

## Phase separation and electronic structure of Hf-silicate film as a function of composition

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Thermal stability and electronic structure of  $x\text{HfO}_2 \cdot (100-x)\text{SiO}_2$  (HfSiO) ( $x=25\%$ ,  $50\%$ , and  $75\%$ ) grown by atomic layer deposition were investigated by various measurement tools. The quantity of incorporated  $\text{SiO}_2$  content changes the binding energy of  $\text{HfO}_2$  as the charging effect in the silicate is enhanced with the quantity  $\text{SiO}_2$ . When the annealing temperature is increased over  $800^\circ\text{C}$ , phase separation between  $\text{SiO}_2$  and  $\text{HfO}_2$  is observed in the films with  $50\%$  and  $75\%$   $\text{HfO}_2$ , while it does not occur in a Hf-silicate film with a high mole fraction of  $\text{SiO}_2$ . The phase separation begins in the surface region via the segregation of  $\text{SiO}_2$ . After the annealing treatment, the quantity of  $\text{SiO}_2$  supplied to the film surface due to interfacial interactions influences the phase separation process, resulting in no phase separation being observed, even at a high annealing treatment of  $900^\circ\text{C}$ .

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Among high dielectric oxides,  $\text{HfO}_2$  is emerging as the material with the greatest potential to substitute for  $\text{SiO}_2$ , because of its high dielectric constant and thermodynamic stability when it forms an interface with Si. However,  $\text{HfO}_2$  films crystallize readily and channel mobility is relatively low, due to its high interfacial trap charge, compared to  $\text{SiO}_2$ .<sup>1,2</sup> In order to increase the crystallization temperature and improve the thermal stability in contact with Si, more recent studies have focused on the Hf-silicate gate stack, which shows a channel mobility close to the universal value and a superior interface stability in contact with Si.<sup>3,4</sup> Although Hf-silicate materials are reported to be thermodynamically stable when in contact with Si, a little understanding has been gained concerning the device fabrication process including high temperature annealing.

Kim and McIntyre recently reported that spinodal decomposition can occur through diffusional phase separation and this expectation was confirmed for a  $\text{ZrO}_2\text{-SiO}_2$  system.<sup>5</sup> Neumayer and Cartier showed that phase separation and crystallization occurs after annealing at a temperature of  $800^\circ\text{C}$  in  $\text{HfO}_2\text{-SiO}_2$  systems with  $\text{HfO}_2$  concentrations over  $50\%$  and even below  $25\%$  at  $1000^\circ\text{C}$ .<sup>6</sup> Based on a previous report on phase separation, Stemmer *et al.* observed two distinctly different phase separated microstructures, consistent with two limiting cases of microstructural evolution: nucleation/growth and spinodal decomposition depending on the  $\text{HfO}_2$  fraction in the Hf-silicate film.<sup>7</sup> However, changes in electronic structure and stoichiometry in the depth direction of Hf-silicate thin films on Si during phase separation have not been studied in detail. Moreover, interfacial reactions between the film and Si substrate during phase separation have not been considered, although reactions in thin films with a thickness of  $\sim\text{nm}$  range can critically affect the

phase separation phenomena depending on  $\text{HfO}_2$  and  $\text{SiO}_2$  contents in the silicate film.

In this study, we focused on the electronic structure and interfacial reactions of Hf-silicate films grown on Si using an atomic layer deposition (ALD) system. We investigated the change in chemical state related to the electronic structure of films as a function of  $\text{SiO}_2$  mole fraction in the film and annealing temperature using x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure (NEXAFS). The stoichiometry in the depth direction was also assessed by medium energy ion scattering (MEIS) using a  $\text{H}^+$  beam with an incident energy of  $101\text{ keV}$ . After the annealing treatment, the typical Hf peak shape resulting from the  $\text{HfO}_2$  film appeared to be largely shifted to high binding energy. The altered Hf peak shape was also dependent on the fraction of  $\text{SiO}_2$  in the films. The change from a distorted Hf peak to a typical shape was not observed in highly  $\text{SiO}_2$  incorporated Hf-silicate films. Moreover, NEXAFS data supported the conclusion that the change in peak shape was caused by the segregation of  $\text{HfO}_2$  from silicate film. MEIS data provided critical proof that the segregation started at surface through  $\text{SiO}_2$  extraction. The diffusion of Si from the substrate increased the Si content of the film surface, which disturbed the phase separation in silicate films with a high  $\text{SiO}_2$  fraction at high temperature.

