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Dielectric Constant Increase of Yttrium-Doped HfO_2 by Structural Phase Modification

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1. Introduction

Hafnium oxide (HfO_2) and Hf-based oxides are promising candidates for the high-κ gate dielectrics. However, further EOT scaling requires the dielectrics with higher dielectric constant (κ). It is theoretically predicted that HfO_2 will have a higher κ in cubic phase (κ ~ 29) or tetragonal phase (κ ~ 70) than that in monoclinic phase (κ ~ 16-18)[1]. Under atmospheric pressure, cubic and tetragonal phases appear only at high temperature, however, it is reported that those phases can be stabilized even at lower temperature by addition of yttrium (Y) [2,3] or iron [4]. In this study, we fabricate Y-doped HfO_2 (YDH) films and systematically investigate the effect of Y incorporation on the dielectric properties of HfO_2 films.

2. Experimental

Yttrium-doped HfO_2 (YDH) films were deposited on HF-last n-Si (100) substrates by RF sputtering of HfO_2 and Y_2O_3 target in argon ambient. The atomic ratio of Y/(Hf+Y) was set to (I) 4% and (II) 17%. The undoped HfO_2 films were also deposited as the references. The post-deposition annealing in 0.1%-O_2+N_2 mixture ambient was performed at 400ºC, 600ºC, 800ºC, and 1000ºC. The composition and thickness of the films were determined by x-ray photoelectron spectroscopy (XPS) and grazing incident x-ray reflectivity (GIXR) measurements, respectively. The physical characteristics of the films were evaluated by x-ray diffraction (XRD) and Fourier transform infrared absorption spectroscopy (FT-IR) measurements. Finally, Au was evaporated to form MIS capacitors.

3. Results and Discussion

Both (I) and (II) YDH films are crystallized by the annealing at 600ºC, as shown in **Fig.1 (a)**. The undoped film crystallized in monoclinic phase, however, both (I) and (II) films show another crystal phase. The observed sharp peak around 30º is attributable to three kinds of phases, cubic, tetragonal, or orthorhombic phase. Since the diffraction patterns for these crystal phases are quite similar, it is difficult to determine the observed crystal phase at the present stage. As shown in **Fig.1 (b)**, the monoclinic phase appears in (I) 4 at.% YDH film due to the phase separation by 1000ºC annealing, whereas 17 at.% Y doping seems to be enough to stabilize the "Y-doped phase" against the phase separation at 1000ºC.

From the FT-IR measurement in the far infrared region, the effect of Y-doping is more pronounced. **Fig.2 (a)** and **(b)** show the IR absorption spectra of the films after 600ºC and 1000ºC annealing, respectively. The undoped HfO_2 films show several peaks corresponding to the monoclinic HfO_2 phonon modes [5]. On the other hand, the YDH films show a broad peak without any characteristic vibration modes. Only the exception is the 4 at.% YDH film annealed at 1000ºC, where the peaks corresponding to the monoclinic phase appear due to the phase separation.

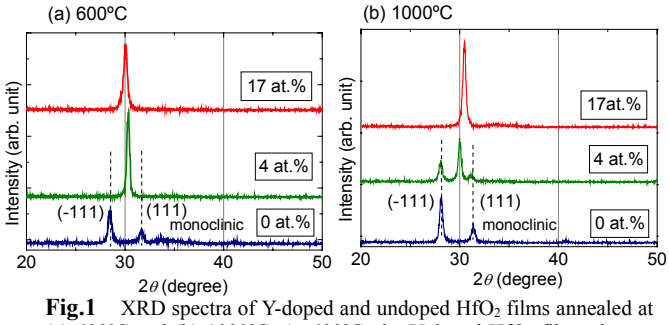

Fig.1 XRD spectra of Y-doped and undoped HfO_2 films annealed at (a) 600ºC and (b) 1000ºC. At 600ºC, the Y-doped HfO_2 films show a sharp peak around 30º whereas the undoped HfO_2 film shows the peaks corresponding to monoclinic phase structure. The peak around 30º can be assigned to the diffraction from cubic (111), tetragonal (111), or orthorhombic (211). In the case of 4at.% doped film, the monoclinic phase appears at 1000ºC by a phase separation.

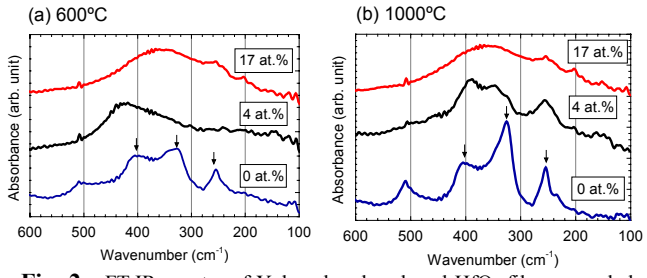

Fig. 2 FT-IR spectra of Y-doped and undoped HfO_2 films annealed at (a) 600ºC and (b) 1000ºC. The undoped HfO_2 films show the peaks at around 400cm^{-1}, 325cm^{-1}, and 260cm^{-1}, which correspond to the monoclinic phase structure [5]. At 600ºC, both Y-doped films show a broad peak without characteristic vibration modes. The spectra for the 4at.% doped film annealed at 1000ºC suggest that the monoclinic phase appeared by a phase separation, although no difference was observed between the 17at.% doped films annealed at 600ºC and 1000ºC.

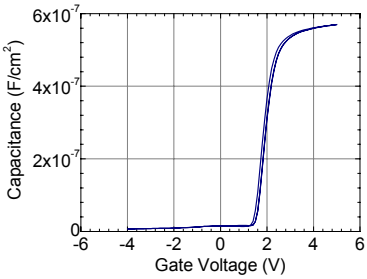

Fig. 3 C-V characteristics of Au/14at.%-YDH/n-Si MIS capacitor. The film was 18.2 nm-thick and annealed at 1000ºC. It shows < 50mV hysteresis and a relatively large positive flatband voltage shift. The CET value is determined from the capacitance at Vg= -5V.

