

# Origin of Structural Phase Transformation of SiO<sub>2</sub>-doped HfO<sub>2</sub>

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## 1. Introduction

It has been so far reported that a small amount of Y<sub>2</sub>O<sub>3</sub><sup>[1]</sup>, La<sub>2</sub>O<sub>3</sub><sup>[2]</sup> and SiO<sub>2</sub><sup>[3]</sup> doping into HfO<sub>2</sub> causes an enhancement of the dielectric constant through the structural phase transformation (cubic or tetragonal phase) of HfO<sub>2</sub>. Recently, the doping effects on HfO<sub>2</sub> have been studied for higher-k dielectric films<sup>[4-6]</sup>. The mechanisms of the phase transformation due to the doping of other ionic oxides have been intensively studied in the ceramics community, in terms of the surface energy<sup>[7-8]</sup>, size effects<sup>[9]</sup> or oxygen vacancy (V<sub>O</sub>) generation<sup>[10]</sup>. Although HfSiO<sub>x</sub> system has attracted much attention for advanced gate dielectric film application in Si ULSI community, the case for SiO<sub>2</sub> doping has been little investigated.

In this paper, we have examined possible origins of the phase transformation of HfO<sub>2</sub> induced by SiO<sub>2</sub> doping. It is significantly important to elucidate its mechanism in order to design and create new higher-k dielectric films for further advanced CMOS as well as to control the current Hf-silicate properties.

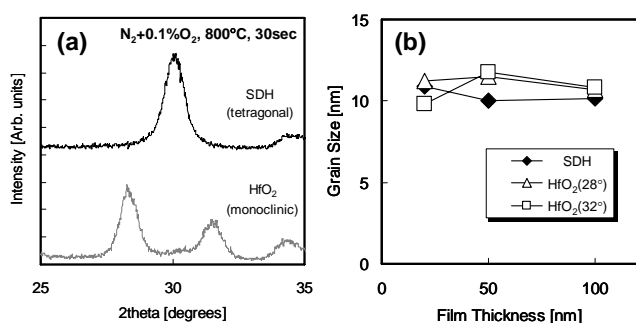
## 2. Experimental

The high-k films were deposited by sputtering technique on FZ-Si wafer. The sputtering targets were HfO<sub>2</sub>, SiO<sub>2</sub> and metal-Hf, which were co-sputtered to fabricate the composite materials of Si-doped HfO<sub>2</sub> (SDH). The thermal annealing process was performed mainly in RTA furnace, while UHV annealing was performed in another chamber in which the base pressure was under 10<sup>-8</sup> Pa.

The film crystal structure and local bonding characteristics were measured by in-plane XRD, and FT-IR measurements.

## 3. Results and Discussion

Typical in-plane XRD spectra and the film thickness dependence of grain size are shown in Fig. 1(a) and 1(b),



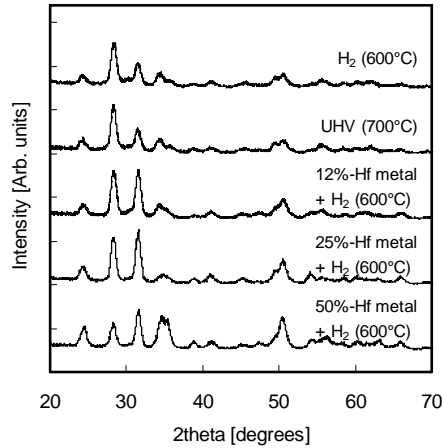
**Fig. 1** (a) Typical in-plane XRD spectra of the tetragonal SDH and the monoclinic HfO<sub>2</sub>. (b) Grain sizes of crystallized SDH and HfO<sub>2</sub> films evaluated with the Scherrer's equation.

respectively. XRD patterns clearly show that SDH and HfO<sub>2</sub> films are crystallized into the tetragonal and monoclinic phase, respectively. The grain size is estimated from the FWHM of XRD peaks with the Scherrer's equation<sup>[11]</sup>. The grain sizes are almost the same between two kinds of phases, and show negligible thickness dependence. This fact is contrary to the reported prediction<sup>[7-8]</sup>, though the applicability of the Scherrer's equation in thin films needs to be considered quantitatively. From the results, it is suggested that the surface energy difference is not the origin of the phase transformation from monoclinic to tetragonal for SDH films.

