# Thickness dependence on crystalline structure and interfacial reactions in HfO$_2$ films on InP (001) grown by atomic layer deposition

Y. S. Kang,[1] C. Y. Kim,[1] M. -H. Cho,[1,a)] K. B. Chung,[2] C. -H. An,[3] H. Kim,[3] H. J. Lee,[3] C. S. Kim,[4] and T. G. Lee[4]

[1]*Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Republic of Korea*
[2]*Department of Physics, Dankook University, Cheonan 330-714, Republic of Korea*
[3]*School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
[4]*Korea Research Institute of Standards and Science, Daejeon 305-540, Republic of Korea*

The crystalline structure and interfacial reactions in HfO$_2$ films grown on InP (001) substrates was investigated as a function of film thickness. High resolution transmission electron microscopy and x-ray diffraction measurements were used to investigate changes in the crystalline structure of the HfO$_2$ films. As the thickness of the HfO$_2$ increased, the crystal structure was transformed from monoclinic to tetragonal, and the interfacial layer between the HfO$_2$ film and the InP substrate disappeared. High resolution x-ray photoelectron spectroscopy was also applied to confirm the existence of an interfacial chemical reaction in HfO$_2$/InP. An interfacial self-cleaning effect occurred during the atomic layer deposition process, resulting in a clear interface with no indication of an interfacial layer between the HfO$_2$ film and the InP surface. Finally, the crystallization process in the HfO$_2$ films was found to be significantly affected by the interfacial energy. © *2010 American Institute of Physics*. [doi:10.1063/1.3506695]

The continuous scaling of Si-based devices with the global trend toward high-speed and low-power is currently reaching its fundamental limits. For achieving high performance metal-oxide-semiconductor (MOS) devices, advanced gate stack structures based on high-k dielectrics and the use of high mobility channel materials such as GaAs, InGaAs, and InP has been widely studied.[1–3] Among the available high-k oxides, Hf-oxide-based materials such as HfO$_2$, HfSi$_x$O$_y$, and HfSiO$_x$N$_y$ are being seriously considered for use as gate oxides on high mobility channel substrates because of their high dielectric constant, wide band gap, and reasonable thermal stability. Studies related to the structural characteristics of high-k films and detailed interface analyses are being actively pursued. In the case of the growth of high-k oxides on III-V substrates (such as GaAs or InGaAs) via an atomic layer deposition (ALD) process, a clean interfacial layer produced as the result of interfacial reaction, has frequently been observed.[4] The crystallization of HfO$_2$ films by a postannealing treatment or interfacial stress are also an issue, due to the increased leakage current in MOS devices.[5,6] In particular, indium phosphide (InP), a potential high mobility channel substrate, is of interest, due to its high electron mobility and high breakdown field. Recent studies related to electrical properties of high-k oxide/InP show that n-channel MOS field effect transistor (MOSFET) on InP substrates have excellent electrical characteristics, which include a large transconductance, large drain current, and low leakage current.[2,3] Although the HfO$_2$/InP structure is under serious consideration for use as a potential candidate for an advanced gate structure in future MOS devices, the structural characteristics and detailed interface analysis of such materials have not yet been reported.

The focus of this study was on the structural stability of HfO$_2$ films grown on InP by ALD and their interfacial reactions as a function of film thickness. A self-cleaning reaction was clearly observed at the interface between the ALD-HfO$_2$ film and the InP substrate. Moreover, the findings herein indicate that the change in the crystal structure of HfO$_2$ during the ALD process is closely related to the interfacial reactions.

