

**Oxidation of hafnium on Si(001): Silicate formation by Si migration**

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The oxidation behavior of 0.6 and 1.1 ML hafnium on Si(001) was studied by using scanning reflection electron microscopy with *in situ* x-ray photoelectron spectroscopy. The submonolayer sample was designed to purposely grow SiO<sub>2</sub> on the partially exposed surfaces, and was compared with a 1.1 ML sample to discriminate the structural and chemical differences between the two samples. This approach revealed that oxygen ions were likely to form Si-O and Hf-O bonding units separately at 400 °C in  $2 \times 10^{-6}$  Torr oxygen, but at 700 °C in  $5 \times 10^{-5}$  Torr oxygen, the bonding priority of oxygen ions transforms into Hf-O-Si bonding units implying silicate formation by Si migration. Despite silicate formation,  $\sim 0.27$ -nm-thick SiO<sub>2</sub>-like layer is believed to have remained underneath silicate layers.

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**I. INTRODUCTION**

In all high-*k* gate dielectrics investigated so far, one of the most serious concerns of ongoing discussion has been the interface between high-*k* dielectrics and Si.<sup>1-6</sup> A thermally stable abrupt interface with Si is a basic requirement,<sup>1</sup> and moreover SiO<sub>2</sub>-like transition<sup>2,3</sup> of the first Si layer might be additionally required to preserve channel carrier mobility. Although this makes investigating the detailed structure and chemistry of the high-*k* oxide/Si interfaces an urgent task, it is critically difficult to clarify the interface features (e.g., phase and composition analyses within only a few monolayers) by using the conventional measurement tools. In fact, there are some ambiguities<sup>4-6</sup> in identifying whether interfacial layers are all based on SiO<sub>2</sub> (or silicate), even in the same material system.

Hafnium oxides and silicates satisfy many of the requirements needed to replace SiO<sub>2</sub> in the next generation silicon devices since they have a high dielectric constant (10–25), a high dielectric breakdown field (15–20 MV/cm), a large band gap (5–6 eV), and are calculated to be thermodynamically stable on silicon.<sup>1</sup> Kinetically, however, interfacial reactions between hafnium oxide and silicon remain a critical issue in determining its applicability in metal-oxide-semiconductor transistors and capacitors.

To clarify the structure and chemistry of the interfacial layer, we devised an experimental scheme to compare the oxidation behavior of a submonolayer (0.6 ML) Hf deposited sample with that of a supermonolayer (1.1 ML) deposited one. Scanning reflection electron microscopy (SREM) confirmed the presence of SiO<sub>2</sub>, which was grown on the par-

tially exposed region in the submonolayer sample, evidenced by the contrast reversion of the alternating ( $2 \times 1$ ) terraces.<sup>7</sup> Comparing the two samples, we concentrated on the structural and compositional changes of SiO<sub>2</sub> phase based on both SREM and *in situ* x-ray photoelectron spectroscopy (XPS). We demonstrate that the oxidation behavior that separately forms Si-O and Hf-O bonding units likely transforms to form Hf-O-Si (silicate) units based on the Si migration above 700 °C.

**II. EXPERIMENT**

Ultrathin hafnium on Si(001) was oxidized in an UHV surface analysis system, and *in situ* analyzed by using SREM, reflection high-energy electron diffraction (RHEED), and XPS. The sample substrates used in this work were cut from Czochralski-grown *n*-type (5–10 Ω cm) Si(001) wafers. Clean Si(001)- $2 \times 1$  surfaces were prepared by flash heating at 1200 °C in a chamber. Electron-beam evaporated 0.6- and 1.1-ML-thick Hf (1 ML = 2.4 Å) were deposited on the clean Si(001)- $2 \times 1$  surface at RT and annealed at 400 °C for 10 min under the low-pressure oxygen (LPO) of  $2 \times 10^{-6}$  Torr. Then, the samples were annealed at 700 °C for 10 min under the high-pressure oxygen (HPO) of  $5 \times 10^{-5}$  Torr. A 30 keV electron beam with a 3 nm beam diameter was used to observe the RHEED patterns on a fluorescent screen using a charge coupled device camera. The SREM images were obtained from the (00) specular spot with a glancing angle of  $\sim 2^\circ$ . In XPS measurements, Mg *Kα* was adopted for the x-ray radiation source and the photoelectrons

