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Effects of heat treatment and in situ high temperature XRD study on the formation of ferroelectric epitaxial HfO_2 based film.

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Abstract

Formation mechanism of ferroelectric orthorhombic phase was investigated for epitaxial HfO_2 based films using by *in-situ* high temperature XRD. Epitaxial $0.07YO_{1.5}$-$0.93HfO_2$ films were grown on (111) ITO-coated (111)YSZ substrates by pulsed laser deposition at room temperature and the following heat treatment process. Films deposited at room temperature were crystallized as paraelectric monoclinic phase. The monoclinic phase changed to tetragonal phase when the temperature increased above 550 ºC. Orthorhombic phase was detected at 300 ºC corresponding to Curie temperature under the cooling process. These results clearly suggest that the formation of tetragonal phase, high temperature paraelectric phase of ferroelectric orthorhombic phase, is a key for the formation of ferroelectric orthorhombic phase.

1. Introduction

Recently, ferroelectricity was observed in HfO_2-based films with orthorhombic phase [1]. This ferroelectric HfO_2-based film has a unique property such as stable large remanent polarization in a small film thickness and receives increased attention for ferroelectric devices using ultra-thin film. Many researchers investigated the stabilization method of ferroelectric orthorhombic phase. Among these stabilizing factor, heat treatment temperature strongly affects the crystal phase of the HfO_2-based films [2]. However, the phase change by the heat treatment temperature dose not fully understand because almost all film consist of the mixture phase of ferroelectric orthorhombic phase and paraelectric phase, such as monoclinic one. Polycrystalline character of the deposited films also make difficult to identify due to the similarity of the crystal structures.

We have already succeeded in growing epitaxial HfO_2 based films on 10 wt.% Sn-doped In_2O_3(ITO) // yttria-stabilized zirconia (YSZ) [3-4]. Ferroelectric orthorhombic phase was stably obtained by selecting $0.07YO_{1.5}$-$0.93HfO_2$ (YHO7) composition. In the present study, we investigated the crystal structures and electric property of epitaxial YHO7 films under various annealing temperature. In addition, in situ HT XRD investigation was used to observe formation process of orthorhombic phase.

2. Experimental procedure

About 15 nm-thick YHO7 thin films were deposited on (111)ITO//(111)YSZ substrates by pulsed laser deposition (PLD) using a KrF excimer laser (λ = 248 nm and fluence of 3 J/cm^2) at room temperature under 10 mTorr O_2 atmosphere. Heat treatment was performed for the as-deposited films at various temperatures under N_2 flow. The heating and cooling rate were 25 °C/s and about 8 °C/s, respectively.

XRD analysis was used to confirm the crystal phase by using laboratory instrument (X'Pert-MRD, Philips, λ= 0.154) and synchrotron facilities (SPring8, BL15, λ= 0.1). A *P-E* hysteresis loop was measured at room temperature under 10 kHz. 100 nm-thick Pt top electrodes were deposited by electron beam evaporation for this measurement.

3. Results and discussion

Figs. 1(a)-(e) show θ-2θ profiles for as-deposited and heat treated YHO7 films on (111)ITO//(111)YSZ substrates and (111)ITO//(111)YSZ substrates. Monoclinic (11-1) diffraction was observed for as-deposited and 600°C- heat treated films. In contrast, orthorhombic or tetragonal phase was observed for 800°C- and 1000°C- heat treated films. It should not be surprising that as-deposited YHO7 film was crystallized because room temperature epitaxial growth of fluorite structure such as YSZ was previously reported.[5]
To identify crystal phase more clearly, we use X-ray 2θ -ψ mappings near *{110}* by using synchrotron facilities due to low diffraction intensity. This mapping allows to distinguish each crystal phases because there is no diffraction from tetragonal phase and peak position is different between monoclinic and orthorhombic phases. Figs. 2 (a) – (d) show the 2θ -ψ mappings. Wide peaks in the ψ direction originating from monoclinic *110* and *011* diffractions were observed for as-deposited and 600°C heat treated films. Both monoclinic and orthorhombic phases were observed for 800°C heat treated film. Finally, single orthorhombic phase was ob-

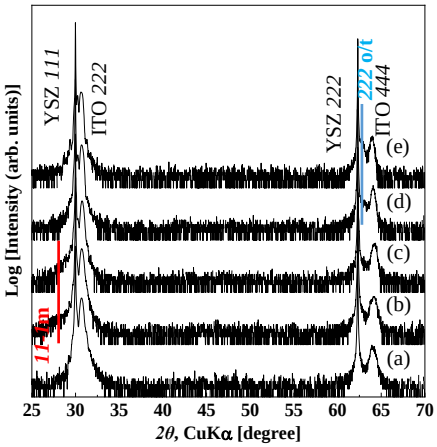

Fig 1 XRD *θ-2θ* profiles for (a) (111)ITO//(111)YSZ substrate, (b) as-deposited, (c) 600°C-, (d) 800°C-, and (e) 1000°C- heat treated YHO films grown on (111)ITO//(111)YSZ substrates.

