

## New Material Approach to Enhance Spontaneous Polarization in Ferroelectric HfO<sub>2</sub>

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### Abstract

We propose and demonstrate new material approach to enhance spontaneous polarization in ferroelectric HfO<sub>2</sub>. While the orthorhombic (*o*-) phase fraction increase and the orientation control have been proposed so far, we focus on the elongation of dipole charge displacement ( $\delta$ ) as a new approach. It is expected that  $\delta$  can be controlled with the unit cell volume of *o*-phase because the dipole originates in the displacement of oxygen in *o*-phase. We found that the unit cell volume of Zr-doped HfO<sub>2</sub> films can be controlled by incorporating carbon content. We experimentally demonstrate that the enlargement of the unit cell volume is effective to further enhance the spontaneous polarization.

### 1. Introduction

Ferroelectric HfO<sub>2</sub> has attracted much attention because of the Si process compatibility. Among various kinds of ferroelectric devices, HfO<sub>2</sub>-based ferroelectric tunnel junction (FTJ) memory is promising for low-power in-memory AI computing [1-3]. One of the most important properties of ferroelectric film for FTJ applications is spontaneous polarization. Polarization ( $P$ ) is expressed with the following equation,

$$P = N \cdot q \cdot \delta \cdot \langle \cos\theta \rangle, \quad (1)$$

where  $N$  is the density of dipole moment ( $q \cdot \delta$ ),  $q$  is the separated charge,  $\delta$  is the charge displacement, and  $\langle \cos\theta \rangle$  is the averaged orientation as shown in the inset of Fig. 1. Because the ferroelectricity comes from the orthorhombic (*o*-) phase in HfO<sub>2</sub>, the *o*-phase fraction increase [4] for higher  $N$  and the orientation control [5] for higher  $\langle \cos\theta \rangle$  have been intensively studied so far. These approaches have been found to be effective for the  $P$  enhancement. However, these factors have upper limits: the highest *o*-phase fraction is 100% and the highest  $\langle \cos\theta \rangle$  is 1. To further increase  $P$ , the dipole moment ( $q \cdot \delta$ ) should be enhanced.

In this paper, as shown in Fig. 1, we focus on the displacement of dipole charge ( $\delta$ ). The origin of dipole is the displacement of oxygen in *o*-phase. Therefore, we consider that  $\delta$  can be controlled with the unit cell volume ( $V$ ) because it can be assumed that the oxygen drastically move in the large unit cell. We established the technique to control  $V$  with carbon content in Zr-doped HfO<sub>2</sub> (HZO) and demonstrated the enhancement of  $P$  with increasing  $V$ .

### 2. Experiment

A 10-nm-thick HZO film was deposited by ALD process on a Si substrate covered with a bottom metal electrode. To control carbon content in the HZO, we changed two process conditions: deposition temperatures (High-T, Middle-T, and Low-T) and oxidation time (Long-O, Middle-O, and Short-O). After deposition of cap metal, post-metallization annealing (PMA) was carried out for the crystallization of the HZO films. Finally, a top metal electrode was formed.

### 3. Results and discussion

Firstly, we measured the carbon content in as-deposited HZO films without the cap metal. Carbon content can be drastically changed with the deposition temperature:  $2.4 \times 10^{21} \text{ cm}^{-3}$  (Low-T) to  $9.0 \times 10^{19} \text{ cm}^{-3}$  (High-T) at Short-O (Fig. 2(a)). As shown in Fig. 2(b), the carbon content is related to not only the deposition temperature but also the oxidation time.

Fig. 3(a) shows the in-plane XRD spectrum for various T and Short-O after the PMA. The  $o/t(111)$  peak at  $\sim 30^\circ$  shifts toward the lower  $2\theta$  direction with lower T, which indicates that lattice space  $d_{111}$  is increased. We analyzed the lattice constant of the *o*-phase by using a whole-powder-peak-deconvolution method for the XRD spectrum. As shown in Fig. 3(b), a universal relationship between the carbon content and the unit cell volume is observed, specifically, the unit cell volume is increased with the carbon content. In our work, the maximum difference of unit cell volume is as large as  $1.8 \text{ \AA}^3$ , which is comparable to the difference of unit cell volume between pure HfO<sub>2</sub> and pure ZrO<sub>2</sub> estimated with DFT calculation ( $\sim 2.4 \text{ \AA}^3$ ) [6]. This result indicates that we can control the unit cell volume for a wide range using the carbon content.

We also checked the monoclinic (*m*-) phase fraction ( $r_m$ ) in the HZO films. As shown in Fig. 4(a), not only  $o/t(111)$  but also  $m(11-1)$  and  $m(111)$  peaks are observed for Long-O and Middle-O at Middle-T. The  $r_m$  was estimated with the following equation,

$$r_m = \{I_{m(11-1)} + I_{m(111)}\} / \{I_{m(11-1)} + I_{o/t(111)} + I_{m(111)}\}. \quad (2)$$

Here,  $I_{m(11-1)}$ ,  $I_{o/t(111)}$ , and  $I_{m(111)}$  are area intensities of  $m(11-1)$ ,  $o/t(111)$ , and  $m(111)$  peaks, respectively. Fig. 4(b) shows the  $r_m$  as a function of the carbon content. The *m*-phase is suppressed with carbon content, which is consistent with the

phase transition from the  $m$ -phase to a highly symmetrical phase reported for HfO<sub>2</sub> with carbon incorporation [7].

