FULL PAPER

Stability of the orthorhombic phase in (111)-oriented YO_{1.5}-substituted HfO₂ filmsTakao SHIMIZU^{1,†}, Kiliha KATAYAMA² and Hiroshi FUNAKUBO^{1,2,3}¹School of Materials and Chemical Technology, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226–8502, Japan²Department of Innovative and Engineered Materials, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226–8502, Japan³Materials Research Center for Element Strategy, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226–8502, Japan

Ferroelectric orthorhombic HfO₂-based films are potential candidates for future ferroelectric applications. The stability of the orthorhombic phase of epitaxial YO_{1.5}-substituted HfO₂ films on (111) yttria-stabilized zirconia substrates was investigated for various compositions, thicknesses and underlying layers. In the case of 14 nm-thick films, only 7 mol % film consisted of a single orthorhombic phase. With decreasing amount of YO_{1.5} or increasing thickness, the paraelectric monoclinic phase formed in the films. On the contrary, the highly symmetric phase was grown by the increasing amount of YO_{1.5}. The effect of the underlying layer was also investigated. Differences in the degree of relaxation of the buffer layer give different amounts of the monoclinic phase. These results imply the importance of the compositions as well as of the strain state to (111)-oriented epitaxial Y-substituted HfO₂ films.

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1. Introduction

Ferroelectric materials continue to show importance due to such attractive properties as large piezoelectric coefficients, dielectric properties, and non-volatile spontaneous polarization in the research and industrial field of electroceramics.^{1)–4)} Among the large numbers of ferroelectric materials, perovskite materials typified by BaTiO₃ and Pb(Zr,Ti)O₃ have occupied especially important positions over the past century since their discovery. Conversely, there are a number of problems, including the “size-effect”, deterioration with downsizing and difficulty of solving with these materials as the sizes of devices and constituent materials have been scaled down.⁵⁾ Miniaturization and integration, in particular, are essential for non-volatile memory applications and sensors. Novel materials that do not deteriorate with downsizing are consequently in high demand.

First reported by Bösch et al. in 2011, HfO₂-based ferroelectrics are novel ferroelectric materials which are suitable for miniaturization.⁶⁾ HfO₂-based dielectric mate-

rials have been used as high-*k* gate insulators for metal–oxide–semiconductor field-effect transistors.^{7),8)} They may offer numerous avenues to fabrication of highly integrated devices, particularly ferroelectric non-volatile memories.

The ferroelectricity in HfO₂-based films originates from the polar orthorhombic phase, which is a meta-stable and non-centrosymmetric phase.⁶⁾ Although the orthorhombic phase is not stable under ambient pressure, chemical substitution into the Hf site stabilizes the orthorhombic phase. For example, the first study on ferroelectricity was demonstrated by Si doping. It was demonstrated that various metal elements, such as Zr, Al, and Y, are efficient for achieving the emergence of ferroelectricity in HfO₂.^{9)–11)} YO_{1.5}-substituted film, in particular, exhibits ferroelectricity with various deposition techniques, such as atomic layer deposition, sputtering, and chemical solution deposition.^{10),12),13)} Furthermore, one remarkable study by Yashima et al. shows that the orthorhombic γ phase was generated in YO_{1.5}-substituted HfO₂ prepared by arc-melting, though the phase had not been attributed to the ferroelectric phase.¹⁴⁾

In order to understand the ferroelectric nature of HfO₂-based ferroelectrics, studies with single crystals or epitaxial films are needed because of the close relationship between ferroelectricity and crystal structures, although polycrystalline ferroelectric films have been used in most

[†] Corresponding author: T. Shimizu; E-mail: shimizu.t.aa@m.titech.ac.jp

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studies in accordance with industrial fabrication processes. We have studied epitaxial and single-axis oriented orthorhombic HfO₂ films, on the other hand, using pulsed laser deposition techniques (PLD) by Y substitution into Hf.¹⁵⁾ These films enabled us to observe the crystal structure in detail. In addition, we have estimated the fundamental properties of HfO₂ films, such as Curie temperature and spontaneous polarization, using epitaxial films.¹⁶⁾ We had already studied the effects of YO_{1.5} concentrations and substrates for (100)-oriented epitaxial films.^{15),17)} However, (100)-oriented films tend to be affected by domain structure destabilizing ferroelectric properties.^{18),19)} To obtain stable ferroelectric properties, using (111)-oriented films is a realistic solution employed for current ferroelectric random access memories with Pb(Zr,Ti)O₃ films. In this study, we investigate the effects of substrates, buffer layers, compositions and thicknesses on the constituent phase with respect to (111)-oriented YO_{1.5}-substituted HfO₂ and investigate the condition for growing orthorhombic HfO₂ films.

