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Growth of epitaxial Y_2O_3-doped ferroelectric HfO_2 films by sputtering method and their characterization

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Abstract

Epitaxial $0.07YO_{1.5}$-$0.93HfO_2$ films were grown on (111)-oriented ITO-coated (111)YSZ substrates by RF magnetron sputtering method. Ferroelectric films were obtained by the room temperature deposition using $0.07Y_2O_3$-$0.93HfO_2$ target under Ar atmosphere and the following heat treatment at 1000 °C under atmospheric N_2 flow. Obtained ferroelectricity was almost compatible with that obtained by pulse laser deposition and the following heat treatment.

1. Introduction

Thin films of hafnium oxide have been widely investigated for gate insulators of FET. Ferroelectricity was reported for the doped hafnium oxide thin films in 2011 [1]. It is pointed out that their ferroelectricity originates to the non-centrosymmetric orthorhombic phase [2]. After this report, ferroelectricity of these films have been payed attention due to their stable properties below 20 nm in thickness and high compatibility with CMOS processes. However, fundamental properties of these films, such as spontaneous polarization (*Ps*), maximum remanent polarization (*Pr*) of these materials, and the Curie temperature (*Tc*), maximum temperature showing ferroelectricity, have not been reported due to the difficulty to obtain phase-pure high quality samples.

We reported on the growth of epitaxial films of Y-doped HfO_2 on ITO-covered yttrium-stabilized zirconia (YSZ) single crystal substrates and ascertained that noncentrosymmetric orthorhombic phase showed ferroelectricity together with the first estimation of *Ps* and *Tc* [3, 4]. In addition, one-axis oriented films, with the polarization components parallel to the applied voltage direction, were successfully grown on Pt-coated Si substrates [5, 6]. These oriented-films are useful to increase the homogeneity of the ferroelectric property even in the small cell size because the ferroelectric property strongly depends on the film orientation. However, all films in the previous study were prepared by pulse laser deposition (PLD) method. This method is not suitable for the mass production due to the small deposition area. One of the best preparation methods for these films appropriate to mass production is a sputtering method due to their high productivity. However, orientation controlled HfO_2-based ferroelectric films have not been scarcely reported by sputtering method. In the present study, growth of epitaxial films with ferroelectric property was successfully demonstrated by sputtering method for the first time. In addition, bottom electrode ITO was also deposited by sputtering method.

2. Experimental Procedure

Ferroelectric films were deposited on ITO-coated (111)YSZ substrates by RF magnetron sputtering method using $0.07YO_{1.5}$-$0.93HfO_2$ target. (111)-oriented yttrium stabilized zirconium oxide (YSZ) was used as a substrate. ITO films were prepared both by RF magnetron sputtering method and PLD as shown in Fig.1. Total pressure and O_2/Ar gas ratio for HfO_2-based films were 200 mTorr, and 0 and 0.02, respectively. Obtained film was heat treated at 1000 °C for 10 min under atmospheric N_2 and O_2 atmosphere.

XRD was used to characterize crystal structure of the obtained films. *110* diffraction spot of ferroelectric phase was mainly used as already reported [3, 4]. Ferroelectricity was characterized after making 100 μmϕ Pt top electrodes.

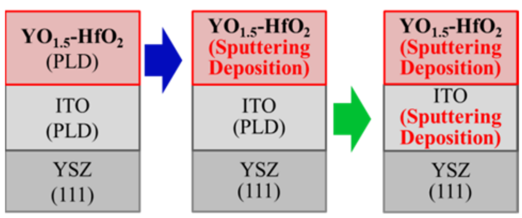

Fig. 1 Experimental flow.

3. Results and Discussion

Fig. 2 shows XRD patterns for 24 nm-thick films prepared on PLD-ITO-coated YSZ substrates under O_2/Ar gas ratio of 0 and 0.02 and the following heat treated under N_2 and O_2 flow. Films deposited under pure Ar consist of orthorhombic phase marked as "110_o" in Fig.1 for both films heat treated under O_2 and N_2 atmosphere. On the other hand, films prepared under O_2 included condition and heat treated under N_2 atmosphere consist of mixed phase of orthorhombic and paraelectric monoclinic phases.

