Study of interfacial structure of HfO$_2$ thin film on Si by grazing incidence x-ray reflectivity

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Abstract The interfacial structures of an HfO$_2$ thin film on a Si substrate were studied by grazing incidence x-ray reflectivity (GIXR) in this work. The HfO$_2$ thin films were fabricated on Si substrates by the sputtering and subsequent oxidization/annealing with different interfacial layers. The GIXR results revealed that the density and thickness of the Hf-silicate interlayer was different for different samples. The composition of the Hf-silicate interlayer was related to the oxygen atoms; more oxygen atoms led to the formation of Si-rich Hf-silicate. The interfacial structures were appropriately obtained by GIXR measurements; these results were in agreement with the results of x-ray photoelectron spectroscopy and cross-sectional transmission electron microscopy.

1. Introduction

As the physical dimensions of metal-oxide-semiconductor field effect transistors (MOSFETs) are being increasingly scaled down, a high-$k$ gate oxide with a thickness of a few nanometers is attracting considerable interest as a suitable alternative to SiO$_2$ [1]. From this point of view, 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 [2, 3]. One of the main issues concerning HfO$_2$ is the interfacial structures that arise after the thermal process because the actual performance of a device strongly depends on the interface formed between the HfO$_2$ layer and Si substrate. Therefore, it is extremely important to understand the interfacial structures that arise after the thermal annealing.

Among the characterization methods for the interface of high-$k$ thin films, grazing incidence x-ray reflectivity (GIXR), which is a nondestructive and quantitative method of monitoring thin film growth with a thickness accuracy in the atomic regime (<0.5 nm) [4], has received considerable attention [5]. An HfO$_2$ thin film on a Si wafer is particularly a suitable candidate for GIXR because it has a higher electron density than the Si substrate underneath. GIXR has been demonstrated as an inline metrology tool for the deposition process of HfO$_2$ gate dielectrics [6, 7], because it does not require sample preparation and the measurements can be made in the production environment. When GIXR is applied to materials characterization, as indicated by the International Technology Roadmap for Semiconductors (ITRS), it is important to construct interfacial models from GIXR data such that these models can be compared to the interfacial models obtained from other methods [8]. However, few GIXR studies have included a comparison of the interfacial structural characterization of high-$k$ thin films with the other characterization methods.

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In the present study, we investigated the interfacial structures of HfO₂ thin films on Si substrates by using GIXR. X-ray photoelectron spectroscopy (XPS) and cross-sectional transmission electron microscopy (CS-TEM) were carried out to compare the interfacial structures with the GIXR results. Based on the comparison, it is confirmed that GIXR is capable of distinguishing interfacial structural change in sub-nanometer order.

2. Experimental

In order to prepare samples with different interfacial structures, the preparation conditions listed in Table I were employed. Sample A was prepared as follows: a HfO₂ film was formed by the reactive sputtering in an Ar/O₂ gas mixture after the deposition of one metal-Hf buffer layer on the Si substrate without native SiO₂; subsequently the film was annealed in a N₂/O₂ gas mixture ambient at 800 °C for 10 minutes. Yamamoto et al. and our group have reported that a predeposited Hf-buffer layer consume the oxygen atoms transported through the HfO₂ overlayer and form an Hf-silicate to keep leakage current low [9, 10]. The deposited thicknesses of the HfO₂ and predeposited metal-Hf layers were approximately 2 nm and 1 nm, respectively; these thicknesses were roughly controlled by the respective sputtering rates. Second, to understand the effects of the subsequent HfO₂ deposition on the predeposited metal-Hf layer, i.e., the interfacial layer, we prepared sample B, which was formed by the sputtering deposition of a thin metal-Hf layer on the Si substrate without native oxide and by performing the same thermal process as that for sample A. Third, to compare the effects of the SiO₂ underlayer on the formation of the interfacial structures, we prepared sample C, which was formed on the Si substrate with native oxide under the same conditions as those for sample B.