The XPS spectra were measured using a monochromatic Al  $K\alpha$  ( $1486.6\text{ eV}$ ) source with a PHI 5700 spectrometer. The binding energy was calibrated with a reference to the position of bulk Si  $2p_{3/2}$  levels at  $E_b=99.2\text{ eV}$  for the energy of each photon. NEXAFS measurement were carried out at the Pohang accelerator laboratory on beamline 8A1 using a synchrotron x-ray source. A MEIS analysis was carried out with a  $101\text{ keV}$  proton beam in a double alignment mode so as to reduce contributions from the crystalline Si substrate, allowing the deconvolution of the spectra into contributions from the  $\text{SiO}_2$  layer and Si signals.

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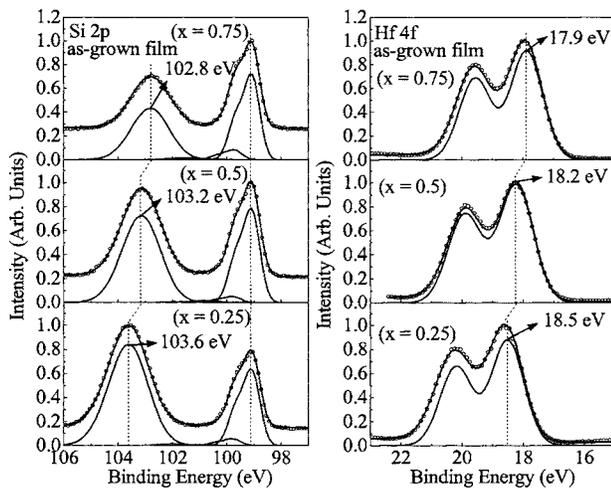


FIG. 1. XPS peak spectra of Si 2*p* (left side) and Hf 4*f* (right side) according to HfO<sub>2</sub> mole fractions ( $x=0.25, 0.5, 0.75$ ) in as-grown Hf-silicate films. The binding energies of Si 2*p*<sub>3/2</sub> and Hf 4*f*<sub>7/2</sub> of the silicate films are indicated in the spectra.

The metal oxides were grown using an atomic layer deposition (ALD) system, which has a vertical warm wall reactor with a showerhead and a heated susceptor. SiO<sub>2</sub> and HfO<sub>2</sub> films were each grown at temperatures below 280 °C using tris(dimethylamido)silane and Tetrakis(ethylmethyldamido) hafnium, respectively, as precursors. O<sub>3</sub> vapor (flow rate=450 sccm) served as the oxygen source and N<sub>2</sub> (flow rate=450 sccm) was supplied as the purge and carrier gas. The SiO<sub>2</sub> incorporated Hf-Si-O were grown by the alternate ALD process repeating the number of cycles for HfO<sub>2</sub> and SiO<sub>2</sub> to mix the SiO<sub>2</sub> content in a controlled manner. Four-nanometers-thick (HfO<sub>2</sub>)<sub>*x*</sub>(SiO<sub>2</sub>)<sub>1-*x*</sub> films on Si with three different compositions, 25 mol % HfO<sub>2</sub>-75 mol % SiO<sub>2</sub> ( $x=0.25$ ), 50 mol % HfO<sub>2</sub>-50 mol % SiO<sub>2</sub> ( $x=0.5$ ), and 75 mol % HfO<sub>2</sub>-25 mol % SiO<sub>2</sub> ( $x=0.75$ ), respectively, were deposited by ALD. The films were annealed using rapid thermal process system in a N<sub>2</sub> ambient from 800 to 1000 °C.