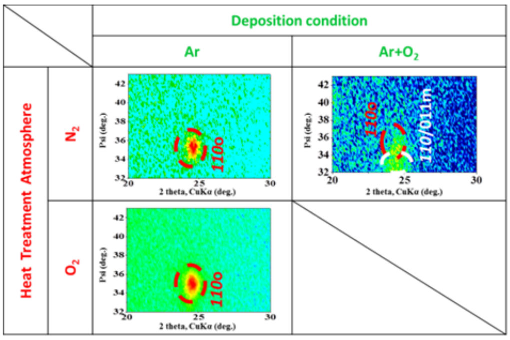

Fig. 2 XRD patterns near *110* diffraction peaks.

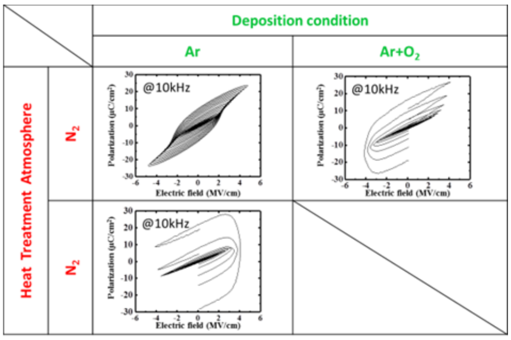

Fig. 3 *P - E* loops measured at 10 kHz for the films shown in Fig. 2.

Fig. 3 shows polarization-electric field (*P - E*) loops measured at 10 kHz for the films shown in Fig. 2. Saturated hysteresis loops originated to ferroelectricity was observed only for the films prepared under Ar and post heat treated under N_2 atmosphere. Obtained ferroelectricity was almost compatible to that obtained by pulse laser deposition and the following heat treatment [4].

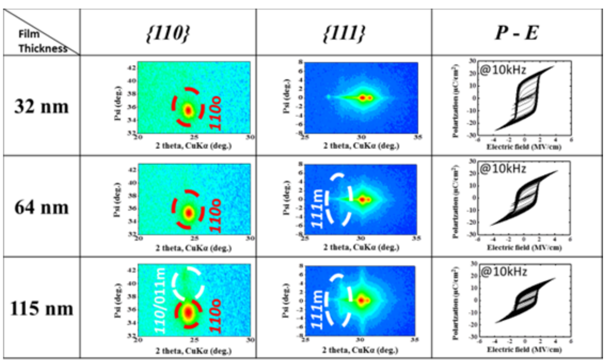

Fig. 4 XRD patterns near *110* and *111* diffraction peaks, and *P - E* loops measured at 10 kHz for various thickness films.

Fig.4 shows the XRD patterns near *110* and *111* diffraction peaks for films on sputtered ITO-coated YSZ substrates with various film thicknesses deposited under Ar atmosphere and heat treated in N_2. Near *111* diffraction results is also shown in Fig. 4 because impurity monoclinic phase is easier to detect. 32 nm-thick films were found to consist of the single phase of orthorhombic one, while 64 nm- and 115 nm-thick films consist of the mixed phase of orthorhombic and paraelectric monoclinic phases. Fig. 4 also shows the *P - E* loops of these films. All films show the hysteresis loops originated to the ferroelectricity. Obtained ferroelectricity was almost compatible with that obtained by pulse laser deposition and the following heat treatment.

4. Conclusions

Epitaxial $0.07YO_{1.5}$-$0.93HfO_2$ films were grown on (111)-oriented ITO-coated YSZ substrates by RF magnetron sputtering method. Ferroelectric films were obtained by the room temperature deposition using $0.07Y_2O_3$-$0.93HfO_2$ target under Ar atmosphere and the following heat treatment at 1000 ^{o}C under atmospheric N_2 atmosphere. Obtained ferroelectricity was almost compatible with that obtained by PLD deposition and the following heat treatment.

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