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Permittivity Enhancement of $Hf_{(1-x)}Si_xO_2$ Film with High Temperature Annealing

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1. Introduction

$Hf_{(1-x)}Si_xO_2$ film is one of the most attractive materials for CMOS gate dielectrics. However, it is widely believed that $Hf_{(1-x)}Si_xO_2$ film has a lower permittivity (κ) than the pure HfO_2 because SiO_2 has a low permittivity ($\kappa \sim 3.9$). On the other hand, it has been found that a slight amount of yttrium (Y) doping into HfO_2 enhances the film permittivity, which is associated with the structural phase transformation from the monoclinic phase to the cubic one [1]. Furthermore, it has been reported that silicon (Si) doping changes the HfO_2 crystal structure [2]. From those results, it is possible that $Hf_{(1-x)}Si_xO_2$ film has a higher permittivity. In this work, we investigated the permittivity change of $Hf_{(1-x)}Si_xO_2$ films as functions of Si concentration and annealing temperature.

2. Experimental

$Hf_{(1-x)}Si_xO_2$ films were deposited on two kinds of wafers. One is a floating-zone Si wafer for the transmission IR absorption and XRD measurements, and the other is a 100 nm Pt film on SiO_2/Si wafer for the permittivity measurement. All the films were deposited by co-sputtering method with HfO_2 and SiO_2 targets in Ar plasma. The samples were annealed at 400 - 800 ºC in N_2 + 0.1 % O_2 ambient for 30 seconds at the atmospheric pressure. For structural analysis, we used the transmission FTIR and XRD measurements. To determine the film permittivity, we measured the capacitance of Au/$Hf_{(1-x)}Si_xO_2$/Pt MIM structure. The film thickness was determined with glazing incidence X-ray reflectmetry.

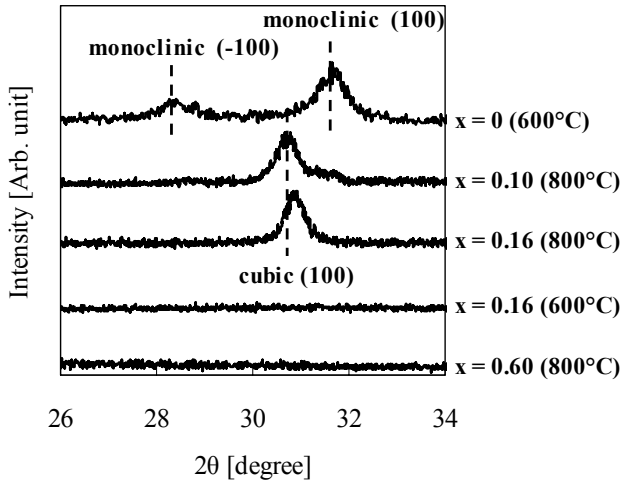

Fig. 1 XRD results of $Hf_{(1-x)}Si_xO_2$ (x = 0, 0.10, 0.16 and 0.60) film. Samples were annealed at 600 °C and 800 °C.

3. Results

Fig. 1 shows the results of XRD measurement for $Hf_{(1-x)}Si_xO_2$ films. Here, we can observe two important effects with Si doping into HfO_2. One is a suppression of the crystallization. The pure HfO_2 crystallizes at least over 600 °C, while $Hf_{(1-x)}Si_xO_2$ (x = 0.16 and 0.60) dose not crystallize at 600 °C and 800 °C, respectively. The other is the phase transformation. By 800 °C annealing, $Hf_{(1-x)}Si_xO_2$ (x = 0.10 and 0.16) crystallizes into the cubic phase, while the pure HfO_2 (x = 0) crystallizes into the monoclinic one. The trend of this phase transformation is similar to the case of Y doped HfO_2 [1].

