Effect of internal-strain caused by monoclinic phase formation on ferroelectric phase formation of ZrO₂

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Abstract

Ferroelectric phase formation in ZrO_2 thin films is demonstrated with the help of the heterogeneous nucleation of monoclinic phase ZrO_2 . This fact strongly supports our view that the internal strain induced by nucleated monoclinic phase to originally existing tetragonal one is a key to making the binary oxide ferroelectricity to appear, including ZrO_2 as well as HfO₂.

Introduction

It was recently reported that HfO_2 ferroelectric properties were achieved by forming the non-centrosymmetric orthorhombic structure, $Pca2_1$ [1,2]. In addition, it was found that HfO_2 has a universal kinetic pathway for the phase transition; cubic (c)/ tetragonal (t) \rightarrow orthorhombic (o) \rightarrow monoclinic (m), and the ferroelectric phase in HfO_2 is likely to be formed at the coexistence condition of t- with m-phases [3]. Moreover, it has been recently reported that un-doped ZrO₂ also shows ferroelectric properties in the coexistence condition of t- with m-phases [4]. Now, we need a more general guideline to control the ferroelectricity of HfO_2 and ZrO_2 binary oxides.

In this paper, we discuss the effect of *m*-phase on the ferroelectric phase appearance in ZrO_2 . We think that a study of ZrO_2 should help us to clarify the physical origin of the ferroelectric phase formation, because *t*-phase only appears in thin ZrO_2 films in general conditions.

Experiments

p⁺-Ge(001) or Pt substrate was used as the bottom electrode. After conventional chemical cleaning of substrates, non-doped ZrO_2 were deposited by rf-sputtering at several deposition temperatures (T_{depo}), followed by the post-deposition annealing (PDA) at 600°C for 30 s in N₂ ambient. Finally, Au was deposited for the top electrode.

Results and discussion

According to the phase diagram of ZrO_2 [5], *m*-phase is the ground state of ZrO_2 at room temperature and under atmospheric pressure. Since it is well known that oxygen vacancy may help to transform from *m*- to *t*- or *c*-phase [6], we first tried to reduce the oxygen vacancy by high pressure O₂ PDA. In fact, no change was, however, unfortunately detected. Next, by considering that the surface energy contribution in a small crystalline grain make it more symmetric phase such as *t*- or *c*-phase, 80-nm-thick ZrO_2 was grown. *m*-phase was reasonably observable as shown in **Fig. 1(a)**, and ferroelectric *P*-*E*

curve was observed (Fig. 1(b)).

Above fact suggests that the *m*-phase appearance in thin films could also form the ferroelectric phase in ZrO_2 . Therefore, the next step is how to form *m*-phase ZrO_2 in thin film region. We have paid attention to the heterogeneous nucleation rather than the homogeneous one. Two methods were tested in this work. One was (1) the high temperature sputtering [4], and the other was (2) room temperature sputtering on Pt substrate. Figs. 1(a) and 1(b) also show XRD pattern and *P*-*E* curve of Pt substrate case. The *m*-phase formation and ferroelectric *P*-*E* hysteresis were both observed for Pt substrate case.

Most of the results so far reported including HfO₂ cases indicate that *t*-phase associated with *m*-phase is crucial for making ferroelectric properties to appear. This will give us a hint for controlling the ferroelectric phase. Therefore, we next discuss why *m*-phase is needed for the ferroelectric phase formation. **Figure 2** shows XRD pattern change of un-doped ZrO₂ with the increase in the substrate temperature during the sputtering. The symmetric phase o/t(111) diffraction peak shifts toward the lower 2θ direction together with the *m*-phase appearance. **Figure 3** shows the 2θ of o/t(111) peak $(2\theta_{111})$ and its lattice spacing (d_{111}) as a parameter of *m*-phase fraction, r_m , which was estimated in the followed equation,

 $r_m = \{I_m(11-1)+I_m(111)\}/\{I_m(11-1)+I_{n/t}(111)+I_m(111)\}.$ (1) Here, $I_m(11-1)$, $I_{0/t}(111)$, and $I_m(111)$ are area intensities of m(11-1), o/t(111), and m(111) peaks, respectively. Fig. 3 includes the data of un-doped ZrO₂ with several deposition temperature, in addition to thick ZrO₂ and Pt substrate cases. It is observable that $2\theta_{111}$ monotonically decreases with the increase in *m*-phase fraction. Regardless of the homogeneous or heterogeneous *m*-phase nucleation, $2\theta_{111}$ shifts along on a given line. It is inferred from this result



Fig. 1(a) XRD patterns and (b) *P*-*E* curves measured at 100 kHz for samples of 80-nm-thick ZrO_2 on p⁺-Ge(001) and 30-nm-thick ZrO_2 on Pt, respectively. ZrO_2 film was sputtered at room temperature.



Fig. 2 XRD patterns of ZrO₂ deposited with several temperatures, followed by PDA. o/t(111) peak shift toward lower 2θ direction with m-phase formation is observable.



that *m*-phase nucleation may locally affect *t*-phase to induce the other phase nucleation with the help of an internal strain due to crystallographic shape mismatch.

To quantitatively discuss the internal strain effect on the ZrO₂ ferroelectricity, the strain in the out-of-plane direction is evaluated by the following equation,

$$\varepsilon_{\text{out-of-plane}} = (d_{111} - d_{111,t})/d_{111,t} \times 100 \ (\%).$$
 (2)

Here, $d_{111,t}$ means d_{111} of t-phase, which was estimated from $2\theta_{111}$ extrapolated to $r_m=0$ in Fig. 3. Also, ZrO₂ ferroelectricity is estimated from the switchable polarization $(P_{sw}=P_r^+-P_r^-; P_r^+)$ and P_r^- are positive and negative remanent polarization, respectively). Figure 4(a) shows P_{sw} as a parameter of $\varepsilon_{out-of-plane}$. Since $\varepsilon_{out-of-plane}$ is positive, the crystalline configuration of t- and m-phases in ZrO₂ should be a columnar type as schematically shown in Fig. 4(b) when the hydrostatic pressure condition is assumed. Note that P_{sw} increases with the increase in ε_{out} of-plane up to ~0.5 %, while it decreases in the region of ε_{out} of-plane more than ~0.5 %. This result indicates that the internal strain should enhance the ZrO₂ ferroelectricity, while the large internal strain stabilizes m-phase transformation.

Our view proposed in this study seems to be naturally applicable to HfO₂ as well. Namely, the crucial point for realizing the ferroelectric phase is how to make the internal strain feasible in *t*-phase HfO₂ (ZrO₂) films with the help of *m*-phase.



Fig. 3 2 θ position and lattice spacing of o/t(111)diffraction peak of ZrO₂. The data of ZrO₂ with several T_{depo} , thick-ZrO₂, and Pt substrate cases are included.

m

-plane

Fig. 4 (a) switchable polarization, P_{sw} as a parameter of out-of-plane strain, *ɛ*out-of-plane. Since $\varepsilon_{out-of-plane}$ is positive, the crystalline configuration of t- and m-phases in ZrO₂ should be a columnar type as schematically shown in (b).

Conclusion

This work has discussed the most critical point in the recent binary oxide ferroelectricity. That is why the ferroelectric phase in binary oxides is likely to be formed in the condition of coexistence of t-phase with m-phase. By investigating un-doped ZrO₂ ferroelectricity, we strongly suggest that the origin of ferroelectric ZrO₂ (HfO₂ as well) is from the structural cooperation of *t*-phase with *m*-phase ZrO₂.

Acknowledgments

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