Interdiffusion studies for HfO$_2$/Si by GIXR and XPS

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Abstract Interdiffusion at the interface between an HfO$_2$ thin film and a Si substrate was studied using grazing incidence x-ray reflectivity (GIXR) and x-ray photoelectron spectroscopy (XPS). HfO$_2$ thin films were deposited on Si substrates by the sputtering of a metal-Hf layer, and then they were oxidized/annealed in a N$_2$/O$_2$ gas mixture with different O$_2$ concentrations. The GIXR and XPS results showed that the out-diffusion of Si atoms from the substrate increased with the oxygen concentration during high temperature annealing, and consequently, it resulted in the formation of a Si-rich Hf-silicate interlayer, i.e., lower-density Hf-silicate with greater thickness. The GIXR results of the interfacial structures were in agreement with the results of XPS and cross-sectional transmission electron microscopy.

1. Introduction

Due to the downscaling of complementary metal-oxide-semiconductor (CMOS) field effect transistors (FETs), leakage current levels arising from the direct tunneling of electrons through the SiO$_2$ gate oxide become unacceptable [1]. A high-$k$ gate oxide with a thickness of a few nanometers, as an alternative to SiO$_2$, has attracted considerable attention [2]. Hafnium oxide (HfO$_2$), one of the most promising materials due to its high dielectric permittivity ($k = 25$), large band gap, and high thermal stability, has been extensively studied [3, 4, 5]. Since the actual performance of a device strongly depends on the interfacial state, the interface between the HfO$_2$ layer and Si substrate is one of the main issues in HfO$_2$ studies.

In the conventional CMOS process flow, a particularly demanding step is the dopant activation anneals ($T \leq 1050$ °C), which the gate dielectric must survive without degrading. The high annealing temperature is likely to produce film decomposition and/or crystallization, as well as concomitant interdiffusion between the HfO$_2$ thin film and Si substrate, which forms the interlayer of Hf-silicate or Hf-silicide or compounds containing other elements. It has been reported that Hf-silicate was formed due to the out-diffusion of Si from the substrate and its reaction with Hf and oxygen atoms near the interface during high-temperature annealing [6]. It is also known that Hf-silicide is formed under oxygen-deficient conditions [7]. Therefore, the interfacial structure attributed to the interdiffusion between the HfO$_2$ and Si substrate during thermal annealing is closely related to the oxygen amount. Although the interfacial structure of HfO$_2$/Si has been extensively studied, the relation between the interdiffusion and oxygen at the HfO$_2$/Si interface has not yet been completely understood, and few articles have systematically researched this issue. Furthermore, as mentioned above, since the actual performance of a device strongly depends on the interfacial state, it is necessary to clarify the interfacial structure unambiguously.
In the present study, in order to clarify the effects of oxygen content on interdiffusion at the interface of the HfO$_2$ thin film and Si substrate, metal-Hf layers were deposited on Si substrates by the sputtering and then were oxidized/annealed in a N$_2$/O$_2$ gas mixture with different oxygen concentrations. The interfacial chemical structures were investigated by x-ray photoelectron spectroscopy (XPS). In order to investigate the physical structure of the interface, we used grazing incidence x-ray reflectivity (GIXR), which is a non-destructive and quantitative measurement of monitoring thin film growth with thickness accuracy in the atomic regime (<0.5 nm) [8]. In this study, we also demonstrated the application of GIXR to the structural evaluation of HfO$_2$ thin films on Si substrates.

2. Experimental
The HfO$_2$ thin films were formed by the sputtering deposition of thin metal-Hf layers on the Si substrates without native oxides and then oxidized/annealed in a N$_2$/O$_2$ gas mixture. The substrates of p-type Si(100) wafers were cleaned with a diluted HF (1%) solution to remove native oxides and contaminations. The Hf thin films were deposited by a radio-frequency (RF) magnetron sputtering system (base pressure: 7.0 × 10$^{-8}$ Pa) with a 3 in. metallic Hf (99.9% purity) disc as the sputtering target. High purity argon was used as the plasma generation gas. After Hf deposition, the oxidization/annealing process was carried out in the same chamber with a N$_2$/O$_2$ gas mixture at 800 °C for 30 min at a pressure of 7.5 × 10$^{-2}$ Pa. We prepared two samples—#1: oxidized/annealed in the N$_2$/O$_2$ gas mixture with a flow rate of 9.9 and 0.1 standard cubic centimeters per minute (SCCM) and #2: oxidized/annealed in the N$_2$/O$_2$ gas mixture with flow rate of 9.9 and 0.1 standard cubic centimeters per minute (SCCM) and 9.5 and 0.5 SCCM.