We measured the  $P$ - $V$  of the fabricated MIM capacitor (inset of Fig. 5(a)) and extracted the maximum remnant polarization ( $2P_r$ ). Fig. 5(a) shows the  $2P_r$  as a function of the  $m$ -phase fraction. In Fig. 5(a), we can see a reasonable trend of  $2P_r$  decrease with increasing  $r_m$ . The dashed line in Fig. 5(a) is the fitting result with  $2P_r = A'N = A(1-r_m)$  for each plot. Note that the fitting parameter ( $A$ ) corresponds to the terms except for  $N$  in eq. (1). These lines are separated from each other because they have different  $A$  values. This indicates there is an additional factor besides  $r_m$  to enhance  $2P_r$ . Then, we summarized the  $2P_r$  as a function of unit cell volume in Fig. 5(b). As expected,  $2P_r$  increases with unit cell volume as shown in Fig. 5(b). In this way, we successfully demonstrated the effectiveness of unit cell volume enlargement for higher  $P_r$  in doped HfO<sub>2</sub>.

#### 4. Conclusions

We focused on the elongation of dipole charge displacement ( $\delta$ ) as a new material approach to enhance spontaneous polarization. We experimentally demonstrated that increasing unit cell volume with carbon content improves the  $2P_r$  as a result of the increased displacement of oxygen atoms in  $o$ -phase. Therefore, in addition to the control of the  $o$ -phase fraction and the orientation,  $\delta$  engineering with unit cell volume is a key to further enhance spontaneous polarization in ferroelectric HfO<sub>2</sub>.

#### References

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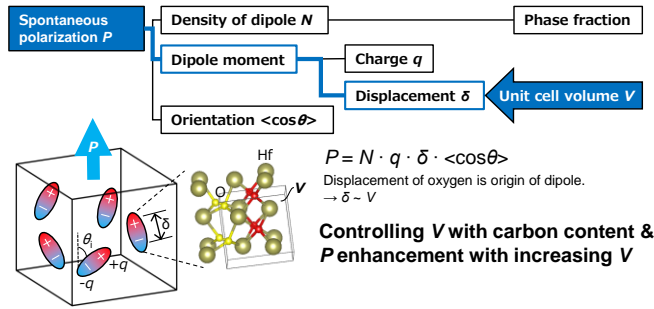


Fig.1 Concept of this work.

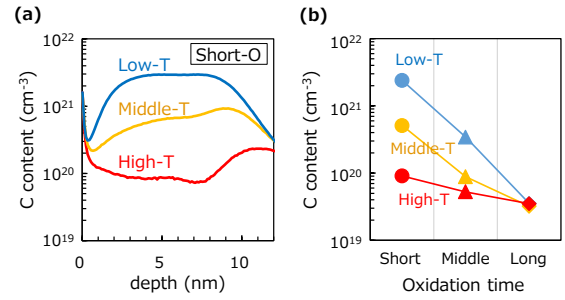


Fig.2 (a) SIMS depth profile and (b) C content in the HZO.

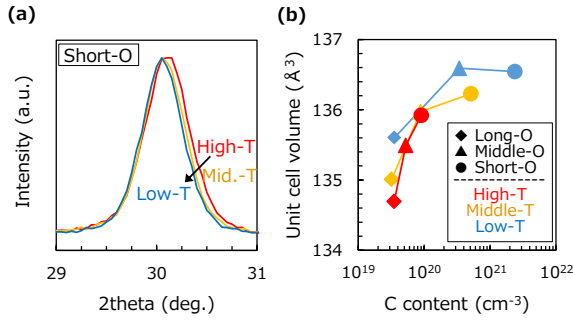


Fig.3 (a) In-plane XRD spectrum for the HZO (Short-O) and (b) unit cell volume of  $o$ -phase as a function of C content in the HZO.

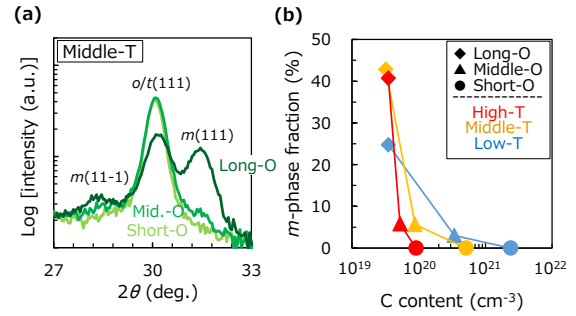


Fig.4 (a) In-plane XRD spectrum for the HZO (Middle-T) and (b)  $m$ -phase fraction as a function of C content.

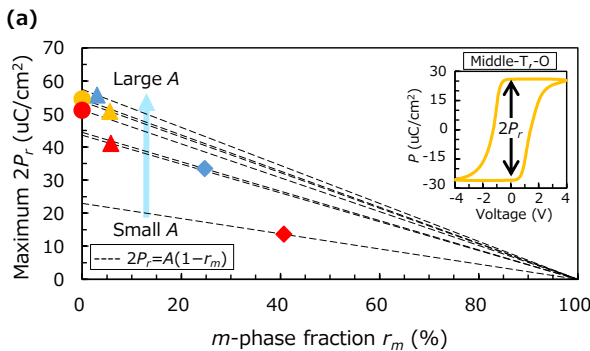


Fig.5 Maximum  $2P_r$  for the HZO as a function of (a)  $m$ -phase fraction and (b) unit cell volume. Inset of (a) shows typical  $P$ - $V$  curve.