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Characterization of Hafnium Diffusion into Thermally-Grown SiO_2 on Si(100)

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1. Introduction

The continuous scaling of CMOS devices to the sub-100nm technologies will force the implementation of a higher dielectric constant (high-k) gate dielectric to achieve a required capacitive coupling between the gate and Si(100) below some limit on the gate leakage. Transition metal or rate earth oxides and their silicates and aluminates have been extensively studied so far as high-k candidates to replace conventional SiO_2 or Si oxynitride-based gate dielectrics[1]. With practical requirements for the gate dielectric application such as the thermal stability and interfacial properties, Hf(or Zr)-silicates are attracting much attention as the most promising alternatives [2, 3] although their dielectric constant are at most three times larger than that of SiO_2. The technological importance of such silicates has been demonstrated from enhanced dielectric constants with incorporation of a few at.% Hf (or Zr) into the SiO_2 network and consequently reduced tunneling currents. The relationship between dielectric constants in SiO_2-rich Hf(or Zr)-silicates and local bonding arrangements, especially the coordination of Hf (or Zr) atoms in the network, has been discussed [4]. We previously studied the Zr incorporation into SiO_2 from Zr-rich oxide by thermal annealing and reported the chemical bonding features of diffused Zr atoms into SiO_2 and diffusion constant of Zr into SiO_2 [5] for an insight on thermal stability against phase separation.

In this work, we have extended our research to the Hf diffusion into ultrathin SiO_2 on Si(100) from Hf-rich oxides and studied the electronic structure of Hf-incorporated SiO_2 from the depth analysis using x-ray photoelectron spectroscopy. The influence of the Hf incorporation on the gap states has also been examined by total photoelectron yield measurements.

2. Experimental

A ~3.4nm-thick SiO_2 layer was grown on wet-chemically cleaned Si(100) at 1000°C in 2% O_2 diluted with N_2. Amorphous HfO_x (x~1.4) films with a thickness of ~1.0nm were formed on SiO_2/Si(100) so-prepared by thermal evaporation in ambient O_2 at ~$1x10^{-3}$Pa. Subsequently, thermal annealing in dry N_2 was performed in the temperature range from 750 to 1000°C. For the removal of the top HfO_x and the thinning of the underlying SiO_2 layer after the annealing, a wet-chemical etching using a 0.1%HF solution was carried out repeatedly. The etch rate of HfO_x was as high as ~0.03nm/s, which is faster than that of SiO_2 by a factor of 6. Very uniform oxide thinning was confirmed by AFM measurements before and after the HF-etching steps.

3. Results and Discussion

From the changes in Hf4f, Si2p and O1s spectra with progressive HF-dipping time, we judged the beginning the thinning of the underlining silicon oxide layer. For the sample annealed at 750°C for 60min (Fig. 1), HF-dipping for 20s causes significant decreases in the Hf4f signal intensity and O1s signals attributable to Hf-O bonds, but in contrast quite a little reduction in the Si2p and O1s signals from Si-O bonds is only observable. In the case of HF-dipping for 120s, the reductions in the Si2p and O1s signals from Si-O bonding units becomes appreciable, indicating that the underline SiO_2 etching proceeds successively after the removal of top HfO_x layer. The Si2p signals reduced in the lower binding energy side of Si^{4+} originating from pure SiO_2 network are attributed to Si-O-Hf bonding units formed at HfO_x/SiO_2 interface in consideration of the effect of 2nd nearest-neighbors on the chemical shift. Note that almost no spectral change in Hf4f signals is observed with further progressive oxide thinning, taking into account the fact that Si^{4+} signals are shifted gradually toward the lower binding energy side due to the reduced charge-up effect (Fig. 2). The result indicates the incorporation of Hf^{4+} into SiO_2 network. For the sample annealed at 1000°C for 20min shown in Fig. 2, Hf4f signals is hardly detected by HF-dipping for 60min, which corresponds to 1.2nm in the remaining SiO_2 thickness. As shown in Fig. 3, by fitting a complementary error function, which shows the constant-surface-concentration diffusion, to the measured Zr depth profiles for the samples annealed below 750 °C, the diffusion constant of Hf was crudely estimated to be