In the case of Y doping, two reasons have been considered for the phase transformation from monoclinic to cubic. One is the size effect of cation, in which Y<sup>3+</sup> ion has slightly larger ionic radius than Hf<sup>4+</sup> ion. This means that the Y doping enhances the  $r_{\text{cation}}/r_{\text{anion}}$  ratio and makes it close to an ideal value for the cubic structure ( $r_c/r_a \sim 0.735$ ). The other reason, which is the main factor, is the V<sub>O</sub>-induced stabilization with Y<sup>3+</sup> ion introduction. Since the valences of Hf and Y are 4 and 3, Y<sup>3+</sup> doping inevitably introduces the V<sub>O</sub> to keep the charge neutrality. Therefore, V<sub>O</sub> with Y<sup>3+</sup> doping is stable in the material and stabilizes the high temperature phase of HfO<sub>2</sub>.

On the other hand, since Si ionic size is much smaller than Hf one and the same valence as Hf, it is suggested that the mechanism to stabilize the high temperature phase in the Si doping case may be essentially different from that in the Y doping case. Nevertheless, three kinds of HfO<sub>2</sub> films were prepared to examine the V<sub>O</sub> effect on the tetragonal phase transformation; (i) HfO<sub>2</sub> film annealed in N<sub>2</sub> + 1%-H<sub>2</sub> at 600°C for 30 minutes, (ii) HfO<sub>2</sub> film annealed in UHV condition at 700°C for 60 minutes, and (iii) Co-sputtered film of HfO<sub>2</sub> with metal-Hf annealed in N<sub>2</sub> + 1%-H<sub>2</sub> at 600°C for 30 minutes (x Hf + (1-x) HfO<sub>2</sub>; x was controlled to be 0.12, 0.25 and 0.5, respectively). These procedures should reduce the O content and create a number of V<sub>O</sub> sites in the film. The XRD results, however, indicate that all the samples were crystallized into the monoclinic HfO<sub>2</sub> (Fig. 2). This fact implies that the phase transformation cannot be brought about only by the incorporation of V<sub>O</sub>, as expected above.

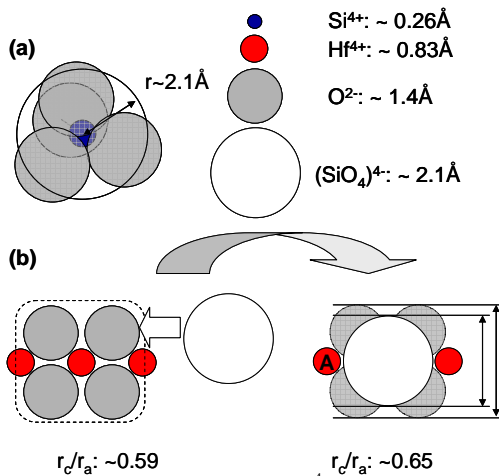
It is well known that Si is bonded with O predominantly through the covalent bonding, which is quite different from Hf-O ionic bonding. Here, we have considered that the doped Si forms the complex ion of (SiO<sub>4</sub>)<sup>4-</sup> tetrahedron in the HfO<sub>2</sub> matrix, which is similar to the case of HfSiO<sub>4</sub> (Hf<sup>4+</sup>-(SiO<sub>4</sub>)<sup>4-</sup> structure). This complex ion picture for the Si-O bonding has been successfully applied for the bulk SiO<sub>2</sub> analysis as well<sup>[12]</sup>. Here, we consider  $r_c/r_a$  ratio for



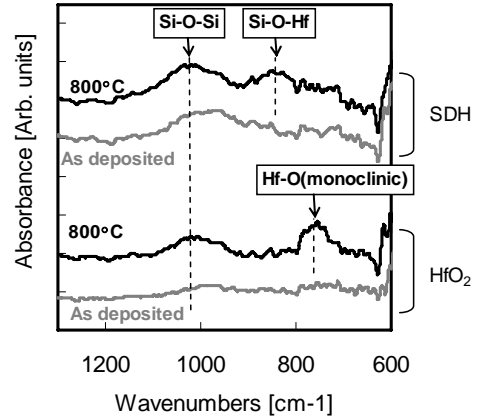
**Fig. 2** In-plane XRD spectra of oxygen defective HfO<sub>2</sub> films. The thickness of all the samples was controlled to be 20nm.

