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Effect of Stress on Ferroelectricity of $(Hf_{0.5}Zr_{0.5})O_2$ Thin Films

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Abstract

Ferroelectricity was investigated for 17 and 55 -nm thick $(Hf_{0.5}Zr_{0.5})O_2$ thin films prepared by Pulsed MOCVD. Ferroelectricity strongly depended on the film thickness and the kinds of substrates. This suggests that the formation and the volume fraction of ferroelectric orthorhombic phase strongly depended on the stress applied to the films from the substrate.

1. Introduction

Ferroelectricity of thin films of HfO_2-based materials have been demonstrated by substituting various ions, such as Si, Y, Al, Zr, Gd, and Sr [1-3]. Most noticeable feature of these films compared to the previous ferroelectric films, such as $Pb(Zr, Ti)O_3$ and $SrBi_2Ta_2O_9$ films, is the appearance of ferroelectricity less than 10 nm in thickness even in polycrystalline film form. This feature is possible to realize not only low voltage operation of capacitor-type ferroelectric memories due to the very thin film thickness, but also ferroelectric transistor-type one due to the good compatibility of HfO_2-based insulators with CMOS. In addition, atomic layer deposition (ALD) technique is applicable for HfO_2-based ferroelectric films with three dimensional capacitors that are essential to realize high density capacitor-type ferroelectric memories.

Origin of the ferroelectricity is pointed out to be the non-centrosymmetric orthorhombic phases. This phase is non-equilibrium phase, but is pointed out to be stabilized in thin film form. Two stabilization factors are pointed out from the previous reports; one is the crystallite size and the other is the stress from the substrates. Crystalline size is systematically investigated by Hwan's groups [4], but the stress effect from the substrate has been hardly reported. In the present study, we investigated the effect of the stress from the substrate by changing the kinds of substrates and film thickness.

2. Experimental Procedure

$(Hf_{0.5}Zr_{0.5})O_2$ thin films were prepared on the (111)Pt/SiO_2 -coated substrates by pulsed metal organic chemical vapor deposition (MOCVD). $Hf(NMe_2)(C_8H_{17}N_2)$ (Tosoh Corp.) and $Zr(NMe_2)(C_8H_{17}N_2)$ (Tosoh Corp.) were supplied alternately as Hf and Zr source materials, respectively. The substrate temperature and chamber pressure during film growth were maintained at 350 °C and 4 Torr, respectively. The Hf/Zr ratio in the films was checked by the wavelength dispersive X-ray fluorescence. Details of the film deposition are already reported [5, 6]. Fused silica (SiO_2), (100)Si and (100)CaF_2 with the thermal expansion coefficient (α) of 0.5, 4.5, and 22 × 10^{-6}/K, respectively, were used as substrates and (111)Pt and amorphous SiO_2 layers were prepared on these substrates by RF magnetron sputtering methods. Deposited $(Hf_{0.5}Zr_{0.5})O_2$ thin films were heat-treated at 700 °C for 10 min under atmospheric O_2 atmosphere.

Crystal structural characterization was performed by X-ray diffraction θ-2θ method. Electrical properties of the $(Hf_{0.5}Zr_{0.5})O_2$ films were investigated by the ferroelectric tester (Toyo Corp.) for *P* - *E* hysteresis measurement and by impedance analyzer (Agilent 4194A) for dielectric measurement. Low temperature measurement was performed using temperature-controlled prober station.

3. Results and Discussion

Figure 1(a) shows XRD θ-2θ patterns of 17 nm-thick films prepared on three kinds of substrates. Figure 1 (b) shows the enlarged one in the range of 2θ= 28° - 34°. Peak position of Pt *111* decreased with increasing α value of the substrates. This indicates that the out-of plane lattice spacing of Pt layer was increased with increasing α value of the substrates. This means that in-plane lattice spacing of Pt layer was decreased with increasing α value due to the thermal stress from the substrates.

Diffraction peaks from the films were also observed for all films shown in Fig. 1. However, the intensity ratio of orthorhombic *111*/tetragonal *101* to monoclinic *111* of the films on SiO_2 substrates was smaller than that of the films on Si substrate. On the other hand, orthorhombic *111*/tetragonal *101*was hardly observed for films on CaF_2 substrates.

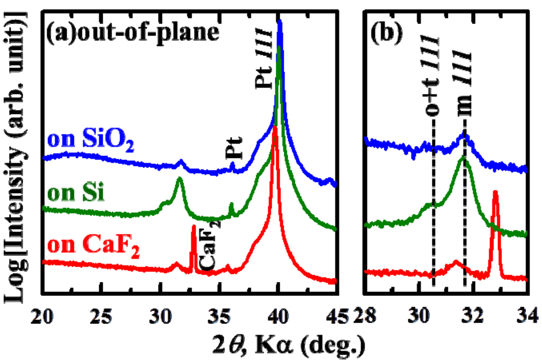

Fig. 1 XRD θ-2θ patterns of 2θ=20 - 45 ° and 28 - 34 ° for 17 nm-thick films prepared on three kinds of substrates.