n-type InP (001) substrates doped with sulfur (doping concentration $\sim 7 \times 10^{17}$ cm$^{-3}$) were prepared. Prior to the deposition of HfO$_2$, the InP substrates were cleaned with a buffered oxide etching (BOE) (NH$_4$F:HF=6:1) solution for 5 min to remove native oxides. The HfO$_2$ films were grown using an ALD system, with tetrakis (ethylmethylamido) hafnium as the precursor. H$_2$O vapor also served as the oxygen source. Three different thicknesses of films were grown on InP; approximately 2 nm, 6 nm, and 11 nm, respectively. The structural properties of the HfO$_2$ films on InP were characterized by high resolution transmission electron microscopy (HR-TEM) and x-ray diffraction (XRD). Electronic structure was investigated by high resolution x-ray photoelectron spectroscopy (HR-XPS) with the monochromatic Al $K\alpha$ (1486.6 eV) source at the Korea Basic Science Institute (KBSI), Jeonju.

Figure 1 shows cross-sectional HR-TEM images of ALD-HfO$_2$ films grown on cleaned InP substrates. The thicknesses of the HfO$_2$ layers without interfacial layers were approximately 2 nm, 6 nm, and 11 nm, respectively. It is noteworthy that a thin interfacial layer was observed in the 2 nm thick HfO$_2$ film, while an atomically sharp interface without any interfacial layer between HfO$_2$ film and the InP substrate were observed in the HfO$_2$ films with thicknesses of 6 and 11 nm. The formation of a clean interface strongly indicates the effect of "self-cleaning." For the growth of Al$_2$O$_3$ or HfO$_2$ using ALD on GaAs and InGaAs, previous studies reported that an interfacial "self-cleaning" reaction process
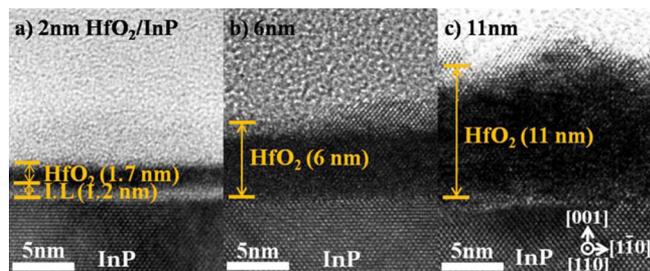
FIG. 1. (Color online) HR-TEM images of HfO$_2$ films grown on BOE treated InP with film thicknesses of (a) 2 nm (b) 6 nm, and (c) 11 nm, respectively. During the ALD growth, the interfacial oxide was removed and a crystal structure was observed.



FIG. 3. (Color online) Crystalline image of monoclinic and tetragonal structures: the monoclinic structure is transformed into a tetragonal structure when the film thickness increases from 6 to 11 nm. The simulated image is in good agreement with the crystalline HRTEM images. (c) Fast Fourier transform (FFT) image of 11 nm thick HfO$_2$ film. (d) Lattice mismatch between 11 nm thick HfO$_2$ film and InP substrate.

effectively reduces the level of native oxides at the interface of high-k/III-V.[4] However, the reaction process does not mainly occur during the initial growth stage, as shown in the interfacial layer of the 2 nm thick HfO$_2$ layer, i.e., the native oxides were not completely removed under the self-cleaning process because the removal process continues after the initial growth stage. Therefore, it is obvious that this reaction process is generated during the ALD growth process under conditions of constant thermal heating on the substrate with the low temperature of 350 °C. Another interesting result is that the relatively thick HfO$_2$ films grown on InP spontaneously crystallized without any postdeposition annealing treatment, while an evidence of any atomic ordering was not observed in the case of a relatively thin 2 nm HfO$_2$ film. This result indicates that film thickness is closely related to the formation of a crystalline structure during the growth process, i.e., the interfacial reaction process affects the crystallization process because of the interfacial strain between the film and substrate.

