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Understanding wet annealing effect on phase transition and ferroelectric phase formation for $Hf_{1-x}Zr_xO_2$ film

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Abstract

The effect of wet annealing on phase transition and ferroelectric phase formation for $Hf_{1-x}Zr_xO_2$ film was discussed. We found that the phase transition of $Hf_{1-x}Zr_xO_2$ caused by wet annealing follows the phase diagram with including the film thinning effect of HfO_2-ZrO_2 system. The key effect of wet annealing to progress the phase transition and form ferroelectric phase is considered as suppression of the film thinning effect based on thermodynamics.

1. Introduction

ZrO_2 is an attractive material for ferroelectric memory application, because (1) it has already been used for DRAM application, (2) its crystalline phase is thermally stable, and (3) its cost is lower than HfO_2 [1, 2]. However, owing to its high thermal stability of the initially formed phase, the ferroelectric orthorhombic phase formation for ZrO_2 film especially by post deposition process is difficult. Recently, we reported that wet O_2 annealing drastically promotes the phase transition; tetragonal (*t*) → orthorhombic (*o*) → monoclinic (*m*) for both HfO_2 and ZrO_2 rather than dry O_2 annealing, resulting in the appearance of ferroelectric property for undoped ZrO_2 film [3]. However, remanent polarization, P_r of ZrO_2 is not sufficiently large. To improve the ferroelectricity of ZrO_2, it is important to reveal the key role of wet O_2 annealing on promoting the phase transition.

In this study, we discussed the effect of wet O_2 annealing on the phase transition and the ferroelectric phase formation of $Hf_{1-x}Zr_xO_2$ films because HfO_2-ZrO_2 system which is a solid solution of HfO_2 and ZrO_2 is a good example to investigate the transition process on the way from HfO_2 to ZrO_2.

2. Experiment

In this work, $Hf_{1-x}Zr_xO_2$ films were prepared by RF co-sputtering on p^+-Ge. The film thickness was 15±2 nm which was estimated by X-ray reflection. The Zr content was estimated by X-ray photoelectron spectroscopy. The films were annealed at 600 °C in N_2 for 30 sec for crystallization. Then, for phase control, post crystallization annealing (PCA) was performed at 300 or 500 °C for 5 min in dry or wet O_2 ambient. The crystalline structure of poly-crystalline $Hf_{1-x}Zr_xO_2$ was characterized by grazing incidence X-ray diffraction (GIXRD). Finally, Al was deposited for the capacitor electrode. Polarization-electric field (*P*-*E*) curves were measured at 10 kHz.

3. Results and discussion

First, we discuss the effect of dry and wet O_2 PCA on the phase transition of $Hf_{1-x}Zr_xO$ films. Figure 1(a) shows GIXRD results of $Hf_{0.56}Zr_{0.44}O_2$ films that did not undergo PCA and that underwent dry PCA at 300 °C and wet PCA at 300 °C and 500 °C. For the sample that did not undergo PCA, only diffraction peak of $o111/t101$ is observed. It is found that the phase transition from *o*/*t*-phase to *m*-phase is dramatically progressed by wet PCA rather than dry PCA, which is consistent with the previous report [3]. However, wet PCA at a lower temperature much progresses the phase transition. This phase transition tendency is not consistent with HfO_2 [4]. To understand physical reason, the peak deconvolution was carried out as shown in Fig. 1 and the *o*/*t* phase ratio, $r_{o/t}$ was estimated from the followed equation,

$$r_{o/t} = I_{o111/t101} / \left(I_{m11\bar{1}} + I_{o111/t101} + I_{m111} \right) \times 100\ (\%). \quad (1)$$

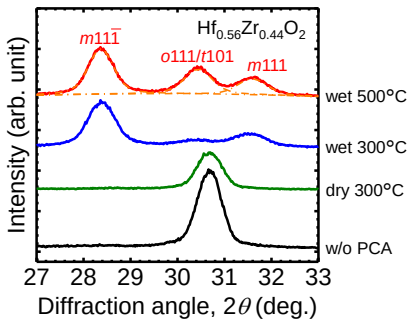

Fig. 1 GIXRD profiles of $Hf_{0.56}Zr_{0.44}O_2$ that did not undergo PCA and underwent dry PCA at 300 °C and wet PCA at 300 °C and 500 °C. Peak deconvolution was performed as shown in the sample that underwent wet PCA at 500 °C.