2. Experimental

YO_{1.5}-substituted HfO₂ films were grown by PLD with a KrF excimer laser ($\lambda = 248$ nm) at 700°C. The oxygen pressure was kept at 10 mTorr. The (111) yttria-stabilized zirconia (YSZ), Sn-doped In₂O₃ (ITO) covered (111) YSZ substrates, and Pt-covered (111) YSZ substrates were used for film growth. ITO was deposited by PLD, while, Pt were deposited by sputtering. 5, 6, 7, and 8 mol % substituted ferroelectric films were chosen due to their potential for forming the orthorhombic phase as postulated based on a previous study on powders and epitaxial films on (100) YSZ substrates.¹⁷⁾ Ceramics targets were prepared by a typical solid-state reaction method. The compositions used in this study were the nominal composition of the targets.

The analysis of the crystal structures of the deposited films was performed at room temperature. The X-ray diffraction (XRD) θ -2 θ diffractogram was measured with a high-resolution XRD set-up (Smart Lab, Rigaku). XRD 2-axis mapping measurements were conducted using XRD equipment (D8-discover, Bruker) with a large-area 2-dimensional (2D) detector (VANTEC-500). The thicknesses were investigated by X-ray reflectivity.

3. Results and discussions

Figure 1(a) shows the XRD θ -2 θ diffractograms from 10 to 80° measured on 14 nm-thick YO_{1.5}-substituted HfO₂ films with various YO_{1.5} concentrations. 111 and 222 reflections from YO_{1.5}-substituted HfO₂ films were observed at around the 111 and 222 peaks from YSZ substrates. To make the peaks from YO_{1.5}-substituted HfO₂ films more easily visible, the magnified XRD patterns between 59 and 66° are depicted in Fig. 1(b), showing clear 222 reflection peaks. Although the thickness of all films was almost the same, the peak intensities were quite different. Weak peak intensities were observed for 5 mol % YO_{1.5}-substituted film, in particular. On the other hand, 8 mol % YO_{1.5}-substituted film showed the strongest 222

Fig. 1. (a) XRD θ -2 θ patterns from 10 to 80° measured for 14 nm-thick 5, 6, 7, and 8 mol % YO_{1.5}-substituted HfO₂ films on (111) YSZ substrates. (b) Magnified XRD patterns for the YO_{1.5}-substituted HfO₂ films.

reflection. In addition, the 222 peak of the 8 mol % YO_{1.5}-substituted film was located at a higher angle compared to the other films. It is difficult to determine the constituent phases of these films from only XRD θ -2 θ diffractograms, however, because they include diffractions parallel to the surface normal direction of the substrates. Hence, it is unclear whether the difference in the intensities is attributable to the crystallinities or constituent phases.

To determine the constituent phase, XRD 2D mapping is a powerful tool, because it can collect more Bragg reflections. Utilizing a large-area 2D detector can dramatically reduce the measurement time required to acquire the peaks from wide reciprocal space. Although the sample rotation employed in the previous study is effective for conducting measurements at once, the intensities become weaker for thin films.¹⁵⁾ Measurement was therefore carried out without a rotating sample in this study. To distinguish the stable monoclinic, ferroelectric orthorhombic, and highly symmetric tetragonal or cubic phases, 2D mapping was performed at the two different inclination angles (ψ s) of 0 and 35°. **Figure 2** shows a schematic model of the orthorhombic and monoclinic phases grown epitaxially on (111) YSZ substrates. 2D mapping at ψ of 0° allowed us to measure around surface normal 111 YSZ peaks. The monoclinic angle deviated from 90° forces to peak splitting into 111 and 11 $\bar{1}$ peaks in the monoclinic phase. As illustrated in Fig. 2, both (111)- and (11 $\bar{1}$)-oriented films are expected, and the (111) and (11 $\bar{1}$) planes tend to tilt with respect to the (111) plane of the substrate. In addition, the 111 and 11 $\bar{1}$ peaks in the monoclinic phase are located at a distance from the YSZ 111 peak because of the large difference in d values. The tilting and different d values lead the peaks into wing-shaped peaks on the 2D maps. On the other hand, orthogonal axes in other phases require a single 111 peak to remain with a d value similar to that of the substrate, and this (111) has plane less tilt, as indicated in Fig. 2. Thus, the mapping measurement enables us to judge the existence of the monoclinic phase. 2D mapping at ψ of 35° is used to identify the orthorhombic phase. The orthorhombic phase diffracts the 110 Bragg peak owing to its lower symmetry as compared with the