The substrates of p-type Si(100) wafers were treated by two methods. For the deposition on substrates without native oxides, the Si wafers were dipped in a diluted HF (1%) solution to remove the native oxides and contaminants. For the deposition on the native oxides, the substrate was cleaned with a hot H₂SO₄:H₂O₂ (4:1) solution to remove the contaminants and rinsed in deionized water. The Hf and HfO₂ thin films were deposited using a radio-frequency (RF) magnetron sputtering system (base pressure: 7.0 × 10⁻⁸ Pa) with a 3 in. metallic Hf (99.9% purity) disc used as the sputtering target. After deposition, the oxidization/annealing process was carried out in the same chamber in a N₂/O₂ gas mixture under flow rate of 9.7 and 0.3 SCCM (standard cubic centimetres per minute) at 800 °C for 10 minutes at a pressure of 7.5 × 10⁻² Pa.

The thickness, density, and roughness of the prepared films were determined by the GIXR. GIXR measurements were carried out using a high-resolution x-ray reflectometer [11]. 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. Subsequently, the beam was compressed and monochromated using an asymmetric channel-cut Ge(111) monochromator to select Kα 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 by 0-2θ scans. The films were also characterized by CS-TEM and XPS with a monochromatized Al Kα source at a take-off angle of 0° with respect to the surface normal to compare these results with those of GIXR analysis.

Table I. Summary of the fabrication process for each sample.

| Sample | Substrate | Deposition process | Oxidization/Annealing |
|--------|-----------|--------------------|-----------------------|
| A      | Si(100) without native SiO₂ | Metal-Hf predeposition→HfO₂ | 800 °C for 10 min in N₂/O₂ gas mixture |
| B      | Si(100) with native SiO₂    | Metal-Hf deposition       |                        |
Table II. Thickness of layers of each sample obtained by CS-TEM.

| Sample | Thickness (nm) |
|--------|----------------|
| HfO₂   | 2.1            |
| A      | Interlayer     | 2.7 |
|        | Total          | 4.8 |
| HfO₂   | 2.0            |
| B      | Interlayer     | 1.2 |
|        | Total          | 3.2 |
| HfO₂   | 2.1            |
| C      | Interlayer     | 1.7 |
|        | Total          | 3.8 |

3. Results and Discussion

Figure 1 shows the CS-TEM images of the samples. Table II lists the thicknesses of each layers obtained from CS-TEM observations. Sample A has a thicker interlayer as compared to the other two samples. It indicates that HfO₂ deposition after the predeposition of a metal-Hf layer increased the formation of the interlayer after annealing. The interlayer of sample C is thicker than that of sample B because of the existence of the native SiO₂ layer underneath.

In order to investigate the interfacial chemical structure of the samples, XPS analyses were carried out. Figure 2 shows the XPS Si 2p core-level spectra of the three samples and 2-nm thermal-oxidized SiO₂ for purpose of comparison. The charging shifts were calibrated by referring to the binding energy of bulk Si²p3/2 (99.3 eV). As shown in Fig. 2, for sample A, the component located around 103.6 eV is dominant in the spectrum. Since this position is consistent with the binding energy of the SiO₂ film, as shown in the bottom in Fig. 2, it is considered that SiO₂ is present at the interface of sample A. The component located around 103.1 eV, which correspond to the peak position of Si-O-Hf, can also be observed. In the case of samples B and C, the dominant components are located around 102.4 eV and 102.8 eV, respectively. It is known that the Si 2p core-level in Si-O-Hf shifts to a higher binding energy with a decrease in the Hf concentration [12, 13]. Therefore, it can be concluded that the Hf content decreased in the order of the samples B, C, and A, i.e., sample B has Hf-rich Hf-silicate interlayer, while sample A has Si-rich Hf-silicate interlayer. From Hf 4f core-level spectrum of sample...
B, no metal-Hf and Hf-silicide was observed. It has been reported that O diffuses downwards most easily as compared to the diffusion of Si and Hf atoms [14]. Thus, interfacial layers of sample A consists of an Hf-silicate interlayer on SiO2 interlayer.

