Ferroelectric Properties of Hafnium-Zirconium-Dioxide Prepared by Chemical Solution Process for MFM and MFS Structures

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【Introduction】

Ferroelectric hafnium zirconium dioxide (HZO) thin films have attracted much attention since they were first reported by Muller et.al. [1]. The most widely used fabrication method for HZO thin films is atomic layer deposition (ALD). On the other hand, chemical solution process (CSD) is one of the promising techniques due to low cost and simple equipment. In this work, yttrium doped HZO (Y-HZO) films were fabricated by CSD and electrical properties of metal-ferroelectric-metal (MFM) and metal-ferroelectric-semiconductor (MFS) structures were characterized.

【Experiments】

Y-HZO (Y:5%) films were fabricated on Pt/Ti/SiO_2/Si substrate (platinized silicon substrate) by the procedure as we reported previously [2]. The solution of Y-HZO was prepared by mixing $Hf(acac)_4$, $Zr(acac)_4$ and $Y(acac)_3$ in propionic acid (PrA) The source solution of ITO was prepared by mixing $In(acac)_3$ and $Sn(acac)_2$ in PrA. The source solution of Y-HZO was spin-coated on the platinized substrate, followed by drying on a hot plate at 225 ^{o}C for 3 min in air. The crystallization of samples was performed by RTA at 800 ^{o}C for 3 min in vacuum, N_2 and O_2 environments. Finally, Pt top electrode with 100 nm thickness and 300 um in diameter was deposited by sputtering to fabricate Pt/Y-HZO/Pt MFM structures. To fabricate MFS structures, source solution of ITO was spin-coated on vacuum annealed Y-HZO, followed by drying on the hot plate in air at 100 ^{o}C for 3 min. Then, the samples were annealed in RTA at 600 ^{o}C for 15 min in O_2 atmosphere. The thickness of ITO was 5.8 nm. Top Pt electrodes are patterned by lift-off process and area of the Pt/ITO/YHZO/Pt MFS structures was 10000 μm^2.

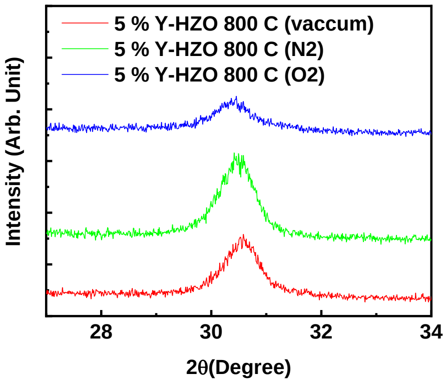

Fig. 1. XRD patterns of Y-HZO films

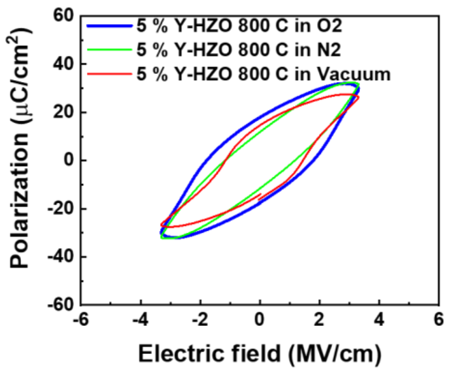

Fig. 2. P-E loops of Pt/Y-HZO/Pt MFM structure

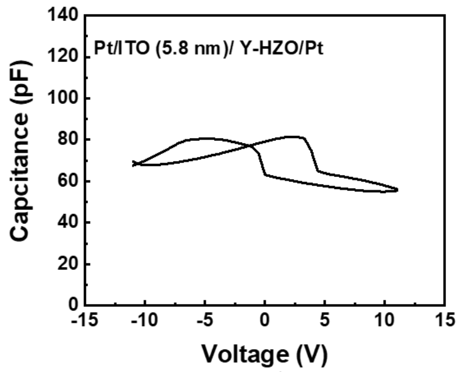

Fig. 3 C-V curve of Pt/ITO/Y-HZO MFS structure

【Results and Discussion】

Figure 1 shows XRD patterns of Y-HZO films annealed at various annealing environments. All samples show a diffraction peak around 30.5° which suggests the formation of o(111)/c(111), where o and c mean orthorhombic and cubic phases. The formation of orthorhombic phase is necessary to obtain ferroelectricity in the films. It is interesting to note that Y-HZO films show negligible diffraction peak from monoclinic-phase (m-phase). Polarization-electric field (P-E) characteristics for MFM structures are shown in Fig. 2. Vacuum annealed (red line) sample shows clear ferroelectric P-E loop as compared to O_2 (blue line) and N_2 (green line) annealed samples. Figure 3 shows capacitance-voltage (C-V) curve for Pt/ITO/Y-HZO MFS structure, where vacuum annealed Y-HZO is used. The C-V curves show clear butterfly shaped loop as observed in ferroelectric materials, with decrease in capacitance on positive voltage side due to depletion of the ITO layer.

【Conclusion】

Y-HZO thin films were fabricated by CSD and electrical properties of MFM and MFS structures were characterized. Vacuum annealed Y-HZO film showed better ferroelectricity than N_2 and O_2 annealed samples. In addition, depletion of the ITO layer was observed in C-V curve of the MFS structure.

【References】

[1] J. Müller et al., Nano Lett.,**12**, 4318 (2012). [2] Mohit et al Jpn. J. Appl. Phys., **59**, SMMB02 (2020).