Thickness dependence on crystalline structure and interfacial reactions in HfO₂ films on InP (001) grown by atomic layer deposition


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The crystalline structure and interfacial reactions in HfO₂ 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 HfO₂ films. As the thickness of the HfO₂ increased, the crystal structure was transformed from monoclinic to tetragonal, and the interfacial layer between the HfO₂ 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 HfO₂/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 HfO₂ film and the InP surface. Finally, the crystallization process in the HfO₂ 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. Among the available high-k oxides, HfO₂-based materials such as HfO₂, HfSiOₓ, and HfSiOₓNₓ 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. The crystallization of HfO₂ films by a postannealing treatment or interfacial stress are also an issue, due to the increased leakage current in MOS devices. 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 the thin MOS field effect transistor (MOSFET) on InP substrates have excellent electrical characteristics, which include a large transconductance, large drain current, and low leakage current. Although the HfO₂/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 HfO₂ 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-HfO₂ film and the InP substrate. Moreover, the findings herein indicate that the change in the crystal structure of HfO₂ during the ALD process is closely related to the interfacial reactions. n-type InP (001) substrates doped with sulfur (doping concentration ~7 × 10¹⁷ cm⁻³) were prepared. Prior to the deposition of HfO₂, the InP substrates were cleaned with a buffered oxide etching (BOE) (NH₄F:HF=6:1) solution for 5 min to remove native oxides. The HfO₂ films were grown using an ALD system, with tetraethylorthosilicate (TEOS) as the precursor. H₂O 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 HfO₂ 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 Kα (1486.6 eV) source at the Korea Basic Science Institute (KBSI), Jeonju.

Figure 1 shows cross-sectional HR-TEM images of ALD-HfO₂ films grown on cleaned InP substrates. The thicknesses of the HfO₂ 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 HfO₂ film, while an atomically sharp interface without any interfacial layer between HfO₂ film and the InP substrate were observed in the HfO₂ 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 Al₂O₃ or HfO₂ using ALD on GaAs and InGaAs, previous studies reported that an interfacial “self-cleaning” reaction process...
TEM, as shown in Fig. 1. When the film thickness was in-
order of crystallization due to the presence of small, locally
protected. This broad peak can be attributed to a short-range
structure of HfO$_2$ started to develop, i.e., the
interfacial layer provides relief for the interfacial energy effect.
XRD measurements were carried out, in order to con-
firm 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°
asigned to the monoclinic structure of HfO$_2$ (121) was de-
dected. 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 in-
creased to 6 nm, a crystalline peak corresponding to the te-
tragonal 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 $m$ (121) 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 af-
fected by compressive stress. As the film thickness is in-
creased 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 $m$ (121),
respectively, it is possible that the crystal structure was trans-
formed as a result of compressive stress. The change in pref-
entially oriented planes parallel to the InP (001) plane from
$m$ (121) to $t$ (002) indicates that the growth system is deter-
mined 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 (121) pre-
ferrential oriented monoclinic structure for a 2 nm thick film
was induced to minimize its surface energy because the in-
fer facial 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 af-
fected 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.\textsuperscript{4},\textsuperscript{5} 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 en-
ergy 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$_2$-(121)||InP(001), while that of tetragonal HfO$_2$ is
$t$-HfO$_2$[110]∥InP[110] and $t$-HfO$_2$(002)∥InP(001). The

![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.](image1)

![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$_2$.](image2)

![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.](image3)
estimated interfacial lattice mismatch is about 0.519% for the \( m\text{-HfO}_2(121)/\text{InP} \) \( \{a[\text{InP}(001)] \times 9 = 74.70 \text{ Å} \), \( a[m\text{-HfO}_2(121) \times 8 = 75.09 \text{ Å} \) and 0.097% for the \( r\text{-HfO}_2(001)/\text{InP} \) \( \{a[\text{InP}(001)] \times 7 = 41.08 \text{ Å} \), \( a[r\text{-HfO}_2(001) \times 8 = 41.12 \text{ Å} \). The lattice mismatch between the 11 nm thick \( \text{HfO}_2 \) film and the \text{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 \( \text{HfO}_2 \) films is significantly affected by the interfacial energy. The crystallization, resulting in minimization in interfacial strain, is very similar to the results for solid phase epitaxial growth between the \( \text{HfO}_2 \) film and \text{GaAs} substrate, i.e., the atomic arrangement between the \( \text{HfO}_2 \) film and the \text{GaAs} adopts a periodic iteration (12 atoms in the \( \text{HfO}_2 \) film on 11 atoms in the \text{GaAs} substrate).