Figure 1 shows Si 2*p* and Hf 4*f* core level spectra of 2-nm-thick Hf-silicate films with various SiO<sub>2</sub> fractions. As the SiO<sub>2</sub> fraction increases, the Si 2*p* and Hf 4*f* spectra shift to higher binding energy.<sup>8</sup> The covalent cation Si is able to affect the charge transfer process in the Hf-Si oxide. In the charge transfer model, one oxygen is shared by molecules of HfO<sub>2</sub> and SiO<sub>2</sub>, connecting to each other: the Hf peak is shifted to higher binding energy, while the Si peak is shifted in the opposite direction from the Hf peak. However, no difference in shift direction between Hf and Si is observed. Moreover, the Si peak caused by silicate, located between Si<sup>4+</sup> and Si<sup>3+</sup>, cannot be differentiated in the spectra as well as it simply shifted to higher binding energy with the SiO<sub>2</sub> fraction, which has a very similar energy shift in the case of an SiO<sub>2</sub> film depending on the SiO<sub>2</sub> film thickness. Moreover, the O peak also shifts to higher binding energy with the SiO<sub>2</sub> fraction (the data are not shown here), indicating that the shift can be caused by same case of SiO<sub>2</sub>: i.e., a considerable shift can be produced by electric charging due to x-ray irradiation thus contributing to the dependence of the SiO<sub>2</sub> fraction of the chemical shift.<sup>9</sup>

Another difference in the peak shape is that the detected HfO 4*f* peak in the silicate films is very broad because of a dispersion effect as a result of intermixing between HfO<sub>2</sub> and

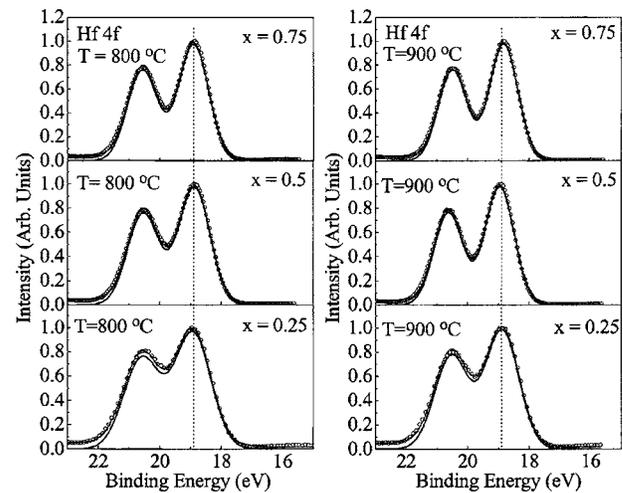


FIG. 2. XPS peak spectra of Hf 4*f* after annealing at temperatures of 800 °C (left side) and 900 °C (right side) according to HfO<sub>2</sub> mole fractions ( $x=0.25, 0.5, 0.75$ ) of Hf silicate films.

SiO<sub>2</sub>. Figure 2 is HfO 4*f* core level spectra of a Hf-silicate film with  $x=0.25, 0.5, 0.75$  after an annealing treatment at 800 and 900 °C. The most interesting finding is that peak broadening changes with annealing temperature and the HfO<sub>2</sub> fraction in the silicate film. The broad peak is changed into the characteristic sharp HfO 4*f* peak in the case of films with a high HfO<sub>2</sub> fraction over  $x=0.5$ , while it is not changed into a sharp Hf peak in the case of the film with low HfO<sub>2</sub> fraction below  $x=0.25$ . Moreover, the degree of the sharpening is dependent on the degree of phase separation such as the amount of SiO<sub>2</sub> fraction contained in the phase separated film. The segregation caused by diffusion of network-modifying species (SiO<sub>2</sub>) is enhanced at high annealing temperatures. However, at an annealing temperature of 900 °C, phase separation is not observed in the silicate film with a low concentration of HfO<sub>2</sub> ( $x=0.25$ ), considering no change in the broad peak. Previously reported findings showed that HfO<sub>2</sub> easily disrupts the silica network even at low HfO<sub>2</sub> concentrations <25%, leading to separation of the HfO<sub>2</sub> and SiO<sub>2</sub> phases, which is a very different result from ours, in which no phase separated at HfO<sub>2</sub> concentrations of 25%.<sup>6</sup> Differences resulting from the use of a MEIS analysis are discussed below.