Figure 3 shows the GIXR profiles of the three samples. Table III shows the GIXR fitting results of the thickness, density, roughness, and R-value, which is the relative standard deviation for fitting. As shown in the CS-TEM images, there was one interlayer in three samples. On the other hand, the XPS results indicated the existence of interlayers of Hf-silicate and SiO2 in sample A. Therefore, we used a 3-layer-model that comprises a contamination layer, the HfO2 layer, and one interfacial layer, and a 4-layer-model that comprises two interlayers of Hf-silicate (Interlayer 1) and SiO2 (Interlayer 2) to fit the GIXR data. It can be observed that the quality of the fit for sample A is improved by using the 4-layer-model. It is considered that a 4-layer-model is more suitable for sample A, which is consistent with the XPS results. This indicates that the interfacial structure between the high-k thin film and Si substrate can be appropriately obtained by GIXR analysis. As shown in the table, the thickness of each sample obtained by 4-layer-model is close to the thickness obtained by CS-TEM. 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. Furthermore, it should be noted that the thickness of the HfO2 layer has almost no change nevertheless the different model.

It is considered that the density of the interfacial layer depends on the stoichiometry of the component. For example, the density of Hf-rich interlayer can be greater than that of Si-rich interlayer. As shown in the Table III, the density of the Hf-silicate interlayer (Interlayer 1) decreased in the order of samples B, C, and A. As described above, XPS results indicated that Hf contents of Hf-silicate interlayer in three samples decreased in the order of B, C, and A. The GIXR results are consistent with XPS results. The Hf-silicate was considered to form due to the out-diffusion of Si atoms from the substrate and reaction with Hf and oxygen atoms supplied for the formation of the HfO2 layer [3, 15]. The XPS and GIXR results revealed the Si-rich Hf-silicate interlayer in sample A, which contained more O atoms due to the HfO2 deposition after the predeposition of metal-Hf layer. In the case of sample B, the Hf-rich Hf-silicate interlayer was formed due to the O atoms supplied only from the

Table III. Thickness, density, roughness, and relative standard deviation (R-value) obtained by GIXR measurements with a 3-layer-model and a 4-layer-model.

|       | Sample | 3-layer-model | 4-layer-model |       |
|-------|--------|---------------|---------------|-------|
|       |        | Thickness (nm) | Density (g/cm³) | Roughness (nm) | R-value (%) | Thickness (nm) | Density (g/cm³) | Roughness (nm) | R-value (%) |
| Contaminants* | A | 0.29 | 0.96 | 0.33 | 0.433 | 0.31 | 0.96 | 0.32 |
| HfO2   |       | 1.86 | 9.53 | 0.33 |       | 1.82 | 9.68 | 0.40 |
| Interlayer 1 |       | 3.15 | 3.35 | 0.26 |       | 1.22 | 3.63 | 0.19 |
| Interlayer 2 |       | -    | -    | -    |       | 1.63 | 2.55 | 0.13 |
| Total (without contaminants) | | 5.01 | -    | -    | 0.259 | 4.67 | -    | -    |
| Contaminants* | B | 0.22 | 0.93 | 0.31 | 0.521 | 0.19 | 0.94 | 0.32 |
| HfO2   |       | 1.68 | 9.96 | 0.48 |       | 1.65 | 9.96 | 0.47 |
| Interlayer 1 |       | 0.83 | 4.85 | 0.23 |       | 0.70 | 5.58 | 0.19 |
| Interlayer 2 |       | -    | -    | -    |       | 0.42 | 2.89 | 0.22 |
| Total (without contaminants) | | 2.51 | -    | -    | 0.497 | 2.77 | -    | -    |
| Contaminants* | C | 0.15 | 0.94 | 0.31 | 0.778 | 0.21 | 0.98 | 0.29 |
| HfO2   |       | 1.83 | 9.71 | 0.38 |       | 1.77 | 9.63 | 0.43 |
| Interlayer 1 |       | 1.26 | 3.59 | 0.28 |       | 1.11 | 3.85 | 0.21 |
| Interlayer 2 |       | -    | -    | -    |       | 0.91 | 2.65 | 0.33 |
| Total (without contaminants) | | 3.09 | -    | -    | 0.561 | 3.79 | -    | -    |

* The contaminants were assumed to be hydrocarbons with lower density like polystyrene from sample container, etc.
annealing ambient. The Hf-silicate interlayer of sample C was richer in Si than sample B, because the O atoms were supplied from the annealing ambient and the native SiO₂ underneath. These results suggest that the composition of Hf-silicate interlayer is related to the amount of oxygen atoms; more oxygen atoms lead to the formation of Si-rich Hf-silicate interlayer.