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 (\( \text{In}_2\text{O}_3 \)) and indium phosphates (\( \text{InPO}_4 \)). Figure 4(a) shows \( \text{InP} \) 3d core level spectra of an \( \text{InP} \) substrate with a high peak intensity caused by \( \text{In}_2\text{O}_3 \). Three oxidation states, \( \text{In}_2\text{O}_3 \) (\( \Delta G \approx -198.6 \text{ kcal/mol} \)), \( \text{InPO}_4 \) (\( \Delta G \approx -610 \text{ kcal/mol} \)), and \( \text{InPO}_4 \) (\( \Delta G \approx -287 \text{ kcal/mol} \)) at room temperature as native oxides of \( \text{InP} \) can be initially formed. In particular, \( \text{In}_2\text{O}_3 \) states as a native oxide were dominantly formed on the \( \text{InP} \) substrate, as shown in Figs. 4(a) and 4(d). An interesting finding is that the \( \text{In}_2\text{O}_3 \) states were greatly decreased and the \( \text{InPO}_4 \) states were increased slightly with increasing \( \text{HfO}_2 \) film thickness. Considering the conversion of \( \text{In}_2\text{O}_3 \) to \( \text{InPO}_4 \) as the ALD process proceeds, the following thermodynamic process is possible. First, the \( \text{InP} \) substrate is oxidized to form \( \text{In}_2\text{O}_3 \) and \( \text{InPO}_4 \): \( 4\text{InP} + 3\text{O}_2 \rightarrow 2\text{In}_2\text{O}_3 + 4\text{P} (\Delta G \approx -323.6 \text{ kcal/mol}) \) and \( 3\text{InP} + 6\text{O}_2 \rightarrow 3\text{In}_2\text{O}_3 + 3\text{InPO}_4 \Delta G \approx -753.4 \text{ kcal/mol} \). Second, following the thermodynamic reactions, indium phosphates are generated during the ALD process: \( 4\text{In}_2\text{O}_3 + 8\text{P} \rightarrow 5\text{InP} + 3\text{InPO}_4 (\Delta G \approx -158.6 \text{ kcal}) \), \( 4\text{In}_2\text{O}_3 + 3\text{InP} + 8\text{In} (\Delta G \approx -11.4 \text{ kcal}) \) and \( 8\text{In} + 4\text{InPO}_4 \rightarrow 3\text{InP} + 9\text{InPO}_4 \Delta G \approx -198 \text{ kcal} \). However, another interesting finding is that the chemical state of \( \text{InPO}_4 \) 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 \( \text{HfO}_2 \) films is about 7–8 nm, the observed \( \text{InPO}_4 \) must have come from the surface region of the \( \text{HfO}_2 \) 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 \( \text{HfO}_2 \) 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 \( \text{HfO}_2 \) 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 \( \text{HfO}_2 \) films grown on \( \text{InP} \) 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 \( \text{HfO}_2/\text{InP} \) system and the self cleaning reaction was completed in the case of a 6-nm-thick \( \text{HfO}_2 \) film. As a result, the \( \text{HfO}_2 \) film on an \( \text{InP} \) 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 \( \text{HfO}_2 \) film, resulting in structural changes with film thickness from monoclinic to tetragonal.

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**FIG. 4.** (Color online) HR-XPS core-level spectra of \( \text{InP} \) (left side) and \( \text{HfO}_2/\text{InP} \) (right side) in \( \text{HfO}_2/\text{InP} \). (d) Since \( \text{InP} \) spectra of an \( \text{InP} \) substrate is overlapped with \( \text{HfO}_2 \), the chemical state is extracted through comparing \( \text{InP} \) spectra with \( \text{HfO}_2 \) spectra. In the \( \text{InP} \) spectra, the In\( _2\text{O}_3 \), In\( _2\text{O}_3 \), and In\( \text{PO}_4 \) 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 \( \text{HfO}_2 \) on \( \text{InP} \).