal/mol}$) at the high-k/InP interface.²⁶ This indium out-diffusion is possibly driven by a relatively lower surface energy of In-oxide with respect to the high-k oxides. Oh et al.²⁸ and Suleiman et al.²⁹ reported a stable monolayer of PxNy (self-limiting growth by plasma-PH3 treatment) on InGaAs prior to ALD, which significantly improves the thermal stability of the high-k/InGaAs interface, indicating it is possible to utilize a P_xN_y layer to isolate the In atoms from high-k oxide. Hence, this may reduce the In outdiffusion upon annealing. While both In and PO₂ diffusion through HfO₂ were observed in previous reports using TOF-SIMS,^{9–11} the detection limit of TOF-SIMS (7×10^7 /cm²) is significantly lower than LEIS (3.3×10^{11} /cm²) and ARXPS (majority of distribution),^{18,30} so it is assumed that the concentration of diffused P is below the limit of detection for LEIS and XPS but sufficient to be detected by TOF-SIMS.

We speculate that the resulting higher P-O concentration at the interface due to indium out-diffusion upon annealing from the high-k/InP stacks is consistent with previous electrical studies of PDA treatments for Al₂O₃ and HfO₂ on InP, where a higher D_{it} was detected after PDA at 400 °C and 500 °C from both of the interfaces.^{8,14} The incorporation of P-N species to mitigate In out-diffusion, and the impact on electrical properties, requires further investigation.

In conclusion, Indium out-diffusion through high-k dielectric films is observed for Al_2O_3/InP and HfO_2/InP stacks by both ARXPS and LEIS. This indium out-diffusion results in a P-oxide rich interface, which is speculated to be correlated to a higher D_{it} profile, which would greatly impact device performance. While an $(NH_4)_2S$ treatment does reduce the concentration of diffused In, it does not appear to completely inhibit In out-diffusion occurring for both Al_2O_3/InP and HfO_2/InP systems. Further investigation is needed to prepare and passivate the InP surface prior to ALD to enhance the thermal stability of the InP/high-k interface.

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