FULL PAPER

Preparation of near-1- μm -thick {100}-oriented epitaxial Y-doped HfO_2 ferroelectric films on (100)Si substrates by a radio-frequency magnetron sputtering method

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Y-doped HfO_2 films with various thicknesses were prepared on (100)-oriented [10 wt.% Sn-doped In_2O_3 , ITO]// (100) [yttria-stabilized zirconia, YSZ], and (111)ITO//(111)YSZ substrates by a radio-frequency magnetron sputtering method. Almost a single phase of orthorhombic symmetry was obtained for all films. {100}-oriented epitaxial films were obtained on (100)ITO//(100)YSZ substrates, while the film orientation changed from {111} to {100} with increasing film thickness on (111)ITO//(111)YSZ substrates. {100}-oriented epitaxial Y-doped HfO_2 films were also obtained on (100)-oriented epitaxial ITO layers on (100)YSZ//(001)Si substrates. Ferroelectricity was observed for all films. Their remanent polarization (P_r) and coercive fields (E_c) were about $5 \mu\text{C}/\text{cm}^2$ and $1 \text{ MV}/\text{cm}$, respectively, indicating that P_r and E_c were almost independent of the film thickness and kind of substrate.

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1. Introduction

Thin films of hafnium oxide (HfO_2) have been investigated as gate insulators with high- κ for field-effect transistors.^{1),2)} Recently, the ferroelectric properties of HfO_2 thin films with thicknesses below 100 nm have been investigated after the first report of ferroelectricity by T. S. Bösccke et al. for SiO_2 -doped HfO_2 thin films below 20 nm in thickness.³⁾ After that report, HfO_2 -based films with various compositions have been reported to show their ferroelectricity.⁴⁾⁻⁷⁾ The origin of ferroelectricity is ascertained to be the metastable noncentrosymmetric orthorhombic phase.³⁾ In addition, ferroelectricity was reported to decrease with the increase in film thickness due to the decrease in the volume fraction of the ferroelectric phase, and it almost disappeared above 100 nm thickness.^{8),9)} Therefore, it is considered difficult to prepare ferroelectric HfO_2 -based films thicker than 100 nm. Thus, ferroelectric HfO_2 -based films are used mainly at thicknesses below 20 nm in applications such as ferroelectric memories and negative capacitance transistors.¹⁰⁾⁻¹²⁾

The disappearance of ferroelectricity in thick films makes it difficult to use them in applications using piezoelectric properties, such as in piezo-micro-electromechanical systems (MEMS), because thicker films of around 1 μm are very important for obtaining large displacement and force or a desired resonance frequency,¹³⁾⁻¹⁵⁾ despite the fact that HfO_2 -based ferroelectric films have good compatibility with the complementary metal-oxide-semiconductor device process, which is an advantage of piezo-MEMS from the perspective of device integration.

Recently we demonstrated the preparation of approximately 1- μm -thick Y-doped HfO_2 ferroelectric films on platinized (100) Si substrates by pulsed laser deposition (PLD).¹⁶⁾ Ferroelectricity was observed for films up to about 1 μm in thickness and was almost independent of thickness for Y-doped HfO_2 ferroelectric films. This shows that the ferroelectric phase of Y-doped HfO_2 films is very stable against film thickness. Thus, these films are promising candidates for piezo-MEMS applications.

Considering industrial applications, the preparation of thick films by the sputtering method is crucial because the sputtering process has been widely commercialized for the ability to grow a film homogeneously over a wide area. It is also important to control the orientation of thick films because large orientation dependence has been reported for various ferroelectric films.¹⁷⁾⁻¹⁹⁾

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In the present study, Y-doped HfO_2 films were prepared by a radio-frequency (RF) magnetron sputtering method. As a result, approximately 1- μm -thick $\{100\}$ -oriented films with good ferroelectricity were successfully grown on (100) Si substrates.

2. Experimental procedure

Y-doped HfO_2 ferroelectric films were prepared at room temperature from a 7%-Y-doped HfO_2 target by a RF magnetron sputtering method under a 10 mTorr Ar atmosphere. The deposition ratio of the films was about 5 nm/min which is about 17 times higher than our previously reported deposition under 200 mTorr.²⁰⁾ (100)-oriented [10 wt.% Sn-doped In_2O_3 , ITO]//(100) [yttria-stabilized zirconia, YSZ], (111)ITO//(111)YSZ, and (100)ITO//(100)YSZ/(100)Si were used as substrates. Epitaxial 100-nm-thick YSZ and 30-nm-thick ITO layers were prepared by a RF magnetron sputtering method. The details have been reported elsewhere.^{21),22)} Film thickness was controlled by the deposition time, and the maximum thickness was about 1080 nm. After film deposition, Y-doped HfO_2 films were heat-treated in atmospheric N_2 at 800°C for 10 s by rapid thermal annealing (RTA).