Fig. 2. Schematic model of the orthorhombic and monoclinic phases with lattice parameters. The relationships with surface planes and (110) plane of the orthorhombic phase, (110) and (011) planes of the (111)-oriented monoclinic phase, and (110) and (011) planes of the (111)-oriented monoclinic phase are schematized.

tetragonal and cubic phases. Reflections expected appear in the maps are 110 from the orthorhombic phase, 110 and 011 from the (111)-oriented monoclinic phase, and 110 and 011 from the (111)-oriented monoclinic phase, as depicted in Fig. 2. Among these, 011 peak from the (111)-oriented monoclinic phase appears at around $\psi = 41^\circ$, while other peaks, including the orthorhombic phase, appear at around ψ in the range from 32 – 36° . The isolated peak at $\psi = 41^\circ$, therefore, also strongly suggests the existence of the monoclinic phase together with the wing-shaped peak at around the near surface normal.

Figure 3 shows XRD 2D maps measured on HfO_2 films with various $\text{YO}_{1.5}$ concentrations. The wing-shape peaks at around $2\theta = 28$ and 31° marked by broken circles suggest the existence of the monoclinic phase in 5 mol % $\text{YO}_{1.5}$ -substituted HfO_2 film. These peaks have different d values from that of the peak in Fig. 1(a), suggesting that the 111 peak in Fig. 1(a) is from the orthorhombic or higher symmetry phases. 110 peaks can be observed in Fig. 3(e) for 5 mol % $\text{YO}_{1.5}$ -substituted HfO_2 film. Because the peak is located at around $\psi = 35^\circ$, it must come from the orthorhombic phase. The peak at around $\psi = 41^\circ$ cannot be seen in the figure, implying that the film includes a small amount of the monoclinic phase. This is due to differences in the structural factors of the 111/111 and 011 Bragg reflections in the monoclinic phase. Based on similar considerations, the 6 and 7 mol %-substituted

HfO_2 films are nearly the single orthorhombic phase because very few wing-shaped peaks appear in Figs. 3(b) and 3(c), and the 110 peaks appear at around $\psi = 35^\circ$. The weaker peak intensities of 5 mol % $\text{YO}_{1.5}$ -substituted HfO_2 film in Fig. 1(b) is result from the small amount of the orthorhombic phase, because the film might include a significantly larger amount of the monoclinic phase than 6 and 7 mol % films.

The 8 mol % $\text{YO}_{1.5}$ -substituted HfO_2 film has quite different features from other films. Figure 3(d) shows no wing-shaped peak and Fig. 3(h) also indicates no 110 peak. The absence of the 110 peak in Fig. 3(h) suggests that the film includes no orthorhombic or monoclinic phase but higher symmetric tetragonal and cubic phases. The different d value (peak position) and strong peak discussed above are due to the highly symmetric phase with relatively high crystallinity. In reality, 0.058° of the full-width half maximum of the rocking curve measurement for 8 mol % $\text{YO}_{1.5}$ -substituted HfO_2 suggests its high orientation degree (see **Fig. 4**).

In order to investigate the stability of the orthorhombic phase with respect to film thickness, we grew 6 and 7 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films with a thickness of 33 nm and performed the same crystal identification by XRD. The reason we chose 6 and 7 mol % films was that these films with a thickness of 14 nm consist of the orthorhombic phase. **Figure 5(a)** shows XRD θ - 2θ diffractograms

Fig. 3. XRD 2θ - Ψ maps measured at around $\Psi = 0^\circ$ for 14 nm-thick (a) 5, (b) 6, (c) 7, and (d) 8 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films and maps at around $\Psi = 35^\circ$ for (e) 5, (f) 6, (g) 7, and (h) 8 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films.

from 10 to 80° measured on 6 and 7 mol % 33 nm-thick $\text{YO}_{1.5}$ -substituted HfO_2 films. As in the case of 14 nm-thick films, enlarged patterns around the YSZ 222 reflections are illustrated in Fig. 5(b).