The thickness, density, and roughness of the films were determined by GIXR. GIXR measurements were carried out using a high-resolution x-ray reflectometer. A rotating Cu anode operated at 15 kW was used as x-ray source. A parabolic multilayer mirror collected x-rays to form a parallel beam. Thereafter, the beam was compressed and monochromatized with an asymmetric channel-cut Ge(111) monochromator to select K$_\alpha$ line. The incident and reflected beams were collimated with 0.05 mm slits, and the reflection intensity was measured by a scintillation counter. The goniometer of a θ-2θ axes were controlled by using a high resolution encoder and calibrated by an auto-collimator with polygon mirror. The angular resolution of the both axes was 0.0001°. The reflectivity profiles were recorded with a θ-2θ scan.

The chemical composition and bonding states were measured by XPS with a monochromatized Al K$_\alpha$ x-ray source at a take-off angle of 0° with respect to the surface normal. High resolution cross-sectional transmission electron microscopy (CS-TEM) was employed in order to verify the GIXR results.

3. Results and Discussion
Figure 1 shows the GIXR profiles of samples #1 and #2. In the GIXR method, a monochromatic x-ray was set at a grazing angle (from 0.2° to 6.2°) with the thin films [9]. The x-ray reflected from the film surface and interface forms interference fringes that reflect the film thickness, density, and roughness. In the GIXR profiles, the angle at which a sudden decrease in reflectivity occurs is referred to as the critical angle. The critical angle is proportional to the electron density of the film. The changes in the oscillation periodicity are related to the film thickness in the following manner: the shorter the periodicity, the thicker the film. The oscillation amplitude suggests a variation at the interface, such as roughness changes or the formation of an interfacial layer. The detailed analysis of these parameters requires data fitting with a model structure. In order to obtain an optimized fit, we used a three-layer-model comprising a contamination layer, HfO$_2$ layer, and interlayer. The density (ρ), thickness (d), and roughness (σ) of each layer, and the R-value, which is the relative standard deviation for fitting, are also shown in Fig. 1. The contaminants were assumed to be hydrocarbons with lower density like polystyrene from sample container, etc. The calculated film density for HfO$_2$ is approximately 9.6 g/cm$^3$ for both samples #1 and #2, which is in good agreement with the theoretical value [10]. The total thicknesses without the contaminants were 2.99 and 3.53 nm for sample #1 and #2, respectively.
Figure 1. GIXR profiles and fitting results of samples #1 and #2.

Table I. Repeated results of GIXR measurements for sample #1.

| Measurement | Thickness (nm) | Density (g/cm³) | Roughness (nm) | R-value (%) |
|-------------|----------------|-----------------|----------------|-------------|
| 1st         |                |                 |                |             |
| Contaminants | 0.17          | 0.96            | 0.40           | 0.442       |
| HfO₂         | 1.67           | 9.67            | 0.37           |             |
| Interlayer   | 1.32           | 4.48            | 0.26           |             |
| Total        | 3.16           | -               | -              |             |
| 2nd         |                |                 |                |             |
| Contaminants | 0.22           | 0.97            | 0.40           | 0.425       |
| HfO₂         | 1.66           | 9.62            | 0.36           |             |
| Interlayer   | 1.28           | 4.55            | 0.25           |             |
| Total        | 3.16           | -               | -              |             |
| 3rd         |                |                 |                |             |
| Contaminants | 0.15           | 0.94            | 0.40           | 0.408       |
| HfO₂         | 1.67           | 9.58            | 0.37           |             |
| Interlayer   | 1.30           | 4.57            | 0.25           |             |
| Total        | 3.12           | -               | -              |             |
| Average     |                |                 |                |             |
| Contaminants | 0.18           | 0.96            | 0.40           |             |
| HfO₂         | 1.67           | 9.62            | 0.37           |             |
| Interlayer   | 1.30           | 4.53            | 0.25           |             |

Standard deviation

| Contaminants | 0.04 | 0.02 | 0.00 | - |
| HfO₂         | 0.01 | 0.05 | 0.01 | |
| Interlayer   | 0.02 | 0.05 | 0.01 | |
Compared with sample #2, sample #1 shows an interlayer with a higher density and lesser thickness. In other words, in the interlayer, the density decreased and the thickness increased with the oxygen concentration during oxidation/annealing process.

