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| **6B-3** | **Nucleation-driven ferroelectric phase formation in ZrO2 thin films** |

-**What is different in ZrO2 from HfO2 ? -**   
Shigehisa Shibayama1, Tomonori Nishimura1, Shinji Migita2, and Akira Toriumi1 1The Univ. of Tokyo, Tokyo, Japan, shibayama@adam.t.u-tokyo.ac.jp   
 2National Institute of Advanced Industrial Science and Technology, AIST

**Abstract**   
Ferroelectric phase formation of ZrO2 thin films is discussed by paying attention to the film deposition

comparing those of HfO2.

Therefore, we have investigated the stabilization mechanism of FE phase of ZrO2.

process and doping into ZrO2, by comparing with the **Experiments**

HfO2 counterpart. The results are showing a considerable difference between ZrO2 and HfO2 in terms of the stability against thermal annealing process. It is inferred that this is likely to be originated from the activation energy difference in the structural phase transitions from tetragonal to orthorhombic and subsequent orthorhombic to monoclinic phase transitions.

(Keywords: ZrO2, HfO2, ferroelectric)

**Introduction**   
It was recently reported that HfO2 ferroelectric (FE) properties was achieved by forming the non-centrosymmetric orthorhombic structure, Pca21 [1, 2]. In addition, it was found that HfO2 had a universal kinetic pathway for the phase transition; cubic (*c*)/ tetragonal (*t*)  orthorhombic (*o*)  monoclinic (*m*) [3]. This phase transition can be controlled by a deformation factor in the structural phase transition. On the other hand, Hf0.5Zr0.5O2 has often been studied as a ferroelectric film because of its broad concentration sensitivity [4]. Moreover, it has been recently reported that non-doped ZrO2 also exhibits FE properties in some conditions, in addition to the fact that it usually indicates anti-ferroelectric (AFE) properties [5-8].

A recent theoretical calculation discusses that AFE hysteresis in ZrO2 is caused by the electric field induced phase transition from tetragonal to non-centrosymmetric orthorhombic phase (Pca21) [5]. Experimentally, it was reported that FE ZrO2 was formed by a stress from the substrate [6, 7]. TiN/MgO(001) or Pt substrates were used for inducing the stress. Another paper reported ~190-nm-thick FE ZrO2, which was formed by the chemical solution deposition method, by focusing on the piezo-electric application [8].

ZrO2 has similar physical properties with HfO2 in terms of ionic radii, electron negativity, and crystalline phases. To elucidate those Zr-related issues, it is needed to understand structural properties in conjunction with FE properties of ZrO2 by

p+-Ge(001) substrate was used as the backside metal because it was reported that p+-Ge backside metal gave a good interface properties compared to other metals [9]. After conventional chemical cleaning of p+-Ge(001) substrate, ~30-nm-thick non-doped ZrO2 were deposited by rf-sputtering at several deposition temperatures (*T*depo). Subsequently, the post-deposition annealing (PDA) at 400–600°C for 30 s in N2 ambient was carried out. Finally, Au was deposited as a top gate. Doped ZrO2 was deposited by rf-co-sputtering, also at room temperature (RT). The crystalline structure was characterized by the grazing angle out-of-plane X-ray diffraction (XRD) method. Both FE and AFE properties were characterized by polarization-electrical field (*P*-*E*) measurements at 100 kHz.

**Results and discussion**   
 *~Stability of tetragonal phase ZrO2~*   
 First, we focus on the effects of annealing and doping on phase transition from *c*/*t* to *m* phase for ZrO2 films deposited at RT, because they are key parameters in FE HfO2 formation. **Figure 1** shows PDA temperature dependence of (a) out-of-plane XRD patterns and (b) *P*-*E* curves. The crystalline structures of ZrO2 films annealed at 400–600°C are all highly symmetric phases with no monoclinic phase. Here, highly symmetric (*h*) phase denotes the phase including cubic, tetragonal and orthorhombic ones, because they are not distinguishable from each other. Fig. 1 (b) shows that AFE hysteresis is more clearly observed by increasing the PDA temperature from 400 to 600°C. Considering AFE property of ZrO2 film is achieved in the tetragonal, the results in Fig. 1(a) show these films are with tetragonal phase. Furthermore, although high temperature XRD measurements were carried out, no monoclinic phase was observed up to 600°C (*not shown*). This fact indicates that the tetragonal phase in ZrO2 is thermally quite stable comparing with HfO2, as expected thermodynamically.

Next the doping effect in ZrO2 is discussed. Since we already demonstrated that Nb5+ doping

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strongly induced the monoclinic phase in HfO2 [3], temperature.

Nb was also introduced into ZrO2. **Figure 2** shows (a) out-of-plane XRD patterns and (b) *P*-*E* curves, of Nb-doped ZrO2. Interestingly, *m* phase is observed, though very slightly and AFE-hysteresis is broadened, in only 2.26 at.% Nb doped ZrO2. A large amount of Nb doping (9.96 at.%) suppresses the crystallization ZrO2. This tendency is substantially different from

**Figure 3** shows the out-of-plane XRD pattern of ZrO2 films deposited at 300, 400, and 500°C, respectively. Both results with and without PDA at 600°C for 30 s in N2 ambient are shown. By increasing the deposition temperature, m-phase formation is clearly observed even for as deposited samples. In addition, it is found that *h*(111) peak

that in HfO2. position shifts toward the lower 2*θ* direction

Neither PDA nor doping is effective to cause the phase transition from *t* to *m* phase in ZrO2. This fact indicates that the activation energy of ZrO2 from *t* to m phase (*Et**m*) is much larger than that of HfO2.

*~Ferroelectric orthorhombic nucleation ~*   
 The sputtering deposition at a low temperature generally leads to a non-equilibrium phase, which is the tetragonal phase in the case of ZrO2. According to a phase diagram of ZrO2, the monoclinic phase is a most stable one at room temperature and atmospheric pressure. Since a higher temperature deposition may enable to achieve an equilibrium one, the m-phase formation is expected by the sputtering at a high

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| Intensity (arb. unit) | **PDA temperature** | | | 2) | | | | 20 | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | | | | | |
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| *m*(11-1) *h(111)* | | | | | | | 2) | 20  -10  -20  0   |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | |  |  |  |  |  |  |
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