The permittivity change of $Hf_{(1-x)}Si_xO_2$ films depending on Si concentration and annealing temperature is shown in **Fig. 2**. Characters a, m and c denote amorphous, monoclinic and cubic, respectively. Si concentration was determined by the HfO_2 and SiO_2 deposition rate. By 800 ºC annealing, the permittivity of pure HfO_2 (x = 0) decreases with the crystallization into the monoclinic phase. Then, it means that the monoclinic HfO_2 has a lower permittivity than the amorphous HfO_2. On the other hand, the permittivity of $Hf_{(1-x)}Si_xO_2$ (x = 0.10 and 0.16) increases. Furthermore, those values exhibit much higher permittivity than the pure HfO_2. To our knowledge, this is the first observation of κ increase in $Hf_{(1-x)}Si_xO_2$ film. By 400 ºC annealing, the permittivity of each film decreases with x. However, the permittivity of $Hf_{(1-x)}Si_xO_2$ is higher than the linear extrapolation line between that of the amorphous HfO_2 and SiO_2. This fact means that the permittivity change of $Hf_{(1-x)}Si_xO_2$ cannot be explained with the simple effective media model.

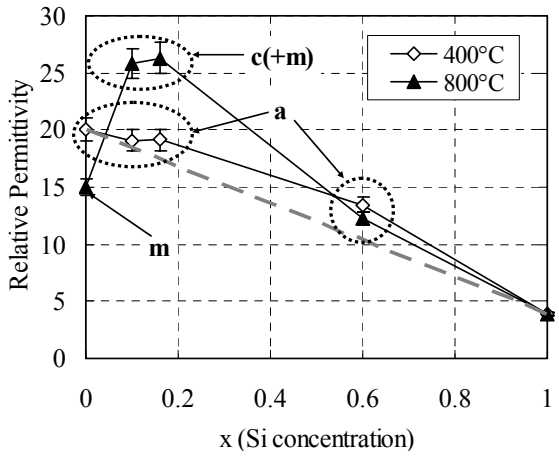

Fig. 2 Permittivity values of $Hf_{(1-x)}Si_xO_2$ films, which were extracted from MIM capacitance. Characters a, m, and c denote amorphous, monoclinic, cubic, respectively.

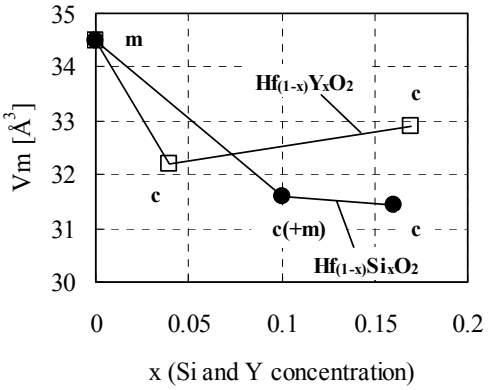

Fig. 3 Molar volume change of $Hf_{(1-x)}Si_xO_2$ annealed at 800 °C. Molar polarizability α_m is extracted from cubic HfO_2 V_m and κ. $Hf_{(1-x)}Y_xO_2$ results are from ref. 1.

3. Discussion

1) permittivity enhancement with structural phase transformation

The κ value is generally expressed in the Clausius – Mosotti equation as follows.

$$\kappa = (1 + 8\pi\alpha_m / 3V_m) / (1 - 4\pi\alpha_m / 3V_m) \qquad (1)$$

Here, α_m and V_m is the molar polarizability and molar volum, respectively. We cannot determine the accurate α_m value experimentally, but can evaluate the V_m value from the lattice parameters determined by XRD in Fig. 1. **Fig. 3** shows the V_m values of $Hf_{(1-x)}Si_xO_2$ film annealed at 800 °C, where the V_m values of Y doped HfO_2 in Ref. 1 are also shown. The V_m values of $Hf_{(1-x)}Si_xO_2$ decrease with x, while those of Y doped HfO_2 has a minimum at x = 0.04. It is suggested that this difference comes from the ionic radius discrepancy among Si (~0.26Å), Hf (~0.97Å) and Y (~1.04Å) atom.