To investigate the reliability of GIXR analysis, we repeated the measurements for sample #1 thrice. Table I shows the repeatability results for sample #1. The average thicknesses of the HfO$_2$ and interlayers are 1.67 and 1.30 nm, respectively, and the standard deviations are 0.01 and 0.02 nm, respectively, indicating that the GIXR evaluation for high-$k$ thin film has excellent repeatability.

In order to verify our GIXR results, CS-TEM images of samples #1 and #2 were taken, as shown in Fig. 2. The thicknesses of the interlayer in samples #1 and #2 were 1.4 nm and 1.9 nm, respectively. The total thickness (HfO$_2$ plus interlayer) estimated by CS-TEM were 3.3 and 4.0 nm for samples #1 and #2, respectively. The agreement of the results from CS-TEM observation and GIXR evaluation is reasonable based on the consideration of the repeatability and an analyzed area of the CS-TEM observation.

Figure 3 shows the XPS spectra for samples #1 and #2 and 2-nm thermal-oxidized SiO$_2$ for comparison. All the charging shifts were calibrated referring to the binding energy (BE) of bulk Si$^0$ 2$p_{3/2}$ (99.3 eV). From the Si 2$p$ core-level spectra shown in Fig. 3(a), samples #1 and #2 shows the dominant component located around 102.4 and 102.8 eV, respectively, which correspond to the peak position of Si-O-Hf (Hf-silicate). The BE of the Si-O-Hf peak increased with the oxygen concentration during oxidation/annealing process. Since the Si 2$p$ core-level shifts to a higher BE when the Hf content decreases in the Hf-silicate compounds [11, 12], the result suggests that the Hf content in the Hf-silicate interfacial layer decreased with increasing oxygen content. In addition, the intensity of the Si-O-Hf peak in sample #1 is lower than that in sample #2. This indicates that a thinner Hf-silicate
interlayer is present in sample #1, which is consistent with the GIXR results. The Hf 4f core-level spectra for samples #1 and #2 are shown in Fig. 3(b). As shown in Fig. 3(b), no metal-Hf and Hf-silicide bond was observed. Figure 3(c) shows the O 1s core-level spectra for samples #1 and #2 and the SiO$_2$ film. Both the spectra of samples #1 and #2 consist of two components: the first one at BE = 530.9 eV is assigned to the O atoms in HfO$_2$, and the second one at a lower binding energy between HfO$_2$ and SiO$_2$ is assigned to the O atoms in Hf-silicate.

From the above results, it can be concluded that the interlayer between HfO$_2$ and the Si substrate was an Hf-silicate layer. Furthermore, both the XPS and GIXR results indicated that the Hf content in the Hf-silicate interlayer decreased; in other words, the Si content increased with the oxygen content during oxidation/annealing process. Formation of the Hf-silicate interlayer can be considered by the out-diffusion of Si atoms from the substrate to the HfO$_2$ layer formed by the reaction between Hf layer and oxygen molecules from ambient. Our results indicate that the out-diffusion of Si occurred easily under the oxygen-rich ambient conditions; more oxygen content, more the out-diffusion of Si and lower the Hf-silicate interlayer density.

4. Conclusions

Interdiffusion between HfO$_2$ thin film and Si substrate was studied by using GIXR and XPS. Both the GIXR and XPS results revealed that the out-diffusion of Si from the substrate increased with the oxygen concentration, and consequently, it formed the interlayer of Si-rich Hf-silicate, i.e., lower-density Hf-silicate with a greater thickness. The GIXR results of the interfacial structures were in agreement with the results of XPS and CS-TEM. In addition, the results of repeated measurements indicated the excellent repeatability of the GIXR technique.

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