

Thickness- and orientation-dependence of Curie temperature of ferroelectric epitaxial HfO₂ based films

Takanori Mimura¹, Takao Shimizu¹, Yoshio Katsuya², Osami Sakata³, and Hiroshi Funakubo¹

¹ Tokyo Institute of Technology

4259, Nagatsuda-cho, Midori-ku, Yokohama 226-8502, Japan

Phone: +81-45-924-5446 E-mail: funakubo.h.aa@m.titech.ac.jp

² Synchrotron X-ray Station at SPring-8, Research Network and Facility Services Division

1-1-1, Kouto, Sayo-cho, Hyogo, 679-5148, Japan

³ Synchrotron X-ray Group, Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS) and Synchrotron X-ray Station at SPring-8, Research Network and Facility Services Division
1-1-1, Kouto, Sayo-cho, Hyogo 679-5148, Japan

Abstract

Curie temperature of ferroelectric orthorhombic phase was investigated for epitaxial 0.07YO_{1.5}-0.93HfO₂ films using high temperature X-ray diffraction. These epitaxial 0.07YO_{1.5}-0.93HfO₂ films with 4.6 – 110 nm film thickness were prepared on (111)YSZ and (100)YSZ substrates by pulsed laser deposition at room temperature and subsequent 1000 °C annealing to obtain ferroelectric orthorhombic phase. This result revealed that Curie temperature was above 300 °C, which is significantly high for the stable operation of memory application regardless of the thickness and orientation.

1. Introduction

Recently, ferroelectricity in HfO₂ based films with non-centrosymmetric orthorhombic phase was discovered [1]. This material has a unique advantage; i.e. stable large remnant polarization in a thin film region below 20 nm. Therefore, ferroelectric HfO₂ based film is considered to be a candidate for highly integrated nonvolatile memories such as FeRAM and FeFET.

Curie temperature (T_C), at which the phase transitions occurs from ferroelectric phase to paraelectric phase, is one of the important properties in ferroelectric materials because the ferroelectricity diminishes at the temperature. This temperature determines the upper limit of operation temperature for the devices, since the stored information should volatilize above

T_C . T_C had been investigated using high temperature X-Ray diffraction (HT-XRD). Park *et al.* reported that the T_C of polycrystalline Si-doped HfO₂ is 600 °C [2], which is compatible with conventional ferroelectric materials. However, several studies on ferroelectric films such as PbTiO₃ [3] and (Bi, Na)TiO₃-(Bi, K)TiO₃ [4] have reported that T_C changes by film thickness and orientation. Therefore, it is necessary to investigate such dependence of T_C for ferroelectric HfO₂ based films. Such investigation requires HfO₂ films having the ferroelectric orthorhombic phase with various thicknesses and orientations. We have already fabricated (100) and (111) oriented epitaxial HfO₂ based films by using (100) and (111) yttria stabilized zirconia (YSZ) substrates, respectively [3,5]. Moreover, stable ferroelectric orthorhombic phase was obtained over the wide film thickness range by choosing 0.07YO_{1.5}-0.93HfO₂ (YHO7) composition [5]. In this study, we reported on T_C for the YHO7 films with various the thicknesses and orientations.

2. Experimental procedure

(111) and (100) oriented YHO7 films were deposited on (111)YSZ and (100)YSZ, respectively by pulsed laser deposition using a KrF excimer laser ($\lambda = 248$ nm) at room temperature under 10 mTorr O₂ atmosphere. YHO7 films with various film thickness were obtained by changing deposition time. To obtain ferroelectric orthorhombic phase, heat treatment was performed for the as-deposited films at 1000 °C for

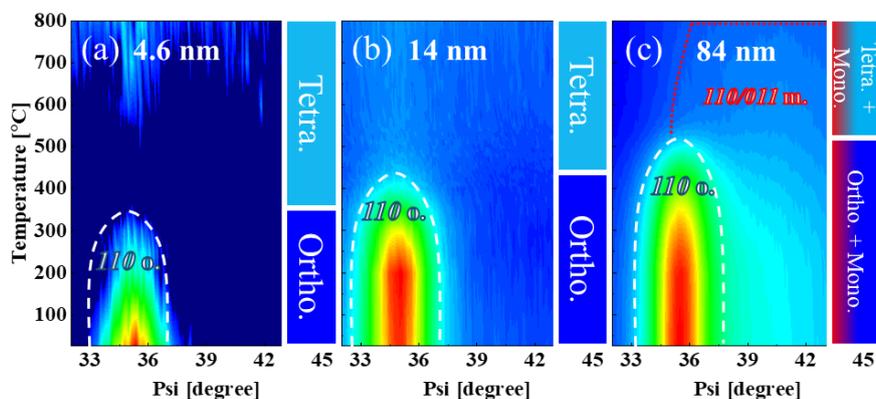


Figure 1 In situ high temperature XRD result for (a) 4.6 nm, (b) 14 nm and (c) 84 nm thick (111) oriented YHO7 films on (111) YSZ measured at various temperatures in the range from 25 °C to 800 °C by Ψ scanning at $2\theta = 13.1^\circ$ ($\lambda = 0.1$ nm).