The crystalline phase was determined by X-ray diffraction (XRD) θ - 2θ scan, pole figure, and 2θ - ψ scan under sample rotation conditions (X'Pert-MRD, Philips and D8 DISCOVER, Bruker), where ψ is a sample inclined axis. To confirm ferroelectricity, the polarization-electric field (P - E) characteristics were measured at 50 kHz using a ferroelectric tester (FCE-Fast, Toyo).

3. Results and discussion

3.1 Deposition on YSZ substrates

Figures 1(a) and 1(b) show XRD θ - 2θ scans of films with different thicknesses deposited on (100)ITO//(100)YSZ and (111)ITO//(111)YSZ substrates. The subscript O. and T. in the figure denote orthorhombic and tetra-

gonal phases, respectively. Only a $\{200\}_{\text{O./T.}}$ peak was observed for films prepared on the (100)ITO//(100)YSZ substrates, as shown in Fig. 1(a). Lattice spacing of $\{200\}_{\text{O./T.}}$ was estimated from the peak position for 340 nm- and 1080 nm-thick films. The change of the lattice spacing was about 0.1%. This small change of the strain with film thickness suggests that strain of both films is relaxed because film thickness was thick enough. X-ray pole figure plots measured at $2\theta = 24.5^\circ$ and $\psi = 0$ - 64° corresponding to $(110)_\text{O.}$ show four clear symmetry spots at $\psi = 45^\circ$, as shown in Fig. 1(c) for a 1080-nm-thick film prepared on the (100)ITO//(100)YSZ substrate. This shows an in-plane alignment of the films, suggesting the growth of epitaxial films with out-of-plane $\{100\}_{\text{O./T.}}$ orientation on (100)ITO//(100)YSZ substrates up to 1080 nm thick.

To ascertain the crystalline phase in detail, 2θ - ψ scans were measured for these two films and are shown in Figs. 2(a) and 2(b). Concentrated spots originating from $\{100\}_{\text{O./T.}}$ out-of-plane orientation were detected, such as ($2\theta = 30.4^\circ$ and $\psi = \sim 55^\circ$) and ($2\theta = 35.3^\circ$ and $\psi = \sim 0^\circ$). This also suggests the $\{100\}_{\text{O./T.}}$ out-of-plane orientation of these films. It must be noted that these spots along the ψ axis become wider with increasing film thickness. This means that the degree of $\{100\}_{\text{O./T.}}$ orientation becomes worse with increasing film thickness.

In the case of films on (111)ITO//(111)YSZ substrates, a $\{111\}_{\text{O./T.}}$ peak was observed together with a minor $\{200\}_{\text{O./T.}}$ one when the film thickness was 300 nm, as shown in Fig. 1(b). The relative intensity of the $\{200\}_{\text{O./T.}}$ one against the $\{111\}_{\text{O./T.}}$ one became strong when the film thickness increased from 300 to 1080 nm. This suggests that the orientation changed to $\{100\}_{\text{O./T.}}$ with the increase in the film thickness. Changes of $\{111\}_{\text{O./T.}}$ and $\{200\}_{\text{O./T.}}$ lattice spacings with film thickness were estimated to be approximately 0.2 and 0%, respectively. This small change of the strain with film thickness suggests that strain of both

Fig. 1. XRD θ - 2θ patterns of Y-doped HfO_2 films with different thicknesses prepared on (a) (100)ITO//(100)YSZ and (b) (111)ITO//(111)YSZ substrates. Inset figure are X-ray pole figure plots measured at $2\theta = 24.5^\circ$ corresponding to $\{110\}_\text{O.}$ for 1080-nm-thick films prepared on (c) (100)ITO//(100)YSZ and (d) (111)ITO//(111)YSZ substrates.