Figure 5(a) shows peaks located at around 28° , which is far from the 111 reflections from the orthorhombic phase. With this peak position taken into account, these peaks can be assigned to monoclinic $11\bar{1}$ reflections. The orthorhombic 222 peaks can be observed from enlarged XRD pattern for the vicinity of the YSZ 222 reflections. The peaks were significantly weaker than those for 14 nm-thick films, however, in spite of greater film thickness. Considering the strong peak from the monoclinic phase and the weaker peak from the orthorhombic phase, we assume that the stability of the orthorhombic phase becomes lower as the thickness increases.

Figure 6 shows XRD 2D maps measured on 33 nm-thick HfO_2 films with 6 and 7 mol % $\text{YO}_{1.5}$ concentrations. Much as in the case of 14 nm-thick films, wing-shaped

Fig. 4. XRD rocking curve measurement of the 222 Bragg peak from 8 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films on (111) YSZ substrates. The solid line is a fitted curve using the pseudo-Voigt function.

Fig. 5. (a) XRD θ - 2θ pattern from 10 to 80° measured on 33 nm-thick 6 and 7 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films on (111) YSZ substrates. (b) The magnified XRD pattern for the $\text{YO}_{1.5}$ -substituted HfO_2 films.

Fig. 6. XRD 2θ - Ψ maps measured at around $\Psi = 0^\circ$ for 33 nm-thick (a) 6 and (b) 7 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films and maps at around $\Psi = 35^\circ$ for (c) 6 and (d) 7 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films.

Fig. 7. Constituent phases plotted against thickness and YO_{1.5} concentrations in YO_{1.5}-substituted HfO₂ films on (111) YSZ substrates.

peaks are observed for both films at around YSZ 111 peaks in Figs. 6(a) and 6(b). In Figs. 6(c) and 6(d), the 110 peaks are located at both $\psi = 35^\circ$ and 41° . These observation show that the 33 nm-thick 6 and 7 mol % YO_{1.5}-substituted films include both orthorhombic and monoclinic phases. The wing-shaped peaks from monoclinic phase in the 7 mol % film in Fig. 6(b) seem relatively weak compared to those in the 6 mol % film in Fig. 6(a). This implies that 7 mol % YO_{1.5}-substituted HfO₂ has a higher-stability of orthorhombic phase than 6 mol % YO_{1.5}-substituted HfO₂.

Figure 7 summarizes the phases formed in this study for different thicknesses and YO_{1.5} concentrations. The single orthorhombic phase was achieved only for 14 nm-thick YO_{1.5} mol % substituted film. Smaller YO_{1.5} concentrations and greater thicknesses destabilize the orthorhombic phase, resulting in generation of the monoclinic phase. This result is slightly different from that of the previous study on epitaxial films on (100) YSZ substrates, which showed that epitaxial films consisting of a single orthorhombic phase were grown for the composition range from 5 to 7 mol % YO_{1.5}-substituted films. Larger YO_{1.5} concentrations, on the other hand, give rise to the tetragonal or cubic phases. This is similar result to those for films on (100) YSZ substrates.¹⁷⁾ Single orthorhombic epitaxial films on (111) YSZ substrate are consequently obtained in a narrower region than those on (100) YSZ substrates. This difference seems to result from the different strain relaxation mechanisms. Indeed, the previous study shows that the buffer ITO layer greatly reduces the monoclinic phase for YO_{1.5}-substituted HfO₂ film on Pt-covered Si substrates. This result implies that the underlying layer strongly affects the stability of the orthorhombic phase through the strain state.

In order to examine the effects of the underlying layer, we grew 7 mol % YO_{1.5}-substituted HfO₂ films on several substrates. In addition to bare (111) YSZ substrates, ITO and Pt-covered (111) YSZ substrates were employed. To investigate the effect of strains, two ITOs with different

Fig. 8. XRD θ - 2θ patterns from 25 to 50° measured on 14 nm-thick 7 mol % YO_{1.5}-substituted HfO₂ films grown on (111) YSZ substrates and substrates with various buffer layers.

strain states, partially relaxed ITO and almost relaxed ITO, were prepared.