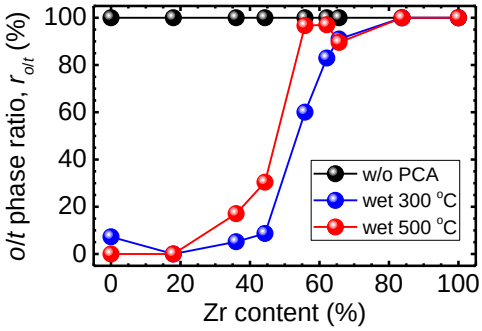

Fig. 2 $r_{o/t}$ as a function of the Zr content for $Hf_{1-x}Zr_xO_2$ films that did not undergo PCA and underwent wet PCA at 300 °C and 500 °C.

Here, $I_{o111/t101}$, $I_{m11\bar{1}}$, and I_{m111} are area intensities of $o111/t101$, $m11\bar{1}$, and $m111$ peaks.

Figure 2 shows $r_{o/t}$ as a function of the Zr content in $Hf_{1-x}Zr_xO$ films. For HfO_2, the $t/o \rightarrow m$ transition is progressed with increasing the wet PCA temperature, which is consistent as so far reported [4]. However, with increasing the Zr content, this tendency changed so as to much progress the $t/o \rightarrow m$ transition at a lower temperature. This phenomenon can be understood based on the phase diagram of $Hf_{1-x}Zr_xO_2$ thin film as shown in Fig. 3. For $Hf_{1-x}Zr_xO_2$, the *m*-phase is most stable at a low temperature, whereas the most stable phase changes to the *t*-phase by increasing temperature. The boundary temperature at which the most stable phase switches from the *m*-phase to *t*-phase decreases along on the way from HfO_2 to ZrO_2. This boundary temperature decreases by film thinning because the contribution of surface energy increases compared to bulk energy [2, 5]. According to the phase diagram, the *t*-phase is likely to be stabilized in the condition of Zr-rich film and high temperature, which well explains GIXRD results.

When the phase transition is followed on the phase diagram, the ferroelectric *o*-phase should appear along on the way from *t*- to *m*-phase according to a previous report [6]. To verify that, we discussed electric properties of $Hf_{1-x}Zr_xO_2$ film. Figure 4 shows *P-E* curves of (a) $Hf_{0.56}Zr_{0.44}O_2$, (b) $Hf_{0.34}Zr_{0.66}O_2$, and (c) $Hf_{0.16}Zr_{0.84}O_2$ films those did not undergo PCA and underwent wet PCA at 300 °C and 500 °C. For comparison, *P-E* curve of $Hf_{0.56}Zr_{0.44}O_2$ film that underwent dry PCA at 300 °C is also shown in Fig. 4(a).

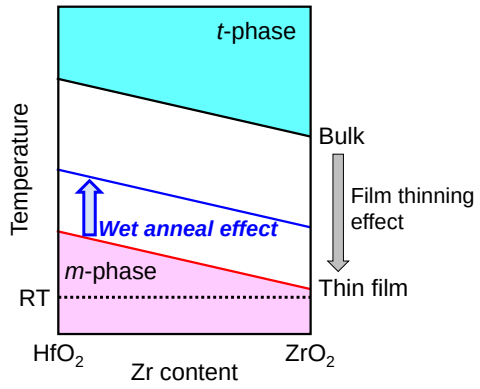

Fig. 3 Schematic phase diagram of $Hf_{1-x}Zr_xO_2$ at atmospheric pressure for both bulk material and thin film. The white region is a transient region from bulk to thin film. It is considered that the effect of wet annealing is to suppress the film thinning effect.