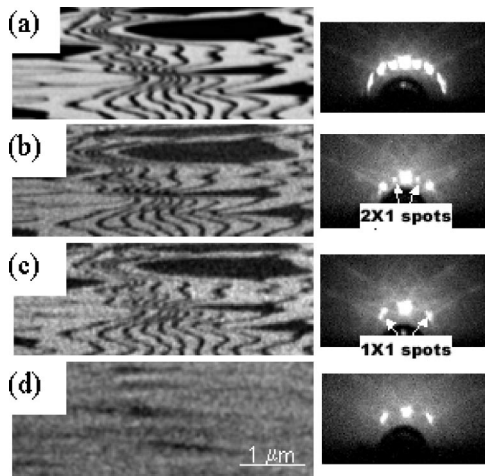


FIG. 1. SREM images and corresponding RHEED patterns for 1.1-ML sample: (a) clean Si(001)- $2\times 1$  surface, (b) Hf/Si interface, and (c) amorphous  $\text{HfO}_x$ /Si interface after LPO. After HPO, featureless image shown in (d) implies possibility of silicate formation due to Si ions migrating from substrate.

were detected at a takeoff angle of  $60^\circ$  with respect to the surface normal.

### III. RESULTS AND DISCUSSION

Figure 1 shows the SREM images along with the corresponding RHEED patterns, which were obtained from the same region on the sample surface. Figure 1(a) shows the clean Si(001)- $2\times 1$  surface with dark and bright contrast corresponding to  $2\times 1$  and  $1\times 2$  terrace regions, respectively. A  $2\times 1$  RHEED pattern was observed for the dark region. Figure 1(b) reveals that the terrace contrast was maintained after 1.1-ML Hf deposition under UHV. Since the monolayer thick hafnium is amorphous in nature,<sup>3,8</sup> this layer did not contribute to the specular spot intensity. The SREM images were obtained by recording the intensity change in reflection spots from the crystalline Si surface covered with an amorphous overlayer, and therefore the interfacial structure could be observed without removing this layer.<sup>7</sup> The preservation of the structure in the SREM image reflects the formation of an atomically flat interface between the hafnium and Si(001). Also noteworthy is that the weak  $2\times 1$  RHEED spots remained despite Hf deposition. This implies that Hf atoms likely dimerize on the Si(001)- $2\times 1$  surface in a similar manner to Si atom dimerization, as already reported<sup>9</sup> in the Al/Si system.

The interface structure remained atomically flat even at a LPO condition of  $400^\circ\text{C}$  [see Fig. 1(c)], as evidenced by the structure preservation as well as the uniform terrace contrast. The preservation of the atomically flat interface indicates that the Hf-covered region likely transformed into  $\text{HfO}_x$  on Si, just as in an  $\text{Al}_2\text{O}_3$ /Si system.<sup>9</sup> This is also evidenced by the Si  $2p$  core-level spectra showing an absence of Si-O bondings (not shown). Therefore, the  $2\times 1$  RHEED spots disappeared but the  $1\times 1$  ones remained. Under HPO at  $700^\circ\text{C}$ , however, it is notable that the terrace structure and contrast drastically disappeared [Fig. 1(d)], inconsistent with