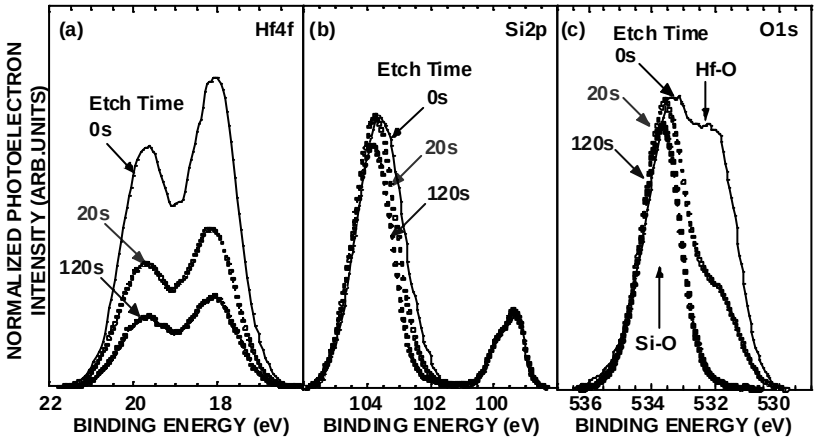

Fig. 1 Hf4f (a), Si2p (b) and O1s (c) spectra taken at each step of oxide thinning in a 0.1%HF solution for the sample annealed at 750°C for 60min. The photoelectron take-off angle was 15°. The biding energy was calibrated by the Si2p peak at 99.3eV from the Si (100) substrate and the photoelectron intensity was normalized by the peak intensity of Si2p signals from the Si(100) substrate

~$1.5x10^{-19}$cm^2/s at 750°C. On the other hand, for the cases annealed at 900 and 1000°C, the measured Hf depth profiles seem to be reproduced well by usage of Gaussian function for a constant-total-dopant diffusion and the Hf diffusion constants at 900 and 1000°C are obtained to be $1.5x10^{-18}$ and $3.5x10^{-18}$cm^2/s, respectively. The obtained values are almost equal to the values previously reported for the Zr diffusion case (Fig. 4). Filled defect states distributed in the energy region corresponding to the Si bandgap were evaluated by measuring total photoelectron yield from the annealed samples (Fig. 5). No significant difference in the yield spectra from the spectrum for thermally-grown SiO_2/Si(100) is observed irrespective of annealing temperature. The result indicates that no filled states in SiO_2 in the energy region corresponding to the Si bandgap are generated by the Hf incorporation.

4. Conclusion

The Hf diffusion constant in thermally-grown (1000°C) SiO_2 is increased with an activation energy of ~1.5eV from $1.5x10^{-19}$ to $3.5x10^{-18}$cm^2/s in the temperature region of 750-1000°C and no increase in the gap states with Hf incorporation into SiO_2 is confirmed by total photoemission yield measurements.

Acknowledgements

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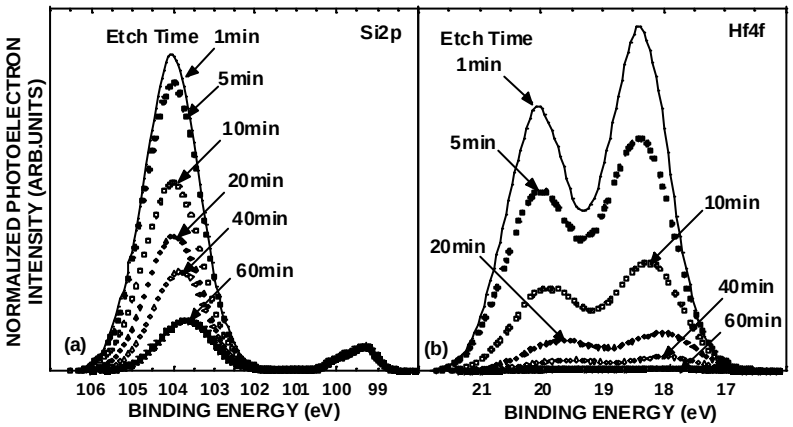

Fig. 2 Si2p (a) and Hf4f (b) spectra measured at each SiO_2-thinning step for the samples annealed at 1000°C for 20min. The photoelectron take-off angle was 15°.