XRD measurements were carried out, in ordered to confirm the crystalline structure of the HfO$_2$ films, as shown in Fig. 2. For 2 nm thick HfO$_2$ films, a broad peak at 41.63° assigned to the monoclinic structure of HfO$_2$ ($\bar{1}$21) was detected. This broad peak can be attributed to a short-range order of crystallization due to the presence of small, locally generated grains, which were not easily observed in HR-TEM, as shown in Fig. 1. When the film thickness was increased to 6 nm, a crystalline peak corresponding to the tetragonal structure of HfO$_2$ started to develop, i.e., the monoclinic and the tetragonal structures of HfO$_2$ are both
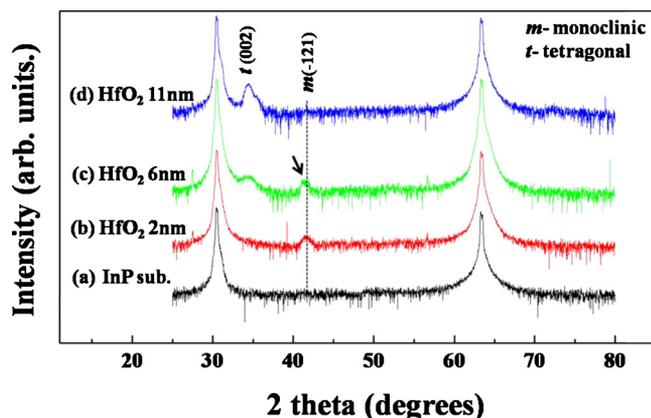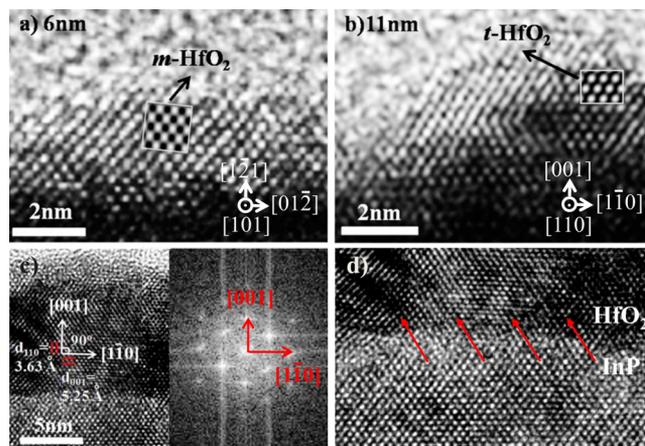
present at this thickness. In particular, the $m$ ($\bar{1}$21) peak is shifted about 0.2° toward a lower diffraction angle as the thickness of the HfO$_2$ film increases from 2 to 6 nm. The shift in peak position indicates that the interplanar distance increases and, consequently, the films of HfO$_2$ had been affected by compressive stress. As the film thickness is increased to 11 nm, the monoclinic structure disappeared and only a tetragonal structure remained. Considering the d-spacing of 2.622 Å for $t$ (002) and 2.171 Å for $m$ ($\bar{1}$21), respectively, it is possible that the crystal structure was transformed as a result of compressive stress. The change in preferentially oriented planes parallel to the InP (001) plane from $m$ ($\bar{1}$21) to $t$ (002) indicates that the growth system is determined by the minimization of the total energy (the sum of the surface energy and the interfacial energy). Considering the TEM and XRD results, we conclude that the ($\bar{1}$21) preferential oriented monoclinic structure for a 2 nm thick film was induced to minimize its surface energy because the interfacial layer provides relief for the interfacial energy effect. As the thickness of the film increases up to 6 nm without any interfacial layer, the crystalline process is dominantly affected by the interfacial energy. Thus, in a 6 nm thick film a (002) preferential oriented tetragonal structure was induced, which minimizes the interfacial energy.