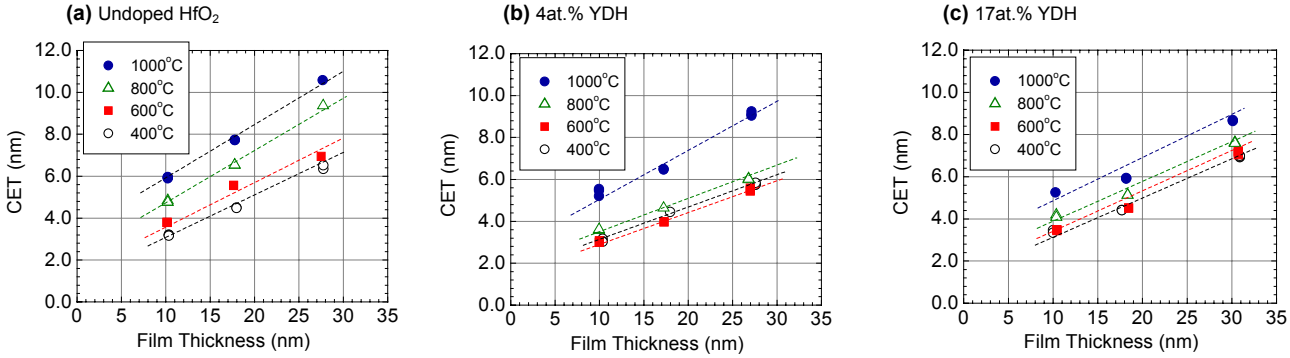

Fig.4 The relationship between CET and film thickness (determined by GIXR) for (a) undoped film, (b) 4at.% Y-doped film, and (c) 17at.% Y-doped film, annealed at 400ºC, 600ºC, 800ºC, and 1000ºC. The dielectric constant (κ) for each film was estimated from the slope.

Figure 3 shows typical C-V characteristics (1MHz) of Au/YDH/n-Si MIS capacitors. The CET value was determined from the accumulation capacitance at V_g = -5V and is plotted as a function of the YDH film thickness in **Fig.4**. The linear relationship between the CET and the film thickness assures the validity of the estimation of κ from the slope. The estimated κ values are plotted in **Fig. 5**. The YDH films show higher κ (27 for the film (I)) than the undoped HfO_2, in spite of the fact that Y_2O_3 (12-15) has a lower κ than HfO_2. It cannot be reconciled with a macroscopic dielectric theory for the mixed materials [6] which assumes that the chemical bonding of constituents does not change with the mixing. So, the structural modification of HfO_2 by incorporation of Y, indicated by XRD (**Fig.1**) and FT-IR measurements (**Fig.2**), must be a key for the anomalous increase of κ in the YDH films.

Another important trend in **Fig.5** is the significant decrease of κ with the high temperature annealing. It is considered to be correlated with the Si uptake from the substrate. Note that such trend seems to be suppressed by the addition of Y. **Fig.6** shows the amount of Si detected by XPS measurement at the film surface. The role of Y should not be the suppression of the Si diffusion, since almost the same amount of Si was detected irrespective of Y content. Then, it is understandable by assuming that κ of the monoclinic HfO_2 is severely decreased by the Si incorporation, but that of "Y-doped phase" HfO_2 is not affected significantly. Finally, it will be worthy of mentioning that this structural modification could improve the mobility as well thanks to the possible disappearance of low energy phonons.

4. Conclusions

We found that Y-doped HfO_2 (YDH) films show higher dielectric constant (κ ~27) than the undoped HfO_2 films, probably due to structural modification of the HfO_2 films by addition of Y. In addition, the decreasing trend of κ with the high temperature annealing is effectively suppressed in YDH films. These results strongly indicate that the structural modification by addition of minor constituents is an effective way to improve the dielectric properties of metal oxides.

Acknowledgements

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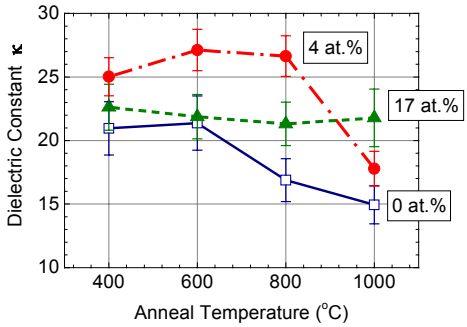

Fig.5 The relative dielectric constant κ of the Y-doped and undoped HfO_2 films annealed at 400ºC, 600ºC, 800ºC, and 1000ºC. The 4at.% doped films show κ ~ 27. The estimated κ decreases severely by the higher temperature annealing in the cases of the undoped and the 4at.% doped film, however, it does not show significant change in the case of 17at.% doped films.

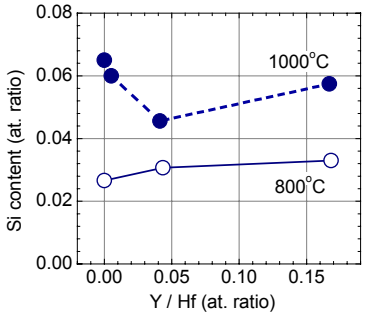

Fig.6 The amount of Si detected by XPS measured at the film surface. Both the Y-doped and undoped films contain certain amount of Si, although the Y-doped films might slightly restrain the Si diffusion at 1000ºC. It suggests that the κ variation with the Y addition (Fig.5) is not caused by the Si content difference.