Figure 8 shows the XRD θ - 2θ patterns for 14 nm-thick 7 mol % YO_{1.5}-substituted HfO₂ films grown on (111) YSZ substrates and those with various buffer layers. The 111 from YO_{1.5}-substituted HfO₂ can be observed in Fig. 8 in the vicinity of the YSZ 111 peaks for the films on (111) YSZ and Pt-covered YSZ substrates. On the contrary, ITO 222 peaks appear instead of the 111 peaks from the YO_{1.5}-substituted HfO₂ films in the XRD patterns for films on ITO-covered YSZ substrates, obscuring the 111 peaks from the films due to their similar d values. In addition to these peaks, additional peaks attributed to $11\bar{1}$ reflections from the monoclinic phase can be observed.

Figure 9 shows XRD 2θ - ψ maps for 14 nm-thick 7 mol % YO_{1.5}-substituted HfO₂ films grown on (111) YSZ substrates and those with various buffer layers. As described above, the films on bare YSZ substrates shows a single orthorhombic phase. Similar results were achieved for the films on partially relaxed ITO layers because the XRD 2D maps in Figs. 9(b) and 9(f) show no wing-shaped peaks from the monoclinic phase or 110 peaks located at $\psi = 35^\circ$. On the other hand, wing-shaped peaks from the monoclinic phase were observed for the films on almost fully relaxed ITO layers. In addition, clear $01\bar{1}$ peaks at $\psi = 41^\circ$ indicate the existence of the monoclinic phase. It is worth noting that there are 110 peaks at $\psi = 35^\circ$, suggesting the presence of the orthorhombic phase, although the 111 peak from the orthorhombic phase is less visible. This difference in the amount of the orthorhombic phase between films on partially and almost fully relaxed ITO layers implies that the formation energy of the orthorhombic phase is greatly affected by the strain state. Both the wing-shaped peak and the $01\bar{1}$ peaks at $\psi = 41^\circ$ from the monoclinic phase are barely visible for the film on the Pt layer in Figs. 9(d) and 9(h), although the $11\bar{1}$ peak from the monoclinic phase appears in Fig. 8. The typical XRD θ - 2θ pattern can acquire diffraction spots for

Fig. 9. XRD 2θ - ψ maps measured at around $\psi = 0$ and 35° for 14 nm-thick 7 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films on (111) YSZ with (a, e) no buffer layer, with (b, f) a partially relaxed ITO layer, (c, g) with an almost fully relaxed-ITO layer, and (d, h) with a Pt buffer layer, respectively.

the surface normal direction, and the resolution of the rocking curve direction is quite high. Hence, the peaks from films with a high crystal orientation become much stronger than those with mosaicity. The 111 peak from the orthorhombic phase accompanies the satellite fringe peaks for the film on the Pt/YSZ substrate, indicating a good orientation. This high orientation could be followed by the monoclinic phase, resulting in the appearance of the $11\bar{1}$ peak from the monoclinic phase.

4. Conclusions

In this study, we address epitaxial growth of $\text{YO}_{1.5}$ -substituted HfO_2 films on (111) YSZ substrates by PLD at 700°C and investigate the effects of the composition, thickness, and underlying layers on the constituent phases of the films using XRD measurement. The single orthorhombic phase was obtained only for 14 nm-thick 7 mol % $\text{YO}_{1.5}$ -substituted HfO_2 film. Decreases in the $\text{YO}_{1.5}$ concentration increased the monoclinic phase for 14 nm-thick films, while, the increases amount of $\text{YO}_{1.5}$ generated highly symmetric tetragonal or cubic phase. When the thickness was increased to 33 nm, the undesired monoclinic phase greatly increased for 6 and 7 mol % $\text{YO}_{1.5}$ -substituted HfO_2 films. The underlying layers also greatly

affected the generated phase of $\text{YO}_{1.5}$ -substituted HfO_2 films. Differences in the fractions of the monoclinic phase between the films on the almost fully relaxed ITO and those on the partially relaxed ITO, in particular, suggest that the strain state is one factor in obtaining the orthorhombic ferroelectric phase.

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