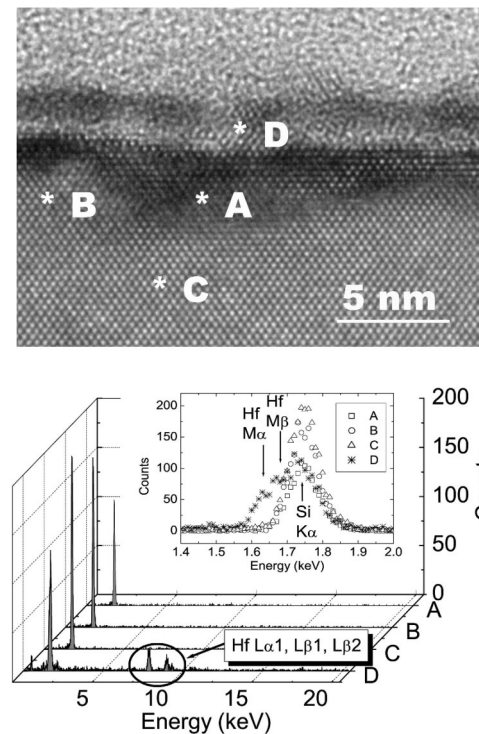


FIG. 2. High resolution transmission electron micrograph with an energy-dispersive x-ray analysis (EDXA) for the annealed  $\text{HfO}_x$ /Si system: (top) The location of four points ("A"–"D") for EDXA is denoted in the micrograph. (bottom) The Si  $K\alpha$  intensities for each points are compared at  $\sim 1.75$  keV position. Electron beam diameter is  $\sim 1$  nm and acceleration voltage is 300 kV.

the  $\text{Al}_2\text{O}_3$ /Si(001) system that shows a reversion of terrace contrast in that same condition. The contrast reversion observed in  $\text{Al}_2\text{O}_3$ /Si means that oxygen ions diffuse through  $\text{Al}_2\text{O}_3$  and form  $\sim 1$ -ML-thick  $\text{SiO}_2$  at the interface in a layer-by-layer fashion, and is caused by the change in the Si-bond direction at the  $\text{SiO}_2$ /Si interface. In our case, however, a featureless image [Fig. 1(d)] was observed along with spotlike RHEED patterns, which reflect the atomic-scale interfacial roughness along the lateral and vertical directions. This implies a possibility of Si migration from the substrate, and silicon ions diffused into hafnium oxide are believed to form Hf-O-Si (silicate) bonding units.

In fact, we could confirm a direct evidence for Si migration into  $\text{HfO}_x$  under a slightly higher thermal budget by using high-resolution transmission electron microscopy with an energy-dispersive x-ray analysis (EDXA). Figure 2 shows a  $\sim 3$ -nm-thick  $\text{HfO}_x$  atop Si(001)- $2\times 1$  after being annealed at  $800^\circ\text{C}$  for 10 min in  $2\times 10^{-5}$  Torr  $\text{O}_2$ . In this sample,  $\sim 1$ -ML-thick hafnium was initially deposited at room temperature on the clean Si(001)- $2\times 1$  in an UHV so as to avoid the silicon oxidation, and then hafnium was deposited in an oxygen ambient. The interesting feature we found is noticeable Si migrations into  $\text{HfO}_x$  (point "D" showing a moderate Si  $K\alpha$  intensity) implying a strong propensity for silicate transformation. The dark fringes underneath the  $\text{HfO}_x$ /Si(001) interface reflect the lattice distortion due to Si loss, which is evidenced from the EDXA showing

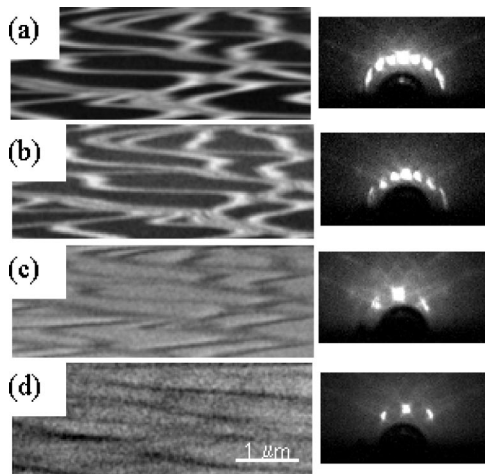


FIG. 3. SREM images and corresponding RHEED patterns for 0.6-ML sample. (a) Clean Si(001)- $2\times 1$  surface. (b) Brighter  $2\times 1$  RHEED spots are shown because Si- $2\times 1$  surface is partially exposed even after deposition. (c) After LPO, the contrast reversion reflects 1-ML-thick  $\text{SiO}_2$  grown on the exposed region. (d) After HPO, propensity for contrast reversion unambiguously weakens.

a stronger Si  $K\alpha$  intensity of point “B” compared with point “A.”