Phase separation phenomena and interfacial reaction were investigated using MEIS spectra to observe stoichiometric changes in the depth direction, providing a high depth resolution of 0.3–0.5 nm, as shown in Fig. 3. When the film is annealed at 800 °C, an Si peak with a narrow width appears at the leading edge of 90.2 eV. The peak width and position indicate that a thin SiO<sub>2</sub> layer, with a thickness less than 1 nm, is segregated at the film surface. Moreover, the energy position and shape of the Hf peak at the leading edge shows that the Hf is also located at the film surface and that the stoichiometry at the surface region of the as-grown silicate film is only changed through the extraction of SiO<sub>2</sub> from the film. The expected shape in the depth direction of the phase separated film through fitting the raw spectra and above information is that small SiO<sub>2</sub> grains intrude into the HfO<sub>2</sub> matrix layer at the film surface. As the annealing temperature increases up to 900 °C, the quantity of extracted SiO<sub>2</sub> at the film surface exceeds the incorporated mole fraction of SiO<sub>2</sub> in the as-grown film. Thus, another source for

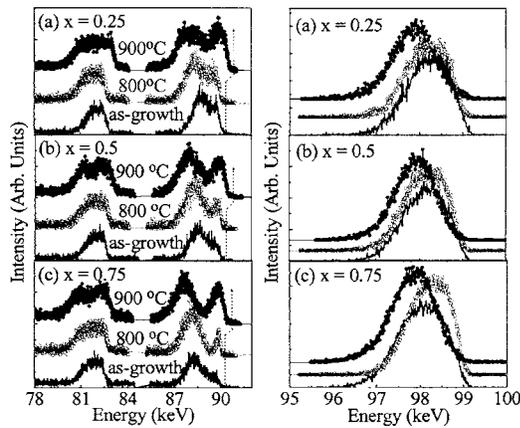


FIG. 3. MEIS spectra for Hf silicate films with different HfO<sub>2</sub> mole fractions ( $x$ ): (a)  $x=0.25$ , (b)  $x=0.5$ , (c)  $x=0.75$ . Left side shows the change in O and Si peaks with mole fractions and annealing temperatures of 800 and 900 °C. Right side is the change in the Hf peak corresponding to the O and Si peaks in the upper line.

the more SiO<sub>2</sub> segregation can be related to diffusion from the Si substrate through the HfO<sub>2</sub> film. The Hf peak change in width and intensity indicates that no movement of Hf occurs, indicating that SiO<sub>2</sub> generated at the interface between the film and Si substrate has diffused to film surface. This tendency, the extraction of SiO<sub>2</sub> at the film surface and diffusion of newly generated SiO<sub>2</sub> at the interface to the film surface, was observed in all samples, including those with low HfO<sub>2</sub> concentration of  $x=0.25$ . Kim and McIntyre, in a simulation, reported that phase separation begins at the interface because of the large local gradient in SiO<sub>2</sub> chemical potential.<sup>5</sup> The result in which the amplitude of SiO<sub>2</sub> concentration decays with increasing distance from the interface is very similar to our MEIS spectra. In our case, the phase separation begins at the surface at an annealing temperature of 800 °C as shown in the high SiO<sub>2</sub> concentration at the film surface and the uniform concentration of HfO<sub>2</sub> in the depth direction. As the annealing temperature and mole fraction of SiO<sub>2</sub> in silicate film increases, interfacial reactions disturb surface directed phase separation, i.e., the amount of SiO<sub>2</sub> at the interfacial region that has diffused into the film surface through the film increases. The interfacial effect can be related to the evolution of a local stress at the interface, resulting in interface directed decomposition.<sup>5,10,11</sup> However, the resulting concentration, a higher concentration of SiO<sub>2</sub> at surface than that at the interface, shows that surface directed phase separation is maintained even though some factors on