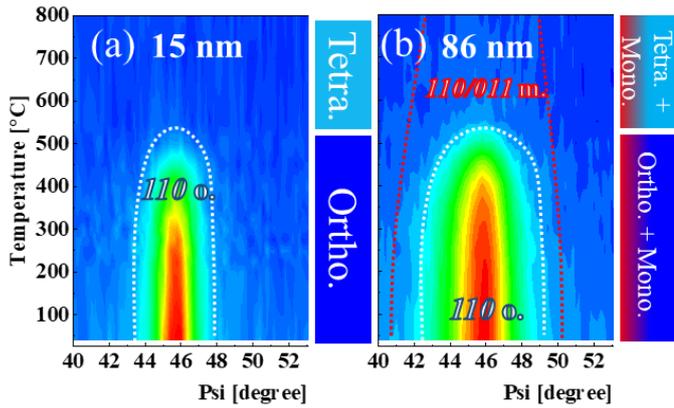


Figure 2 In situ high temperature XRD result for (a) 15 nm and (b) 86 nm thick {100} oriented YHO7 films on (100) YSZ measured at various temperatures in the range from 25°C to 800°C by Ψ scanning at $2\theta = 13.1^\circ$ ($\lambda = 0.1$ nm).

10s under N₂ flow. The heating and cooling rate were 25 °C /s and about 8 °C /s, respectively.

HT-XRD measurement was employed to investigate Curie temperature using laboratory instrument (D8 discover, Bruker, $\lambda = 0.154$) synchrotron facilities (SPRING8, BL 15, $\lambda = 0.1$ nm) with domed hot stage (Anton Paar, DHS 1100) in air.

3. Results and discussion

To observe phase transition from ferroelectric orthorhombic phase to paraelectric tetragonal phase on heating, we use Ψ scan near 110 super lattice reflections at each temperature. The Ψ scan allows us to distinguish crystal phases including orthorhombic, tetragonal phases as described in the previous reports. Note that the super-lattice reflection should appear for the orthorhombic phase, while disappear for the tetragonal phase due to the extinction rule. Figs. 1(a)-(c) shows the temperature dependence of HT-XRD (Ψ scanning at $2\theta = 13.1$) results for (111) oriented YHO7 films from 25°C to 800°C upon heating. The 110_o peaks coming from orthorhombic phase were observed in XRD results for the 4.6, 14, and 84 nm-thick films, which is shown in Figs. 1(a), (b), and (c) respectively. In addition, the broad 110_m/011_m peaks in Fig. 1(c) reveals that the 84 nm-thick film included monoclinic phase. In each film, the 110_o peak intensity decreases as the temperature increases and finally disappears at certain temperature, phase to paraelectric tetragonal phase. The transition temperature (T_C) is 350°C, 450°C and 550°C for 4.6 nm, 14 nm and 84 nm thick YHO7 films, respectively. For (111)-oriented films, T_C decreases with the decrease in thickness. Nevertheless, even 4.6 nm-thick film has significantly high T_C above 300 °C.

Figures 2(a) and (b) show the HT-XRD (Ψ scanning at $2\theta = 13.1$) result for {100} oriented YHO7 films. Both 110_o peaks were observed for 15 nm and 84 nm thick YHO7 films at room temperature after 1000°C heat treatment, indicating that these films include orthorhombic phase. Similar to the (111)-oriented film, 110_m/011_m peaks were observed for 84 nm thick YHO7 film. The 110_o peak disappears above 550°C for both films. Thus the T_C unchanged by change in thickness from 15 nm to 86 nm for the {100}-oriented film, in contrast to the

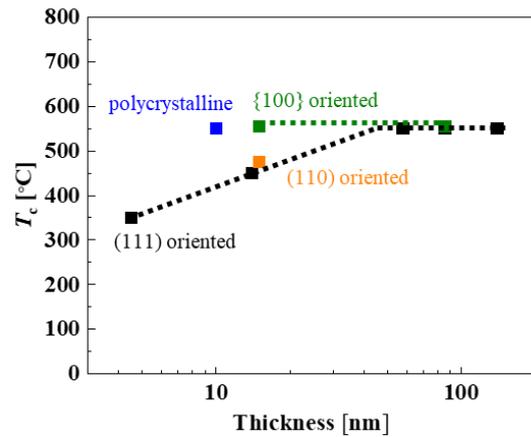


Figure 3 Phase transition temperature, T_C , as a function of film thickness for oriented and non-oriented YHO7 films.

results for (111)-oriented films.

Figure 3 shows the thickness dependence of T_C from the present results including {100} and (111) oriented YHO7 films, together with previous data for (110) oriented film [6] and polycrystalline YHO7 films with random orientation (not shown here). Figure 3 reveals T_C of all films is larger than 350°C, which is significantly high for memory applications. In addition, (111)-oriented films have thickness dependence of T_C , as is observed for conventional ferroelectric films. These thickness dependences are possibly due to the different surface energy or/and strain in the films. Further study will elucidate these effects on T_C .

4. Conclusions

T_C of ferroelectric YHO7 films with various thicknesses and orientations was investigated by using in-situ HT-XRD. Our results revealed that the T_C was larger than 350°C in all films. Thus, the ferroelectric HfO₂ based films have significantly high T_C for using memory applications.

Acknowledgement

This work was partly supported by the JSPS KAKENHI Grant Nos. 17J10208, 17K14807, 18H01701, and 18K19016; and by the Element Strategy Initiative to Form a Core Research Center, Ministry of Education, Culture, Sports, Science, and Technology of Japan (MEXT). The synchrotron radiation experiments were performed at beamline BL15XU with the approval of NIMS (Proposal Nos. 2017A4701).

Reference

- [1] T. S. Boscke *et al.*, Appl. Phys. Lett. **99** (2011) 102903.
- [2] M. H. Park *et al.*, Nanoscale **9**, (2017) 9973.
- [3] S. K. Streiffer *et al.*, Phys. Rev. Lett. **89** (2002) 067601.
- [4] P. Li *et al.*, J EUR CERAM SOC. **36** (2016) 3139–3145.
- [5] T. Mimura *et al.*, Appl. Phys. Lett., **113** (2018) 102901.
- [6] T. Shimizu *et al.*, Appl. Phys. Lett., **107** (2015) 032910.