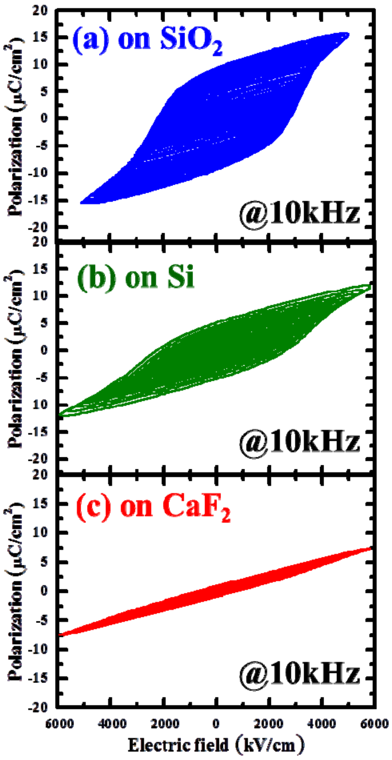

Fig. 2 Room temperature polarization-electric filed ($P - E$) hysteresis loops measured at 10 kHz for 17 nm-thick $(Hf_{0.5}Zr_{0.5})O_2$ films prepared on (a) SiO_2, (b) Si and (c) CaF_2 substrates.

Figure 2 shows the room temperature polarization-electric filed ($P - E$) hysteresis loops measured at 10 kHz for the same films shown in Fig. 1. Hysteresis loops originating from the ferroelectricity were observed for all films. Remanent polarization (*Pr*) value decreased in the following order; films on SiO_2, Si and CaF_2 substrates. This order is in good agreement with decreasing peak position of Pt *111* in Fig. 1. *Pr* value can be understand the intensity ratio of the intensity ratio of orthorhombic *111*/tetragonal *101* to monoclinic *111* as discussed in Fig. 1 because this ratio can be considered to be related to the volume fraction of orthorhombic phase.

Figure 3 show the room temperature polarization-electric filed ($P - E$) hysteresis loops for 55 nm-thick films. Hysteresis loops originateing from the ferroelectricity was observed for films on SiO_2 substrate as shown in Fig. 3 (a). This is thickest $(Hf_{0.5}Zr_{0.5})O_2$ film showing the ferroelectricity within in our survey, although *Pr* value of 55 nm-thick film was smaller than that of 17 nm thick films prepared on the same SiO_2 substrates. On the other hand, hysteresis loops were hardly observed for the films on Si and CaF_2 substrates as shown in Figs. 3 (b) and (c). This change of the ferroelectricity can be explained by the in-plane stress from the substrates; Stress applied from the substrates was relaxed by the increase of the film thickness of $(Hf_{0.5}Zr_{0.5})O_2$ films.

These data show the impact of the stress from the substrates on the ferroelectricity of the $(Hf_{0.5}Zr_{0.5})O_2$ thin films.

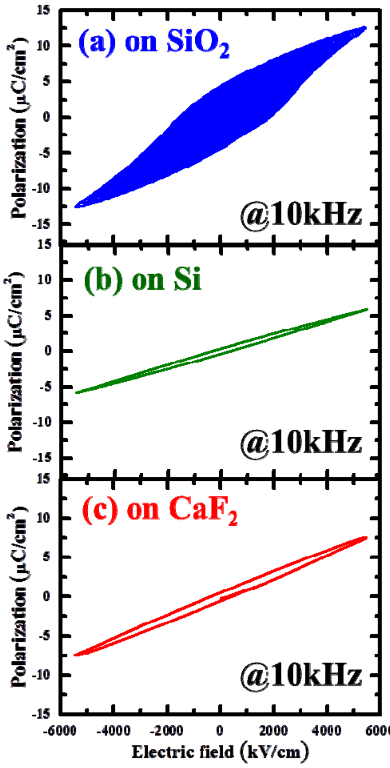

Fig. 3 Room temperature polarization-electric filed ($P - E$) hysteresis loops measured at 10 kHz for 55 nm-thick $(Hf_{0.5}Zr_{0.5})O_2$ films prepared on (a) SiO_2, (b) Si and (c) CaF_2 substrates.

4. Conclusions

Ferroelectricity was investigated for 17 and 55 nm-thick $(Hf_{0.5}Zr_{0.5})O_2$ thin films prepared on Pt/SiO_2-coated SiO_2, Si and CaF_2 substrates. Ferroelectricity was observed for 17 nm-thick films regardless of the kinds of substrates, while only films on SiO_2 substrate showed ferroelectricity for 55 nm-thick films. This can be understood by the volume fraction of orthorhombic phase. These results show the impact of the stress from the substrates on the ferroelectricity of the $(Hf_{0.5}Zr_{0.5})O_2$ thin films.

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