Characterization of high-*k* materials for the advancement of high-speed ULSIs *

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Insulators with high dielectric constants (so-called high-*k*) have been intensively investigated for the replacement of SiO₂ gate dielectric of MOS transistors for high-speed ULSIs in near future. The characterization results of the Hf-silicate gate dielectric, especially in terms of its structural transformation during high temperature annealing, are presented. Phase separation and micro-crystallization in Hf-silicates were evaluated using XPS, TEM, and XRD. Impurity diffusion through the dielectric was also examined using the backside SIMS of the p⁺-poly-Si/Hf-silicate/Si-substrate system. It has also been revealed that such thermal stability problems for Hf-silicates can be solved with nitrogen incorporation in the film using the physical analyses outlined above.
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I. INTRODUCTION

As the device dimensions in ULSIs have been reduced, several intrinsic barriers against further development have emerged. One of these is the leakage current through the SiO₂ gate dielectric due to the quantum mechanical tunneling of the carriers in the inversion layers. This phenomenon results in a high level of power consumption, which is especially problematic in LSIs for mobile applications. Much effort has been expended in developing high-permittivity dielectrics (high-*k* materials) as an alternative gate insulator in order to solve this problem [1]. Among various candidates, silicate is considered to be a promising material due to its modest dielectric constant [2] and relatively good interface properties with the silicon substrate [3]. However, a major drawback of this material is its poor thermal stability [4]. Figure 1 shows that several high temperature annealings following the gate dielectric film deposition is necessary for ULSI fabrication. This report focuses on the characterization of Hf-silicates especially in terms of their structural transformation during high temperature annealing. The electrical property change is also presented in relation to the structural change of this material. The effect of nitrogen incorporation in Hf-silicates on the thermal stability was also evaluated with the characterization technique mentioned above.

II. EXPERIMENT

Hf silicate films were deposited on HF-treated Si(100) substrate using reactive co-sputtering from the Hf and Si targets in Ar+O₂ ambient at room temperature. The

Hf/Si ratio in the film was varied by changing the power imposed on each target. Nitrogen incorporation was achieved by a mixture of N₂ gas in the sputtering atmosphere. Rapid thermal annealing in N₂ at 1000°C for 30 s was performed after the film deposition as the high temperature annealing in this study. High Resolution TEM (Hitachi HF-2000 field emission, 200 keV) was used to observe the structural change in the film. In-plane XRD was performed in order to evaluate the crystallinity of thin (< 10 nm) films. An X-ray beam (Cu K α , 0.154 nm) was incident on the samples at an angle of 0.3° for the total reflection at the sample surface in this measurement. In order to evaluate the chemical bonds in the silicate films, XPS using Al K α (1.487 keV) as the light source was carried out. Backside SIMS measurement was used to evaluate the boron diffusion through thin Hf-silicate films with high temperature annealing. O₂⁺ with an energy of 3 keV was used for the primary ion in this measurement.

For the electrical measurement, highly-doped poly-Si/Hf-silicate/p-Si(100) MOS capacitors have been fabricated. High temperature annealing was carried out at 1000°C for 30 s for the activation and diffusion of implanted Arsenic and Boron inside the gate electrodes. C-

FIG. 1: High temperature processes following the gate dielectric film deposition in the ULSI fabrication.

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FIG. 2: TEM planar view of the Hf-silicate films (a) without nitrogen, (b) with [N] of 5 at.%, and (c) 30 at.%, after the 1000 °C annealing. Relative concentration Hf/Hf+Si was about 25 % for all samples.

V measurement was carried out in order to evaluate the dielectric constant of the films.

III. RESULTS AND DISCUSSION

Figures 2 show the TEM planar view of the Hf-silicate films (a) without nitrogen, (b) with a nitrogen atomic concentration [N] of 5 at.%, and (c) 30 at.% after the 1000 °C annealing. The relative concentration of Hf to Hf+Si (Hf/Hf+Si) was about 25% for all samples. Micro-

FIG. 3: In-plane XRD profile of the Hf-silicate films after 1000 °C annealing. Hf/Hf+Si was about 25 % and the nitrogen concentration in the films was changed.

crystals formed with a diameter of several nanometers inside the film without nitrogen during the annealing as shown in Fig. 2(a). The diameter was decreased with the nitrogen incorporation in the 5 at.% film and uniform amorphous film was obtained for the 30 at.% nitrogen concentration. Figure 3 shows the in-plane XRD profile of the Hf-silicate films including those shown in Fig. 2. The diffraction peaks of crystal formed inside the sample without nitrogen corresponded to those of orthorhombic HfO₂. The average diameter D_{hkl} of the HfO₂ crystal inside the surface plane was calculated by Scherrer's equation,