Fig. 2. XRD 2θ - ψ scans of Y-doped HfO_2 films with (a, c) 340 and 300 and (b, d) 1080 nm in thickness prepared on (a, b) (100)ITO/(100)YSZ substrates and (c, d) (111)ITO/(111)YSZ substrates. Peaks of $\{100\}$ - and $\{111\}$ -oriented phases are enclosed in solid and dotted lines, respectively.

films is considered to be relaxed because films were thick enough. Figure 1(d) shows the X-ray pole figure plots measured at $2\theta = 24.5^\circ$ and $\psi = 0-64^\circ$, corresponding to $\{110\}_O$ for the 1080-nm-thick film prepared on the (111)ITO/(111)YSZ substrate. Three spots, located at $\psi = 35.3^\circ$ and corresponding to $\{110\}_O$ of $\{111\}_{O,T}$ out-of-plane orientation, were observed. This suggests that an epitaxial layer with $\{111\}_{O,T}$ out-of-plane orientation was obtained on the (111)ITO/(111)YSZ substrate. On the other hand, a ring-shaped $\{110\}_O$ pattern located around $\psi = 45^\circ$ was observed, suggesting that this film had an out-of-plane $\{100\}_{O,T}$ preferred orientation with an in-plane random one.

Figures 2(c) and 2(d) show 2θ - ψ scans of these two films to ascertain the crystalline phase in detail. Concentrated spots originating from the $\{111\}_{O,T}$ out-of-plane orientation were detected, such as ($2\theta = 30.6^\circ$, and $\psi = \sim 0^\circ$ and 70.1°) and ($2\theta = 35.2^\circ$ and $\psi = \sim 56^\circ$) together with broader peaks originating from the polycrystalline phase in the case of 300-nm-thick films. When the film reached a thickness of 1080 nm, all of the spots observed on the 300-nm-thick film remained with almost the same intensity, as indicated by the red circles in Fig. 2(c), while stronger and broader spots were observed at ($2\theta = 30.4^\circ$ and $\psi = \sim 54^\circ$) and ($2\theta = 35.2^\circ$, and $\psi = \sim 0^\circ$ and $\sim 90^\circ$). These spots corresponded to the $\{100\}_{O,T}$ out-of-plane orientation.

Figure 3 shows a cross-sectional transmission electron microscope (TEM) image with selected area diffraction patterns of 1080-nm-thick Y-doped HfO_2 film on (111)ITO/(111)YSZ. A layer less than about 100 nm from the interface of the Y-doped HfO_2 film and the ITO layer showed epitaxial growth [see Fig. 3(d)]. However,

Fig. 3. (a) TEM bright field image of cross sectional Y-doped HfO_2 /(111)ITO/(111)YSZ with (b–d) selected area diffraction patterns at the area shown in (a).

random orientation was observed above 100 nm from the interface [see Fig. 3(c)] and finally tended to the $\{100\}_{O,T}$ orientation around 800 nm from the interface [see Fig. 3(b)]. Comparing these with the two 2θ - ψ scans shown in Figs. 2(c) and 2(d), we see that the 1080-nm-thick film on the (111)ITO/(111)YSZ substrate consists of three orientation thickness regions along the film thickness direction. The bottom layer was oriented mainly to $\{111\}_{O,T}$. This layer is considered to have an epitaxial relationship with the underlying ITO layer because the epitaxial growth of $\{111\}_{O,T}$ was ascertained for 45-nm-thick films in our previous study.²⁰⁾ On the other hand, the top layer consists mainly of the $\{100\}_{O,T}$ orientation with in-plane random orientation, and the intermediate layer has a random orientation. These data show that Y-doped films tend to be oriented to $\{100\}_{O,T}$ with increasing film thickness, i.e., they have $\{100\}_{O,T}$ self-oriented characteristics. A similar trend was observed for the previously reported films prepared on (111)Pt/TiO_x/SiO₂/(001)Si substrates by PLD.¹⁶⁾

Figures 4(a) and 4(b) respectively show the P - E characteristics at a maximum electric field of 3 MV/cm for 340-nm- and 1080-nm-thick films on (100)ITO/(100)YSZ substrates. Clear hysteresis loops originating from the ferroelectricity were observed for both films. Figure 4(c) displays the thickness dependence of remanent polarization (P_r) and the coercive fields (E_c) of the films deposited on the (100)ITO/(100)YSZ and (111)ITO/(111)YSZ substrates shown in Figs. 1 and 2. P_r and E_c had almost constant values of about $5 \mu\text{C}/\text{cm}^2$ and 1 MV/cm, respectively, regardless of the film thickness. This thickness-