In the case of interlayer 2, the densities of the SiO₂ interlayers are greater than that of thermally oxidized SiO₂ obtained by GIXR [16]. As mentioned above, Si diffusion from substrate into upperlayer is in competition with the O transport to the interface, which results in the formation of interlayers of Hf-silicate and SiO₂. It has been reported that the transport rate of Si toward the surface through the HfO₂ layer is 1/50 times that of O toward the interface [12]. Although the reason for the higher density of the SiO₂ interlayer of the samples is not yet clear at this moment, it can be considered that some Hf-silicate was embedded in the SiO₂ interlayer due to the different transport rates, thereby increasing the density of the SiO₂ interlayer.

4. Conclusions

The interfacial structures between an Hf-based thin film and a Si substrate were studied by GIXR in this work. Three samples with different interfacial layers were prepared by the sputtering and oxidization/annealing subsequently in a N₂/O₂ gas mixture ambient. The GIXR results revealed that the Hf-silicate interlayers of the samples have different densities and thicknesses. The composition of the Hf-silicate interlayer was related to the oxygen atoms, that is, more oxygen atoms led to the formation of Si-rich Hf-silicate. Interfacial structures, such as density and thickness of interlayer, were appropriately obtained by GIXR measurements; these results were in agreement with the results of XPS and CS-TEM analyses. Based on the comparison, it is confirmed that GIXR is capable of distinguishing interfacial structural change in sub-nanometer order. It is suggested that GIXR is a convenient and reliable nondestructive method to characterize the interfacial structures of high-κ thin films on Si substrates.

References

[1]  G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. App. Phys. 89 (2001) 5243.
[2]  V. V. Afanas’ev, A. Stesmans, and W. Tsai, Appl. Phys. Lett. 82 (2003) 245.
[3]  G. Bae, H. Lee, D. Jung, H. Kang, Y. Roh, and C. -W. Yang, Jpn. J. Appl. Phys. 40 (2001) L813.
[4]  J. -M. Baribeau, Appl. Phys. Lett. 57 (1990) 1748.
[5]  Y. Hwang, K. Heo, C. H. Chang, M. K.Job, and M. Ree, Thin Solid Films 510 (2006) 159.
[6]  S. Ferrari, M. Modreanu, G. Scarel, and M. Fanciulli, Thin Solid Films 450 (2004) 124.
[7]  P. Y. Hung, C. Gondran, A. G. Roy, S. Terada, B. Bunday, H. Yeung, and A. Diebold, J. Vac. Sci. Technol. B23 (2005) 2244.
[8]  International Technology Roadmap for Semiconductors, http://www.itrs.net, 2005.
[9]  K. Yamamoto, S. Hayashi, M. Niwa, M. Asai, S. Horii, and N. Miya, Jpn. J. Appl. Phys. Part 1 42 (2002) 1835.
[10] R. Tan, Y. Azuma, and I. Kojima, Appl. Sur. Sci. 241 (2005) 135.
[11] I. Kojima and B. Li, The Rigaku Journal, 19 (1999) 31.
[12] Y. Hoshino, Y. Kido, K. Yamamoto, S. Hayashi, and M. Niwa, Appl. Phys. Lett. 81 (2002) 2650.
[13] O. Renault, D. Samour, J. -F. Damlencourt, D. Blin, F. Martin, S. Marthon, N. T. Barrett, and P. Besson, Appl. Phys. Lett. 81 (2002) 3627.
[14] W. L. Scopel, Antonio J. R. da Silva, W. Orellana, and A. Fazzio, Appl. Phys. Lett. 84 (2004) 1492.
[15] B. H. Lee, L. Kang, R. Nieh, W. -J. Qi, and J. C. Lee, Appl. Phys. Lett. 76 (2000) 1926.
[16] N. Awaji, S. Ohkubo, T. Nakanishi, Y. Sugita, K. Takasaki, and S. Komiyi, Jpn. J. Appl. Phys. 35 (1996) L67.