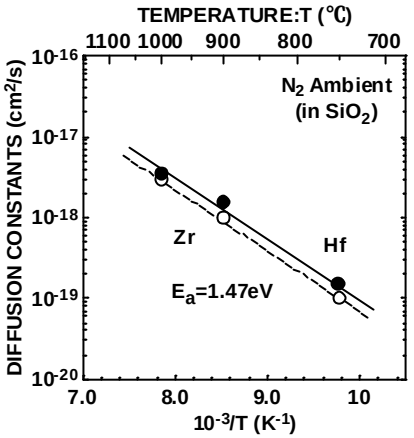

Fig. 4 Hf diffusion constants (solid circles) thermally-grown (1000°C) SiO_2 derived from the curve fitting shown in Fig. 3. Zr diffusion constants (open circles) reported in Ref.5 are also shown.

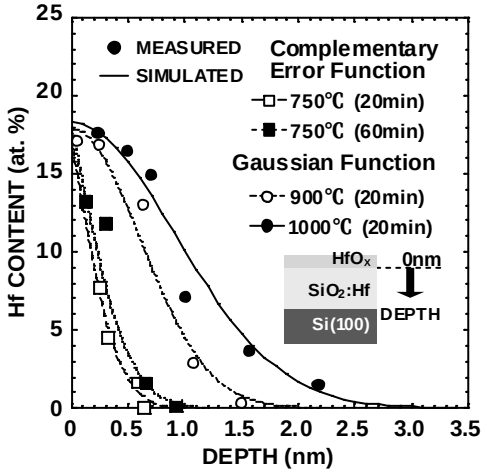

Fig. 3 Hf depth profiles in the SiO_2 films for different annealing conditions, which was obtained the XPS analysis at each SiO_2-thinning step. The curves fitted with experimental data are simulated results using complementary error functions for the 750°C annealing cases and Gaussian functions for 900 and 1000°C annealing cases. The diffusion constants used here are summarized

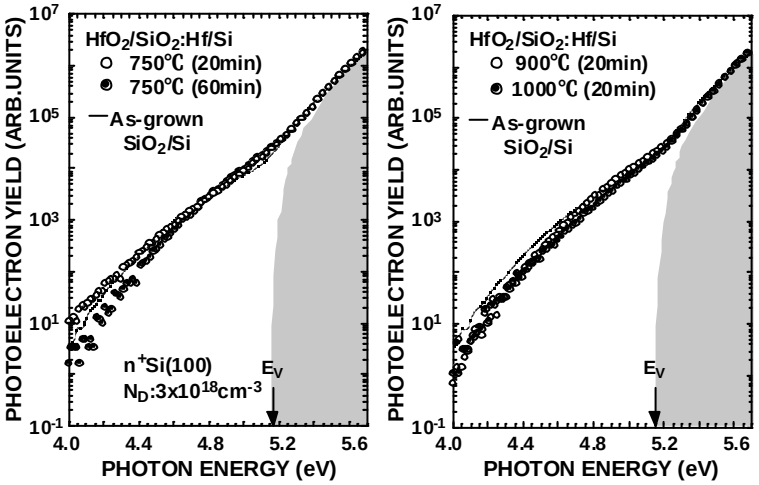

Fig. 5 Total photoelectron yield spectra for as-prepared 1.0nm-thick HfO_x/3.4nm-thick SiO_2/n^+Si(100) and after annealed at 750 – 1000°C. The PYS spectrum for as-grown 3.4nm-thick SiO_2 at 1000°C is also shown as a reference. A gray region denotes the contribution of Si valence electrons to the photoelectron yield and the spectra were normalized by the yield in the photon energy region of 5.7-6.0eV.