Fabrication of ferroelectric hafnium-zirconium dioxide thin films by solution process

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【Introduction】

Ferroelectric hafnium zirconium dioxide (HZO) thin films were first reported by Muller et.al. [1] and extensive research has been conducted. HfO_2 based ferroelectric thin films are compatible with silicon CMOS technology and used as a gate insulator in advance Si-MOSFET. The most widely used method for HZO thin film deposition is atomic layer deposition (ALD). On the contrary, the solution process is one of the promising techniques to deposit oxide thin films with low cost and simple equipment. There are only a few reports on HZO films deposited by chemical solution deposition (CSD). In this work, Yttrium doped HZO (Y-HZO) films were fabricated by the solution process on Pt/Ti/SiO_2/Si substrate (platinized silicon substrate) with Pt top electrode.

【Experiments】

Three kinds of samples, HZO films deposited directedly on Pt, and HZO films with ZrO_2 and yttrium stabilized zirconia (YSZ) buffer layers, were fabricated. The ZrO_2 buffer layer (13 nm) and YSZ buffer layer (12 nm) were deposited by CSD and reactive sputtering, respectively. The source solution of Y-HZO was prepared by mixing $Hf(acac)_4$, $Zr(acac)_4$ and $Y(acac)_3$ in propionic acid (PrA) and the source solution of ZrO_2 was prepared by mixing $Zr(acac)_4$ in PrA. YSZ and ZrO_2 buffer layers were annealed by rapid thermal annealing (RTA) with annealing temperatures of 500 and 700 ºC for 15 and 3 min, respectively. The source solution of Y-HZO was spin-coated on three kinds of substrates, followed by drying on a hot plate at 225 ^{o}C for 3 min in air. Then, all samples were annealed using RTA at 600 and 700 ^{o}C for 3 min in an O_2 environment. Finally, Pt top electrode with 100 nm thickness was deposited by sputtering.

【Results and Discussion】

Figure 1 shows XRD patterns of Y-HZO films annealed at different annealing temperature without and with a buffer layer of YSZ or ZrO_2. All samples show diffraction peak around 30.5° which suggests the formation of o(111)/c(111), where o and c mean orthorhombic and cubic phases. To obtain ferroelectricity, the orthorhombic phase formation is necessary. It is interesting to note that Y-HZO films show negligible diffraction peak from monoclinic-phase (m-phase). Hence Y-HZO films fabricated by CSD tends to suppress the formation of m-phase. In order to confirm ferroelectricity, polarization-electric filed (P-E) and capacitance-voltage (C-V) measurements were carried out. Figures 2(a) and 2(b) show P-E loops and C-V curves of Y-HZO films annealed at 700 °C without buffer layer, respectively. C-V curves show clear butterfly shaped loops as observed in ferroelectric materials. Coercive field, E_C, estimated from C-V curves is 1.22 MV/cm, which is similar to the reported values. Electrical properties of Y-HZO films with ZrO_2 and YSZ buffer layers will be discussed in the meeting.

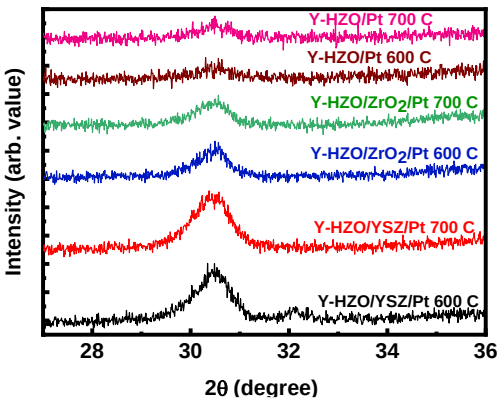

Figure 1. XRD patterns of Y-HZO films

【Conclusion】

Y-HZO thin films were fabricated by CSD with and without ZrO_2 and YSZ buffer layers on platinized silicon substrates. The ferroelectric nature of Y-HZO films fabricated by the CSD method was demonstrated from P-E and C-V measurements.

【Acknowledgement】

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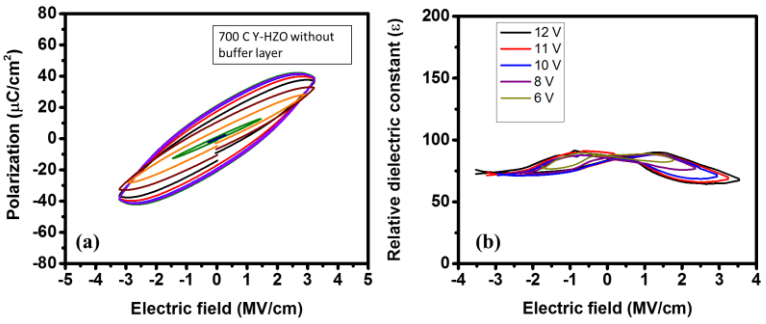

Figure 2. (a) P-E loops and (b) C-V curves of Y-HZO films

【References】

1. J. Müller et al., Nano Lett., vol. 12, no. 8, 2012, pp. 4318–4323.