Fig. 4. Room-temperature P - E hysteresis loops measured at 50 kHz for (a) 340 nm and (b) 1080 nm thick Y-doped HfO_2 films prepared on (100)ITO/(100)YSZ substrates. (c) Film-thickness dependence of remnant polarizations (P_r) (circles) and coercive fields (E_c) (triangles) for Y-doped HfO_2 films prepared on (111)ITO/(111)YSZ (open symbols), (100)ITO/(100)YSZ (closed symbols) and (100)ITO/(100)YSZ/(100)Si (half-closed symbols) substrates.

independent tendency was the same as in the data reported by Mimura et al. for films prepared by PLD.¹⁶⁾ In addition, P_r and E_c values were almost independent of the orientation of the substrates. In the case of films on (111)ITO/(111)YSZ substrates, the $\{111\}_{\text{O,T}}$ -oriented thickness region was less than 100 nm, and most of the thickness region tended to have a $\{100\}_{\text{O,T}}$ orientation, as shown in Figs. 2 and 3. Therefore, a strong orientation dependence of the substrate was not detected in the present study.

3.2 Deposition on (100)Si substrates

We next tried to grow $\{100\}_{\text{O,T}}$ -oriented epitaxial Y-doped HfO_2 films on (100)Si substrate because (100)YSZ layers were reported to grow on (100)Si substrates.²¹⁾

Fig. 5. XRD θ - 2θ scans of (a) 100-nm-thick YSZ film on (100)Si, 30-nm-thick ITO film on YSZ/(100)Si, and 900-nm-thick Y-doped HfO_2 on ITO/YSZ/(100)Si and (b) X-ray pole figure plots measured at $2\theta = 24.5^\circ$ corresponding to $\{110\}_{\text{O}}$ for 900-nm-thick Y-doped HfO_2 film on ITO/YSZ/(100)Si substrate.

Fig. 6. Room-temperature P - E hysteresis loops measured at 50 kHz for 900-nm-thick Y-doped HfO_2 film prepared on (100)ITO/(100)YSZ/(100)Si substrate.

Figure 5(a) shows XRD θ - 2θ scan results of the YSZ layer on (100)Si substrates and ITO layer on YSZ/(100)Si substrates. $\{100\}$ -oriented films were ascertained to have grown. Figure 5(a) also shows XRD θ - 2θ scan results for 900-nm-thick Y-doped HfO_2 films on ITO/YSZ/(100)Si substrates. The $\{100\}_{\text{O,T}}$ -orientation of Y-doped HfO_2 films were confirmed. In Fig. 5(b), the X-ray pole figure plot at a fixed 2θ angle of 24.5° shows four-fold symmetry spots as the $\{100\}_{\text{O,T}}$ Y-doped HfO_2 film on the (100)ITO/(100)YSZ substrate. These results show the successful growth of $\{100\}_{\text{O,T}}$ -oriented epitaxial Y-doped HfO_2 films on a (100)Si substrates: $\{100\}_{\text{O,T}}$ Y-doped HfO_2 / (100)ITO/(100)YSZ/(100)Si.

The ferroelectricity of this film was confirmed by P - E hysteresis loops as shown in Fig. 6. The P_r and E_c values obtained from these loops are also plotted in Fig. 4(c). These data are almost on the same lines of the data for the films on ITO/YSZ substrates. This suggests that Y-doped

HfO₂ films on Si substrates show a crystal structure similar to that of films on YSZ substrates. These results reveal the growth of epitaxial ferroelectric Y-doped HfO₂ thick film on Si substrates by the sputtering method. The results of the present study open the door to the possibility of mass-producing piezoelectric devices using ferroelectric HfO₂-based films.

4. Conclusions

Y-doped HfO₂ films were prepared on (100)ITO// (100)YSZ and (111)ITO//(111)YSZ substrates by a RF magnetron sputtering method. A single phase of orthorhombic symmetry was obtained under all conditions in the present study. {100}_{O/T}-oriented epitaxial films were obtained on (100)ITO//(100)YSZ substrates, while the film orientation changed from {111}_{O/T} to {100}_{O/T} with increasing film thickness on (111)ITO//(111)YSZ substrates. {100}_{O/T}-oriented epitaxial Y-doped HfO₂ films were also obtained on (100) ITO//(100)YSZ/(100)Si substrates. Ferroelectricity was observed for all films, and their remanent polarization (P_r) and coercive fields (E_c) were about 5 $\mu\text{C}/\text{cm}^2$ and 1 MV/cm, respectively. These results suggest that P_r and E_c are almost independent of both the film thickness and the kind of substrate.

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