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Characterization of hafnium and zirconium silicate films fabricated by plasma-enhanced chemical vapor deposition

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INTRODUCTION

In the near future, silicon dioxide would not maintain the insulating property, since direct tunneling dominates the leakage current[1]. In order to overcome this difficulty, several attempts to increase the physical thickness, while keeping the equivalent silicon dioxide thickness, have been carried out using materials with a higher permittivity[2]. Hafnium and zirconium silicates are considered to be attractive for a new material with a higher permittivity[3]. We have tried to deposit hafnium and zirconium silicate films by plasma-enhanced chemical vapor deposition (PECVD), and have successfully obtained good films. In this report, we briefly describe the developed deposition method and discuss electrical properties and chemical structure of the deposited films.

DEPOSITION METHOD

The hafnium or zirconium silicate films were deposited by PECVD using tetraethoxysilane (TEOS: $Si(OC_2H_5)_4$) and hafnium alkoxide or zirconium alkoxide, respectively. Oxygen, used as a carrier and oxidation gas, was excited with a RF power of 13.56 MHz through capacitive coupling. The TEOS was vaporized and transported at 70 °C into the "tail flame" of the oxygen plasma. The TEOS flow rate was controlled with a mass-flow controller (Hitachi Metal, SFC-670). The hafnium and zirconium alkoxides were vaporized and transported at 220 and 200 °C into the oxygen plasma, respectively. Argon gas was used as a carrier and diluent gas for each alkoxide vapor and its flow rate was controlled with a mass-flow controller (Brooks: 5850TR). The films were deposited onto a p-type silicon monocrystal wafer set on a stage whose temperature was kept at 400 °C.

CHARACTERIZATION OF DEPOSITED FILMS

The x-ray photoelectron spectroscopy (XPS) was obtained by a JEOL JPS-90MX spectrometer. Figures 1 (a) and (b) show the Hf_{4f} photoelectron spectra obtained for samples B, C, and D and the Zr_{3d} photoelectron spectra for samples F, G, and H, respectively. Clear peaks are seen around 17.0 eV and 18.5 eV due to Hf-O bonds[4] and around 182.5 eV and 185.0 eV due to Zr-O bonds[4], while there are no peaks due to silicide (Si-Hf and Si-Zr) bonds. The O_{1s} photoelectron spectra exhibit that samples A to E have Hf-O and Si-O bonds and samples F to I have Zr-O and Si-O bonds. Therefore, the samples were confirmed to be silicates without any silicide bonds. The threshold energy of the energy loss spectrum of O_{1s} photoelectrons was assumed to be the energy gap[5]. As shown in Fig.2, the energy gap decreases from 8.2 to 5.7 eV as the hafnium content increases from 0 to 21 atomic %. Similarly, it decreases from 8.2 to 5.3 eV as the zirconium content increases from 0 to 21 atomic %. Electrical properties were examined by measuring capacitance-voltage characteristics at 1 MHz for the samples having evaporated gold electrodes with an effective area of 7.9×10^{-3} cm^2. The relative permittivity was calculated from the capacitance of the accumulation layer. As shown in Fig. 3, the relative permittivity increases from 3 to 15 with an increase in the hafnium content, whereas it increases from 3 to 8 with an increase in the zirconium content. These results indicate that the hafnium silicate has a larger energy gap and a higher permittivity than the zirconium silicate, if we compare the films with the same hafnium or zirconium content. Since this is important for a future gate dielectric material, it is considered that hafnium silicate is more applicable than zirconium silicate.

CONCLUSION

We have succeeded in the deposition of hafnium and zirconium silicate films by PECVD. The deposited films were confirmed to be silicates with Si-O and Hf-O or Zr-O bonds. The deposited hafnium silicates have a larger energy gap and a higher permittivity than the zirconium silicates.

REFERENCES

(1) D. A. Muller et al., Nature, Vol. **399**, pp. 758-761, 1999.
(2) W. J. Qi et al., IEDM Tech. Dig., pp. 145-148, 1 999.
(3) G. D. Wilk et al., J. Appl. Phys., Vol. **87**, pp. 484-492, 2000.
(4) S. Miyazaki et al., Appl. Surf. Sci., **113/114**, pp. 585-589, 1997.

Table I. Elementary compositions of the deposited

sample	elementary composition (atomic %)		
	Hf	Si	O
A	5.3	26	69
B	7.6	23	70
C	16	16	68
D	18	11	71
E	21	9.1	70
	Zr	Si	O
F	5.1	29	66
G	12	21	67
H	19	14	67
I	21	12	67

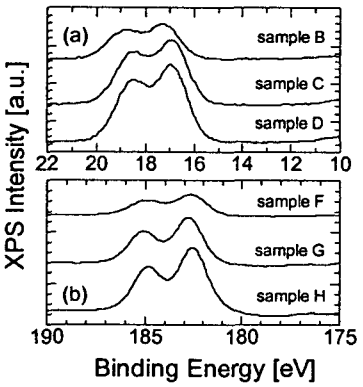

Figure 1. Hf_{4f} (a) and Zr_{3d} (b) photoelectron spectra.

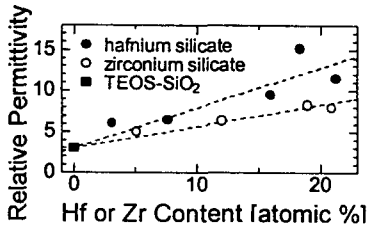

Figure 2. Energy gap as a function of the hafnium or zirconium content.

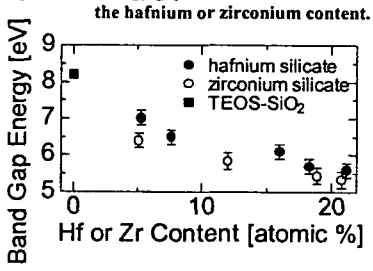

Figure 3. Relative permittivity as a function of the hafnium or zirconium content.