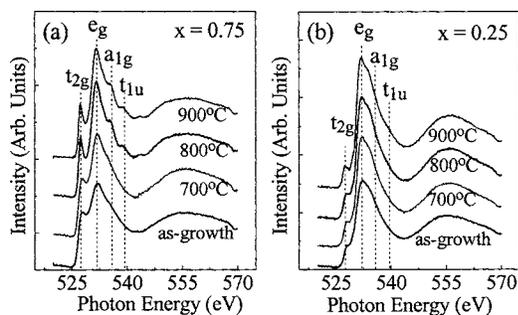


FIG. 4. Change NEXAFS spectra in Hf-silicate films with (a) high HfO<sub>2</sub> mole fraction ( $x=0.75$ ) and (b) low HfO<sub>2</sub> mole fraction ( $x=0.25$ ) at different annealing temperatures of 700, 800, and 900 °C.

the effect of interface directed phase separation influence the phase separation process.

The NEXAFS spectra of the O *K* edge clearly show the change in molecular structure between HfO<sub>2</sub>/Hf-Si-O. The O *K* edge NEXAFS spectrum of HfO<sub>2</sub> is directly related to the oxygen *p*-projected density of states, which consists of four unoccupied hybridized orbitals, under an assumption of an octahedral symmetry.<sup>12,13</sup> The peaks caused by unoccupied hybridized orbitals in HfO<sub>2</sub> are decreased by the amount of incorporated SiO<sub>2</sub> because the spectrum of SiO<sub>2</sub> with a double band caused by O *p* states hybridized with Si 3*sp* states modifies the HfO<sub>2</sub> spectrum.<sup>13,14</sup> The most distinct change with silicate formation is the disappearance of peaks caused by ( $a_{1g}+t_{1u}$ )(Hf 6*sp*+O 2*p*) and a change in  $t_{2g}$  (Hf 5*d*+O 2*p* $\pi$ ) to a broad width and low intensity. The appearance of  $a_{1g}$  and  $t_{1u}$  clearly shows that HfO<sub>2</sub> is extracted from the mixture of SiO<sub>2</sub> and HfO<sub>2</sub> in a film with a high mole fraction of HfO<sub>2</sub> ( $x=0.75$ ) at an annealing temperature over 800 °C, while no change in the spectrum is observed for the film with a low mole fraction of HfO<sub>2</sub> ( $x=0.25$ ) even at an annealing temperature of 900 °C. MEIS spectrum indicates that the quantity SiO<sub>2</sub> supplied at the interfacial region to the film surface is increased as the mole fraction of SiO<sub>2</sub> in the as-grown silicate film and the annealing temperature increase, which can explain why no phase separation is observed in the film with a high SiO<sub>2</sub> mole fraction.<sup>6</sup>

In summary, the chemical state of Hf-Si-oxide films as a function of the mole fraction of HfO<sub>2</sub> was investigated from the point of view of a change in binding energy. Peak changes of Hf and Si indicate that the charging effect is closely related to changes in binding energy. As the annealing temperature increases, phase separation begins through the segregation of SiO<sub>2</sub> at the film surface. At higher annealing temperatures over 900 °C, interfacial interactions influence the phase separation process, supplying SiO<sub>2</sub> from the interface to the surface. The quantity of SiO<sub>2</sub> supplied to the film is dependent on the annealing temperature, resulting in a disturbance of phase separation.

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