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where λ , β , and θ are the wavelength of the X-rays, the full width at half maximum of the (211) peak, and the diffraction angle of the peak, namely 15.2 °, respectively. The average diameter turned out to be about 3.5 nm from this calculation, which was consistent with the TEM results in Fig. 2(a). The orthorhombic HfO₂ peaks were still observed for the sample with [N] of 5 at.%, however, it diminished for samples with [N] more than 16 at.%. Figure 4 shows the XPS O1S spectra for the samples with Hf/Hf+Si of 25 % and [N] of 30 at.% before and after the 1000 °C RTA. It reveals that the main chemical bond component in the film is Hf-O-Si (Silicate bonds). The fact that the XPS profile after 1000 °C N₂ annealing is almost identical to that of sample before the annealing indicates that the chemical bond structure was not changed during the annealing with the presence of nitrogen inside the film. On the other hand, when nitrogen was intentionally replaced by oxygen by the 1000 °C O₂ annealing, which is not used in ULSI process, the Hf-O-Si peak diminished and Hf-O-Hf and Si-O-Si increase their intensi-

FIG. 4: XPS spectra for the samples with Hf/Hf+Si of 25 % and [N] of 30 at.% before and after the 1000 °C RTA.

ties. This result indicates that phase separation occurred in the sample, which is consistent with the nonuniformity observed in the film without nitrogen after annealing in Fig. 2(a).

As a whole, these three analyses revealed that Hf-silicate experiences the phase separation and micro-crystallization of orthorhombic HfO₂ during high temperature annealing, while nitrogen incorporation of about 30 at.% could completely suppress this phenomenon. We believe that nitrogen retards the diffusion of constituent atoms (Si, Hf or both) inside the film. The fact that the diameter of HfO₂ crystals dramatically diminished with the density of crystals unchanged (about $7 \times 10^{12} \text{ cm}^{-2}$) as in Fig. 2(b) ([N]: 5 at.%) indicates the suppression of crystal growth as the result of the slow diffusion.

As the next step, it is necessary to elucidate the influence of the structural change and that of nitrogen incorporation on the electrical properties of the silicate. MOS capacitors with the silicate as the insulator have been fabricated for that purpose. Figure 5 shows the film dielectric constant ϵ_r as a function of Hf/Hf+Si for samples with and without nitrogen incorporation. The dielectric constant ϵ_r generally increases with the increase in Hf/Hf+Si as previously mentioned in the literature [5], however, it degraded for samples without nitrogen through 1000 °C annealing. It has been reported that this decrease can be explained by the modeling of the segregation of orthorhombic HfO₂ (ϵ_r : 20) in the matrix (ϵ_r : changes according to the remaining Hf content) and may increase the propagation delay time of CMOS circuits formed with such a gate dielectric [6]. This figure also shows that nitrogen is very effective in maintaining its high ϵ_r value, due to the preservation of silicate bonds through the annealing as shown in Fig. 4. Note that the ϵ_r value of the

FIG. 5: Film dielectric constant as a function of Hf/Hf+Si for samples with and without nitrogen incorporation. [N] is 25 at.%.

as-deposited sample with [N] of about 25 at.% is larger than that of the sample without nitrogen. This suggests that nitrogen itself can enhance the ϵ_r of the film.

As for the thermal stability of the gate dielectrics, impurity penetration such as that of Boron from the gate electrode through the thin films during high temperature annealing is another issue [7]. Figure 6 shows the Boron profile after 1000 °C annealing for 30 s in the p⁺-poly Silicon/Hf-silicate/Si-substrate system. Hf/Hf+Si was about 30 % and the thickness of the film including the interfacial layer was about 3nm for all three samples. SIMS measurement proceeded from the backside, namely from the Si substrate, in order to extract accurate profiles, avoiding the knock-on effect by the primary ions. The fact that Boron concentration [B] is very high at the interface between the *poly*-Si gate electrode and the Hf-silicate indicates that the high temperature annealing is long enough for the Boron diffusion inside the electrode. However, Boron severely penetrated into the substrate for the film without nitrogen, which is problematic in terms of transistor threshold voltage shift as well as short-channel effect enhancement. This figure also shows that an increase in [N] can successfully suppress the phenomenon and [B] at the interface between the substrate and the dielectric film could be reduced down to about $2 \times 10^{17} \text{ cm}^{-3}$, which could be acceptable in future ULSI devices.

IV. CONCLUSION

Characterization (XPS, TEM, and XRD) of the Hf-silicate gate dielectrics especially in terms of their structural transformation during high temperature annealing have revealed that Hf-silicate shows the phase separation

FIG. 6: Boron profile after 1000 °C annealing for 30 s in the p^+ -poly Silicon/Hf-silicate/Si-substrate system. Hf/Hf+Si was about 30 % and the thickness of the film including the interfacial layer was about 3 nm.

and micro-crystallization of orthorhombic HfO_2 during the subsequent LSI high temperature processes. Related electrical measurement suggested that this phenomenon leads to a decrease in the dielectric constant of the material. Boron diffusion through the dielectric evaluated with the backside SIMS of the p^+ -poly-Si/Hf-silicate/Si-substrate system indicated that Hf-silicate is not a good diffusion barrier for Boron. It was also revealed that such thermal stability problems for Hf-silicates can be solved with nitrogen incorporation in the film. These physical analyses are quite effective in shedding light on nanoscale structural changes inside high- k films and their surrounding system, and they are indispensable in the development

of high- k materials for ultra-high speed CMOS devices.

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