Figure 3 shows the SREM images of the 0.6-ML deposited surfaces. Compared with the 1.1 ML, a much brighter  $2\times 1$  RHEED pattern in Fig. 3(b) appears to reveal a presence of partially exposed Si(001)- $2\times 1$  surface after deposition, and in the LPO condition shown in Fig. 3(c), the terrace contrast is reversed by progress in the oxidation of the first silicon layer at the exposed region. The propensity for contrast reversion unambiguously weakened because the contrast reversion, due to a layer-by-layer growth of  $\text{SiO}_2$ , appearing in the uncovered region was suppressed by an interfacial roughness of the Hf-covered area. The featureless image was also observed after HPO, just as in the 1.1-ML case.

Understanding the bonding sequence and priority of oxygen ions based upon competition between Hf and Si ions is ultimately required in order to elucidate the detailed feature of oxygen bonding at the  $\text{HfO}_x/\text{Si}$  interface after a HPO condition. Under the reasonable assumption that sudden enhancement of the interfacial roughness stemmed from silicate bonding units, the 1.1-ML sample should reveal a clear signature of silicate bonding compared with the submonolayer sample including a large amount of purposely grown  $\text{SiO}_2$ . As a result of the Si  $2p$  core-level study of the suboxide components, Fig. 4(a) and Table I show that a significant increase of  $\text{Si}^{3+}$  (implying dominance of silicate) was observed in the 1.1-ML sample while the  $\text{SiO}_2$  portion decreased.

This result can be understood by a phenomenological view<sup>10,11</sup> of bonding in mixed oxides. Considering the mixing of two oxides (e.g.,  $\text{SiO}_2$  and  $\text{ZrO}_2$ ) to form a complex mixed oxide (zircon,  $\text{ZrSiO}_4$ ), the cation (Zr) of the more ionic metal oxide ( $\text{ZrO}_2$ ) is expected to become even more ionic after formation of the complex oxide, whereas the cation (Si) of the more covalent oxide ( $\text{SiO}_2$ ) should experience

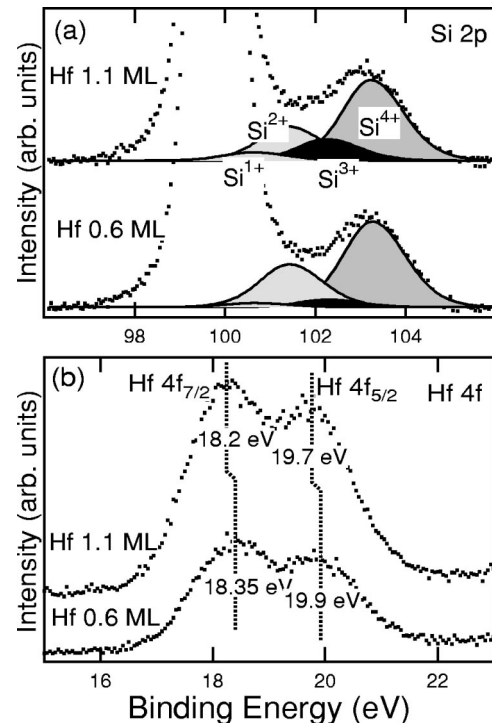


FIG. 4. Si  $2p$  and Hf  $4f$  photoelectron spectra obtained after HPO for 0.6-ML and 1.1-ML samples. The bonding structure of Hf ions corresponds to silicate ( $4f_{5/2} \sim 20$  eV), not metal oxide ( $4f_{5/2} \sim 19$  eV).

a corresponding increase in covalence. In other words, this means that the charge on Si ions should be smaller,<sup>11</sup> i.e.,  $\text{Si}^{4+} \Rightarrow \text{Si}^{3+}$ , in zircon (including silicates) than in  $\text{SiO}_2$  while the charge on Zr ions is expected to be larger. The same feature should be observed in the  $\text{HfO}_x/\text{Si}$  system based upon the chemical similarities between Hf and Zr.<sup>1</sup> The interesting thing we note is that the  $\text{SiO}_2$  portion decreased but still remained above 55% among the interfacial phases in spite of the significant increase of  $\text{Si}^{3+}$  (see Table I).