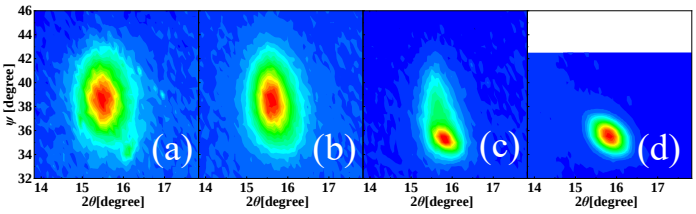

Fig 2 XRD *2θ-ψ* mappings around the YHO7 {*110*} diffraction for (a) as-deposited, (b) 600°C-, (c) 800°C-, and (d) 1000°C- heat treated YHO films grown on (111)ITO//(111)YSZ substrates.

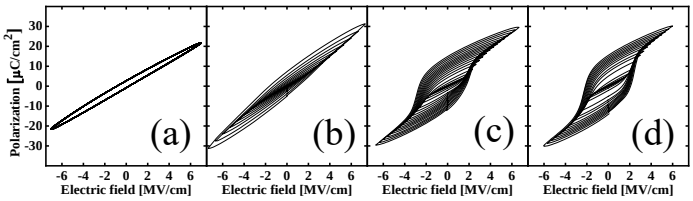

Fig 3 *P-E* hysteresis loops measured at 10 kHz for (a) as-deposited, (b) 600°C-, (c) 800°C-, and (d) 1000°C- heat treated YHO films grown on (111)ITO//(111) YSZ substrates.

tained for 1000°C heat treated film.

Fig. 3 shows the *P–E* loops for the as-deposited and heat treated YHO7 films at various temperature. Clear hysteresis loops associated with ferroelectricity were observed for 800°C- and 1000°C- heat treated films, while as-deposited and 600°C- heat treated films were paraelectricity. Remanent polarization, *Pr*, of 800°C- heat treated film was about 12 μC/cm^2 that was lower than that of 1000°C- heat treated film (about 14 μC/cm^2) due to the coexistence of paraelectric monoclinic phase. The result of *P-E* loops shown in Fig.3 is in good response to that of the crystal structure as shown in Fig.2.

To investigate this heat treatment effect more in detail, XRD measurement at various temperatures was carried out by synchrotron facilities. Fig. 4 shows the in-situ HT XRD (ψ scanning at 2θ = 15.7°) result for room temperature deposited film at the temperature ranging from 25°C to 1000°C upon heating and cooling. Initial as-deposited film was monoclinic phase. As the temperature increases above about 225°C, monoclinic *110* peak intensity increases and become wider. Above ~ 550°C, the monoclinic peak intensity decreases with increasing temperature and almost disappeared above 950 °C. This means the partial phase changes from monoclinic to tetragonal phase and monoclinic phase perfectly transformed to tetragonal phase. To confirm tetragonal phase at high temperature, XRD *θ-2θ* profiles was measured at 1000°C. Tetragonal phase was observed for the film (not shown here). The film was single tetragonal phase during cooling process down to about 300°C. The orthorhombic peak appeared below 300°C. This means the phase change from tetragonal to orthorhombic phase under the cooling process, corresponding to Curie temperature. These results clearly suggest that the formation of tetragonal phase, high temperature paraelectric phase of ferroelectric orthorhombic phase, is a key for the formation of ferroelectric orthorhombic phase.

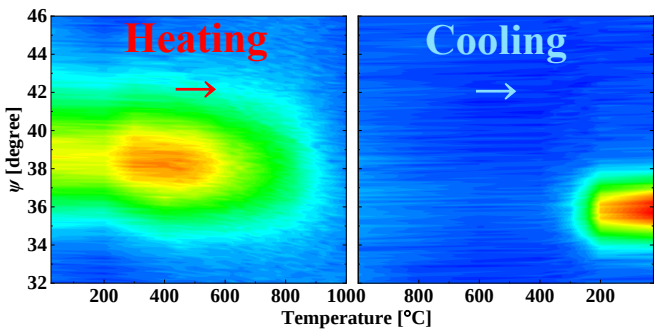

Fig.4 In-situ HT XRD result of as-deposited film.

4. Conclusions

Epitaxial $0.07YO_{1.5}$-$0.93HfO_2$ films were grown on (111)ITO//(111)YSZ substrates by PLD at room temperature. Paraelectric monoclinic phase was detected for as-deposited film. To obtain ferroelectric orthorhombic phase, phase change from monoclinic to tetragonal phase during high temperature heat treatment is found to be a key issue.

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