$Hf_{0.56}Zr_{0.44}O_2$ films those did not undergo PCA and underwent dry PCA show antiferroelectric (AFE) like hysteresis. AFE like hysteresis changes to ferroelectric hysteresis by wet PCA and a large P_r is obtained for the sample that underwent wet PCA at 300 °C, which has a large $r_{o/t}$ value. Next, for the $Hf_{0.34}Zr_{0.66}O_2$ films that underwent wet PCA at 300 °C and 500 °C, which $r_{o/t}$ values are an approximately 90 %, those *P-E* curves show ferroelectric hysteresis with a large P_r although the shape of *P-E* curves is slightly deformed. Then, with increasing Zr content, P_r values are decreased compared to the $Hf_{0.34}Zr_{0.66}O_2$ films as shown in Fig. 4(c). These facts suggest that the ferroelectric *o*-phase is formed along on the way from *t*- to *m*-phase for $Hf_{1-x}Zr_xO_2$ underwent wet PCA.

Finally, we discussed the wet annealing effect from the view point of thermodynamics. The effect of wet PCA is considered as increasing the boundary temperature as shown in Fig. 3. Possible two mechanisms to increase the boundary temperature are oxygen addition in the film and the decrease of the surface energy difference among *t*-, *o*-, and *m*-phases by H_2O adsorption on grain boundaries [7, 8]. Considering that the phase transition is much progressed by wet PCA than dry PCA, the change of the surface energy during annealing would be contributing to progress of the martensitic phase transition.

4. Conclusions

We discussed the effect of wet PCA on the phase transition and the formation of ferroelectric *o*-phase of $Hf_{1-x}Zr_xO_2$ films. It was found that the phase transition of $Hf_{1-x}Zr_xO_2$ caused by the wet PCA follows its phase diagram, and the ferroelectric *o*-phase is formed along on the way from *t*- to *m*-phase. This finding infers that the key role of wet annealing for this system is to suppress the film thinning effect, resulting in promotion of the phase transition.

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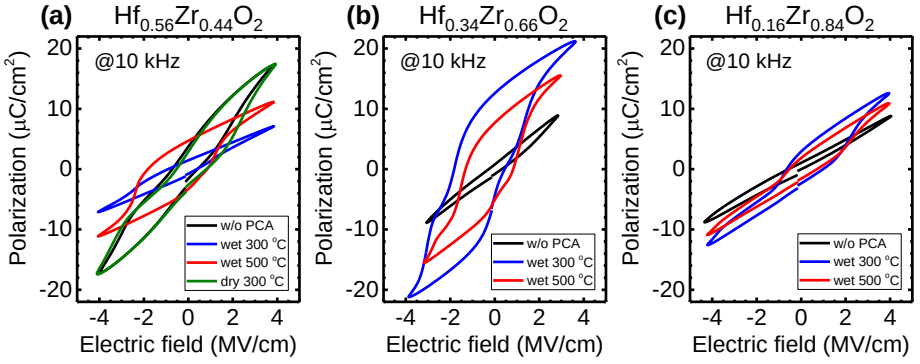

Fig. 4 *P-E* curves measured at 10 kHz for samples of (a) $Hf_{0.56}Zr_{0.44}O_2$, (b) $Hf_{0.34}Zr_{0.66}O_2$, and (c) $Hf_{0.16}Zr_{0.84}O_2$ films that did not undergo PCA, and underwent wet PCA at 300 °C and 500 °C. For the $Hf_{0.56}Zr_{0.44}O_2$ film, *P-E* curve of the sample underwent dry PCA at 300 °C was also shown in (a).