A plausible explanation of this behavior is the possibility of initial  $\text{SiO}_2$  growth prior to silicate formation at the  $\text{HfO}_x/\text{Si}$  interface. Recent work<sup>2</sup> based on electron-energy-loss spectroscopy in a scanning transmission electron microscope supports our appraisal by probing a presence of  $\sim 0.3$ -nm-thick  $\text{SiO}_2$ -like layer underneath Zr silicate. Despite a different approach to sample preparation, the thickness of  $\text{SiO}_2$ -like layer was estimated to be  $\sim 0.27$  nm in our

TABLE I. XPS intensities of Si  $2p$  components normalized by  $\text{Si}^0$  intensity,  $\text{SiO}_2$  portion (S) among interfacial phases, and estimated composition of each sample.

Sample	$\frac{\text{Si}^{1+}}{\text{Si}^0}$	$\frac{\text{Si}^{2+}}{\text{Si}^0}$	$\frac{\text{Si}^{3+}}{\text{Si}^0}$	$\frac{\text{Si}^{4+}}{\text{Si}^0}$	S <sup>a</sup> (%)	Composition
0.6 ML	0.008	0.075	0.013	0.149	61.1	$\text{Hf}_{0.6}\text{SiO}_{3.9} \cdot (\text{SiO}_2)_{1.5}$
1.1 ML	0.016	0.066	0.041	0.155	55.7	$\text{Hf}_{0.9}\text{SiO}_{4.2} \cdot (\text{SiO}_2)_{1.3}$

<sup>a</sup>Portion of  $\text{Si}^{4+}$  with respect to total amount of  $\text{Si}^{1+} - \text{Si}^{4+}$ .

work,<sup>12</sup> consistent with their observation. The presence of a SiO<sub>2</sub>-like layer implies a *compositional gradient* for silicate formation, and is advantageous for application as a gate dielectric in scaled device technology in the event of achieving the expected channel mobility.<sup>1–3</sup> Previously, chemically selective scanning tunneling microscopy confirmed that a compositional gradient could occur in 1–2 nm thickness range by thermal annealing of 1-ML-thick Hf deposited on 1-nm-thick SiO<sub>2</sub>.<sup>3</sup> Compositionally graded features were varied from topmost HfO<sub>x</sub>-like to SiO<sub>2</sub>-like at the interface with Si.

Our results show that as hafnium increases, a slight shift of Hf 4*f* doublets (4*f*<sub>7/2</sub> and 4*f*<sub>5/2</sub>) to the low-energy side [Fig. 4(b)] is observed to reveal an increase of Hf-O bonding units in silicate network, as shown in Table I, while a portion of SiO<sub>2</sub> decreases. Although silicate formation was previously reported<sup>13</sup> to depend upon the oxygen pressure, annealing above a certain temperature must be critically necessary to transform the bonding feature of oxygen ions into the silicate type since we have not observed a silicate tendency at HPO condition below 500 °C.

#### IV. SUMMARY

The oxidation behavior of ultrathin hafnium on Si(001) was studied by using scanning reflection electron microscopy with *in situ* x-ray photoelectron spectroscopy. The bonding sequence and priority of oxygen ions were found to depend upon the oxidation temperature and pressure. Under the low-pressure oxygen ( $2 \times 10^{-6}$  Torr) at 400 °C, oxygen ions were likely to form Si-O and Hf-O bonding units separately, but at 700 °C in the high-pressure oxygen ( $5 \times 10^{-5}$  Torr), the bonding feature of oxygen ions transformed into Hf-O-Si bonding units (implying silicate formation by Si migration). The presence of  $\sim 0.27$ -nm-thick SiO<sub>2</sub>-like layer underneath silicate layers revealed a possibility of compositional gradient.

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