Fig. 4 shows the κ values calculated from V_m in Fig. 3. Here, two cases are considered. One is the case of a constant α_m, and the other is the case the α_m is proportional to x (the additivity rule conventionally used[3]). In Fig. 4, κ values determined experimentally are also shown. There is a good agreement between calculated κ values with a constant α_m and experimental ones. This fact indicates that the permittivity enhancement of $Hf_{(1-x)}Si_xO_2$ film (x < 0.16) mainly results not from the polarizability change, but from its molar volume shrinkage.

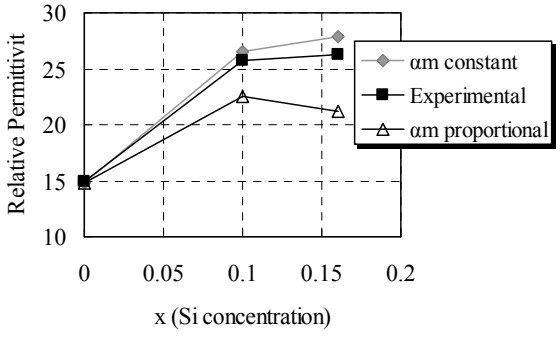

Fig. 4 permittivity of $Hf_{(1-x)}Si_xO_2$ annealed at 800 °C. Black squares denote experimental results and the others denote calculated ones.

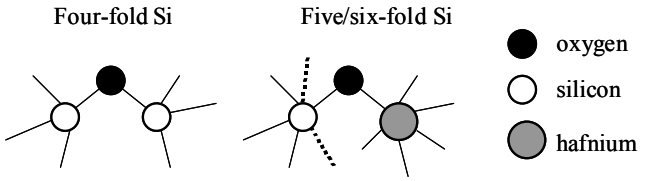

Fig. 5 A schematic description for the increase of Si coordination number with Hf doping.

2) non-linear decrease of permittivity in amorphous film

The permittivity of $Hf_{(1-x)}Si_xO_2$ films (400 ºC annealed) is also higher than that of the linear extrapolation between HfO_2 and SiO_2, while the film structure keeps amorphous in all x region. This behavior can be also explained with the change of V_m. Assuming the conventional additivity rule, the V_m value, especially x = 0.60, is slightly smaller than the values evaluated with the effective media model.

This V_m shrinkage is similar to the reported case in ZrO_2/SiO_2 system, where it is suggested that the increase of coordination number of Si with Hf atom mixing rapidly reduces the V_m values [4].

The molar volume of SiO_2 decreases with its coordination number and structural change from ~37.75Å^3 (four-fold/α quartz) to ~23.32Å^3 (six-fold/Stishovite). It is suggested that the mixture of SiO_2 with HfO_2 increases both Si ionicity and its coordination number (**Fig. 5**). This bond connectivity increase would reduce the V_m value of $Hf_{(1-x)}Si_xO_2$. Further experimental confirmation of the V_m change should be required.

4. Conclusion

We investigated the permittivity change of $Hf_{(1-x)}Si_xO_2$ film. As a result, by 800 °C annealing, it was found that $Hf_{(1-x)}Si_xO_2$ permittivity increases by a small amount of Si doping. This is the first observation of the permittivity enhancement in the $Hf_{(1-x)}Si_xO_2$ system We also investigated the structural change with Si doping, and revealed that the permittivity enhancement of $Hf_{(1-x)}Si_xO_2$ film comes from the structural phase transformation from the monoclinic HfO_2 to the cubic one, and its molar volume shrinkage. The permittivity of amorphous $Hf_{(1-x)}Si_xO_2$ films is also higher than the values expected by the effective media model. It is suggested that the increase of coordination number should reduce the V_m values and increase the κ value.

Those results mean that we can control the film permittivity and its crystallinity by adjusting Si concentration and thermal treatment condition.

Acknowledgements

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References

[1] K. Kita, *et. al.*, Appl. Phys. Lett. **86**, 102906 (2005).
[2] K. Tomida, *et. al.*, Ext. Abst. of SSDM, pp. 790 (2004).
[3] R. D. Shannon, J. Appl. Phys. **73**, 348 (1993).
[4] R. A. B. Devine and A. G. Revesz, J. Appl. Phys. **90**, 389 (2001).