SiO<sub>2</sub>-doped HfO<sub>2</sub>. The average ionic size of (SiO<sub>4</sub>)<sup>4-</sup> is estimated to be about 2.1 Å (**Fig. 3 (a)**). From the electrical neutrality viewpoint, one Hf<sup>4+</sup> and four O<sup>2-</sup> ions can be substituted to one (SiO<sub>4</sub>)<sup>4-</sup> ion (**Fig. 3 (b)**). This fact implies that the average anion size is effectively decreased for the neighbor Hf<sup>4+</sup> ion (denoted “A” in Fig. 3(b)), which increases the effective  $r_o/r_a$  ratio and locally stabilizes the cubic or tetragonal phase thanks to the size effect. Although the concentration of Si is less than 10%, it is enough for triggering the structural phase transformation through the whole dielectric film.

In this model, O atoms surrounding a doped Si atom should be bonded to Hf atoms to form Hf<sup>4+</sup>-(SiO<sub>4</sub>)<sup>4-</sup> bonding. **Figure 4** shows FT-IR spectra of HfO<sub>2</sub> and SDH films. The samples were annealed at 800°C in N<sub>2</sub> for 30 seconds. After annealing, a small peak at 1030 cm<sup>-1</sup> is detected in the sample of HfO<sub>2</sub>/Si, which can be assigned to Si-O-Si bonding. On the other hand, SDH sample before annealing show a broad peak at 980 cm<sup>-1</sup>, which indicates Si-O-Si bonding and partial Si-O-Hf bonding. This peak is split into 1030 cm<sup>-1</sup> and 860 cm<sup>-1</sup> after annealing. Compared to the



**Fig. 3** (a) Schematic view of (SiO<sub>4</sub>)<sup>4-</sup> structure. The average ionic size of (SiO<sub>4</sub>)<sup>4-</sup> is estimated as a radius of sphere that occupies the total volume of Si<sup>4+</sup> and four O<sup>2-</sup> ions. (b) Substitution of (SiO<sub>4</sub>)<sup>4-</sup> ion for Hf<sup>4+</sup> and four O<sup>2-</sup> ions. Considering one Hf<sup>4+</sup> ion surrounded by six O<sup>2-</sup> and one (SiO<sub>4</sub>)<sup>4-</sup> ions, the effective  $r_c/r_a$  ratio increases to 0.65.



**Fig. 4** FT-IR spectra of SDH/Si and HfO<sub>2</sub>/Si. RTA process was performed in N<sub>2</sub> ambient for 30 seconds at 800°C.

annealed HfO<sub>2</sub>/Si sample, it is suggested that the peak at 1030 cm<sup>-1</sup> originates from SiO<sub>2</sub> interfacial layer, while the peak at 860 cm<sup>-1</sup> results from the Si-O-Hf bonding. This means that the SiO<sub>2</sub> doping does not bring about a phase separation, but (SiO<sub>4</sub>)<sup>4-</sup> complex ions are distributed in the SDH film. As a result, it is very consistent with the fact that the covalent nature caused by Si-O bonding does not affect the crystal structure of SDH film but that more symmetric high temperature phase of HfO<sub>2</sub> appears at a relatively low temperature.

#### 4. Conclusion

We have investigated the origin of the tetragonal phase transformation of Si-doped HfO<sub>2</sub>. It has been experimentally revealed that neither the surface energy nor the oxygen vacancy effect has an influence on the structural phase transformation of HfO<sub>2</sub>.

The mechanism of the tetragonal phase transformation can be qualitatively explained by considering the complex ion formation of (SiO<sub>4</sub>)<sup>4-</sup> tetrahedron in the HfO<sub>2</sub> matrix. The (SiO<sub>4</sub>)<sup>4-</sup> ion can decrease the effective anion size and increase the  $r_c/r_a$  ratio, which can stabilize the 8-fold coordinated structure without V<sub>O</sub> formation.

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