The crystalline structure in the images of HfO$_2$ films combined with the XRD data was investigated in detail, and the results are shown in Fig. 3. The simulated monoclinic structure at the (101) zone axis and a tetragonal structure at the (110) zone axis were identified in both 6 and 11 nm thick films. The observed structural change with film thickness is also in good agreement with data previously reported by Cho *et al.*,[6] which reported that the crystallization of HfO$_2$ films depends on the film thickness and the annealing temperature, i.e., an increase in stress with film thickness can contribute to structural changes, in the case where the crystallization energy is not high. Considering the orientation relationship between HfO$_2$/InP in XRD and HR-TEM, the atomic arrangement of monoclinic HfO$_2$ is $m$-HfO$_2$[101]$\|$InP[110] and $m$-HfO$_2$-($\bar{1}$21)$\|$InP(001), while that of tetragonal HfO$_2$ is $t$-HfO$_2$[110]$\|$InP[110] and $t$-HfO$_2$(002)$\|$InP(001). The



FIG. 2. (Color online) XRD data for HfO$_2$ films as a function of film thickness. The observed peak positions of HfO$_2$ and the peak width changed, as the film thickness increased. In (c) 6 nm HfO$_2$, the arrow at 41.43° shows the shifted peak position of $m$-HfO$_2$.
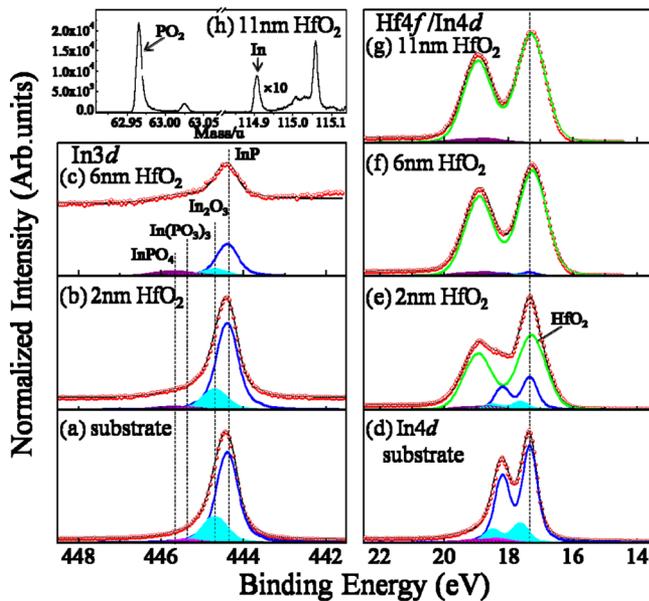
FIG. 4. (Color online) HR-XPS core-level spectra of In 3*d* (left side) and Hf 4*f*/In 4*d* (right side) in HfO$_2$/InP. (d) Since In 4*d* spectra of InP substrate is overlapped with Hf 4*f*, the chemical state is extracted through comparing In 3*d* spectra with In 4*d* spectra. In the In 3*d* spectra, the InP, In$_2$O$_3$, In(PO$_3$)$_3$, and InPO$_4$ bonding states correspond to binding energies at 444.4 eV, 444.7 eV, 445.4 eV, and 445.7 eV, respectively. (h) TOF-SIMS spectra of In and PO$_4$ atoms in 11 nm HfO$_2$ on InP.

estimated interfacial lattice mismatch is about 0.519% for the $m$-HfO$_2$($\bar{1}$21)/InP {$a$[InP(001)]$\times 9 = 74.70$ Å, $a$[$m$ -HfO$_2$($\bar{1}$21)$\times 8 = 75.09$ Å}and 0.097% for the $t$-HfO$_2$(001)/InP {$a$[InP(001)]$\times 7 = 41.08$ Å, $a$[$t$ -HfO$_2$(001)$\times 8 = 41.12$ Å}. The lattice mismatch between the 11 nm thick HfO$_2$ film and the InP substrate was confirmed in HR-TEM images, as shown in Fig. 3(d). This result shows that the crystal structure is transformed from monoclinic to tetragonal and that this transformation minimizes the interfacial energy through a change in lattice mismatch from 0.519% to 0.097%. Consequently, the crystallization process in the HfO$_2$ films is significantly affected by the interfacial energy.[7] The crystallization, resulting in minimization in interfacial strain, is very similar to the results for solid phase epitaxial growth between the HfO$_2$ film and GaAs substrate, i.e., the atomic arrangement between the HfO$_2$ film and the GaAs adopts a periodic iteration (12 atoms in the HfO$_2$ film on 11 atoms in the GaAs substrate).[8]

The detailed chemical state of the materials was investigated using HR-XPS, as shown in Fig. 4. Through the deconvolution process in comparing the peak shapes with the film thickness, it is possible to extract the two peaks caused by indium oxides (In$_2$O$_3$) and indium phosphates (InPO$_4$). Figure 4(a) shows In 3*d* core level spectra of an InP substrate with a high peak intensity caused by In$_2$O$_3$. Three oxidation states, In$_2$O$_3$ ($\Delta$G ~ −198.6 kcal/mol), In(PO$_3$)$_3$ ($\Delta$G ~ −610 kcal/mol), and InPO$_4$ ($\Delta$G ~ −287 kcal/mol) at room temperature as native oxides of InP can be initially formed.[9] In particular, In$_2$O$_3$ states as a native oxide were dominantly formed on the InP substrate, as shown in Figs. 4(a) and 4(d). An interesting finding is that the In$_2$O$_3$ states were greatly decreased and the InPO$_4$ states were increased slightly with increasing HfO$_2$ film thickness. Considering the conversion of In$_2$O$_3$ to InPO$_4$ as the ALD process proceeds, the follow-

ing thermodynamic process is possible. First, the InP substrate is oxidized to form In$_2$O$_3$ and In(PO$_3$)$_3$: 4InP+3O$_2$ →2In$_2$O$_3$+4P ($\Delta$G ~ −323.6 kcal/mol) and 3InP+6O$_2$ →In(PO$_3$)$_3$+In$_2$O$_3$ ($\Delta$G ~ −753.4 kcal/mol).[9] Second, following the thermodynamic reactions, indium phosphates are generated during the ALD process:[9] 4In$_2$O$_3$+8P→5InP +3InPO$_4$ ($\Delta$G ~ −158.6 kcal), 4In$_2$O$_3$+3InP→3InPO$_4$+8In ($\Delta$G ~ −11.4 kcal) and 8In+4In(PO$_3$)$_3$→3InP+9InPO$_4$ ($\Delta$G ~ −198 kcal). However, another interesting finding is that the chemical state of InPO$_4$ is gradually increased with increasing film thickness, up to 11 nm, as shown Fig. 4(g), which is consistent with a thermodynamically controlled reaction process. Since the depth of penetration of HR-XPS into the HfO$_2$ films is about 7–8 nm, the observed InPO$_4$ must have come from the surface region of the HfO$_2$ film, not from the interfacial region. The HR-XPS results are consistent with the clean interface in the HR-TEM image. Using time-of-flight secondary ion mass spectroscopy (TOF-SIMS), we were able to confirm that In and P atoms are present on the surface region of HfO$_2$ films as a function of film thickness, as shown in Fig. 4(h). The TOF-SIMS results indicate the diffusion of In and P into the film surface through the HfO$_2$ film, because TOF-SIMS data include information related to the secondary ions that are emitted from the surface region to a thickness of about 1–2 nm.

In conclusion, we investigated the interfacial chemical state and crystalline structure of HfO$_2$ films grown on InP substrates as a function of film thickness. During the ALD process, the self-cleaning effect of the surface on group III-V compound semiconductors was applied in this HfO$_2$/InP system and the self cleaning reaction was completed in the case of a 6-nm-thick HfO$_2$ film. As a result, the HfO$_2$ film on a InP substrate has an abrupt interfacial layer over the 6 nm film thickness. The presence of a clean interface significantly affects the crystallization process of the HfO$_2$ film, resulting in structural changes with film thickness from monoclinic to tetragonal.

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