Relationship between the Waking-up Effect and Structural Distortion in Ferroelectric HfO₂ characterized by X-ray Diffraction

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Abstract

The possible origin of the waking-up effect in ferroelectric (FE) HfO₂ was investigated via the analysis of structural distortion using X-ray diffraction. We found a remarkable increase in the difference in the in-plane and out-of-plane interplanar spacing ($d_{spacing}$) with the increase in the waking-up ratio of FE-HfO₂. Although the mechanism has not been clarified yet, the result provides evidence of the relationship between the waking-up ratio and the amount of structural distortion in FE-HfO₂.

1. Introduction

Since the discovery of FE-HfO₂, it has become one of the hottest functional oxides in CMOS applications due to its high compatibility with the current Si-technology.[1] While bulk HfO₂ crystallizes into the none polar monoclinic (m-) phase, the non-centrosymmetric polar orthorhombic (o-) phase can be induced and stabilized by external factors, such as dopants and surface energy.[2,3] Despite the intensive investigation on the fabrication process of FE-HfO₂, it is commonly observed that the switchable polarization (P_{sw}) of FE-HfO₂ often increases during the device operation, so-called the waking-up effect. It was suggested that the waking-up of P_{sw} is the result of the evolution of defect distribution and phase transformation during bipolar cycling.[4] In this study, we are focusing on the relationship between the waking-up ratio of FE-HfO₂, and the difference between the difference of in-plane and out-of-plane $d_{spacing}$.

2. Experimental Method

It has already been studied that the amount of o-phase in HfO₂ can be controlled by Y-doping concentration.[5] Hence, three types of 30 nm-thick HfO₂ MIM capacitors with different Y-doping concentrations were fabricated: pure-HfO₂, Y-doped HfO₂ (Y-HfO₂), and high Y-doped HfO₂ (high Y-HfO₂). The Y-concentrations of Y-HfO₂ and high Y-HfO₂ were estimated by XPS to be in the range of 1.5 -4.5% and >7% cation ratio, respectively. All capacitors were fabricated by rf-sputtering HfO₂ on heavily doped p-Ge substrates, where the Y-dopant was introduced by co-sputtering HfO₂ and Y₂O₃. Then, post-deposited-annealing (PDA) was performed at 600°C in N₂ ambient for 30 s, followed by the deposition of Au top electrodes. The waking-up effect of FE-HfO₂ was characterized by 12 V pulse bipolar cycling at the frequency of 10 kHz. The structure of HfO₂ was analyzed using in-plane XRD and conventional out-of-plane XRD with $2\theta/\theta$ scan.

3. Result and Discussion

Fig. 1(a) shows the P-V characteristics of Y-HfO₂ at different stages during cycling, and the changes in P_{sw} during cycling are summarized in Fig. 1(b). The waking-up ratio ($r_{wake}= 1-P_{sw,\ pristine}/P_{sw,\ max}$) was used to quantify the amount of waking-up effect. A significant waking-up effect ($r_{wake}=0.37$) was observed on Y-HfO₂; whereas, a slight waking-up effect ($r_{wake}=0.05$) is observed in pure-HfO₂. For high Y-HfO₂, the Y-incorporation lead to the transition tetragonal (t-) and cubic (c-) phase, therefore is paraelectric.[5]

An example of Y-HfO₂'s in-plane and out-of-plane XRD patterns are shown in Fig. 1(c). From the figure, there is a significant shift in the peak position to a lower angle when the measurement was made in the in-plane diffraction. This indicates that there is a remarkable difference in $d_{spacing}$ that is parallel (out-of-plane) and perpendicular (in-plane) to the HfO₂'s surface. We hypothesize that there is a significant lattice distortion in the FE-HfO₂ structure.
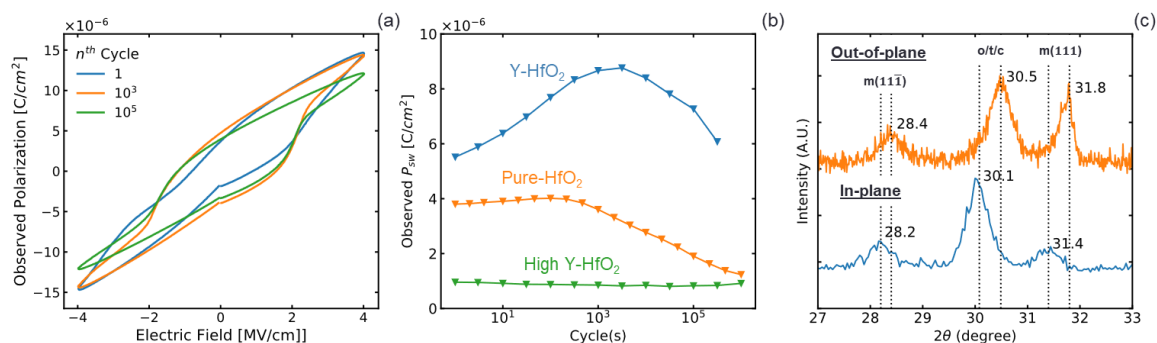

Fig. 1 (a) P-V and I-V characteristics of Y-HfO₂ at its pristine, 10³, and 10⁵ cycles. The change in P_{sw} during bipolar voltage cycling at 12 V and 10 kHz. (c) Out-of-plane and in-plane XRD (with incident angle of 0.45°) of Y HfO₂. Note that all XRD data were made without neither the top Au electrode nor electrical treatments.

To estimate the amount of structural distortion, we compared the observed in-plane and out-of-plane d_{spacing} of the higher symmetric (o/t/c) phases. The in-plane d_{spacing} seems slightly larger than the d_{spacing} of the reported values of relaxed t-[6] and c-[7] phase, which is indicated in Fig. 2(a). It is known that the stabilization of the polar o-phase in HfO$_2$ is closely related to the introduction of tensile strain in HfO$_2$ film during the annealing process.[8,9] Our results show that there was a slight expansion in the in-plane d_{spacing}. On the contrary, the out-of-plane d_{spacing} was anomalously shrunk when compared with the in-plane d_{spacing} and the reported values.

One might expect that the tensile strain induced by the substrate to have a depth dependence. Fig. 2(b) shows the depth dependence of HfO$_2$'s in-plane d_{spacing} measured by in-plane XRD at various incident angles. In the shallow region, there is a decrease in the Y-HfO$_2$'s and pure-HfO$_2$'s in-plane d_{spacing}. As expected from a PDA condition, there is relaxation of d_{spacing} as it moves further away from the substrate. Despite the relaxation, the in-plane d_{spacing} of Y-HfO$_2$ is still larger than its out-of-plane d_{spacing} as opposed to the in-plane d_{spacing} of pure-HfO$_2$ that approaches its out-of-plane d_{spacing}. On the other hand, the in-plane d_{spacing} of high Y-HfO$_2$ was almost unaffected by its depth. It is important to notice that there is still a large difference between the in-plane and out-of-plane d_{spacing} of high Y-HfO$_2$, despite being paraelectric.

Fig. 3 The relationship between r_{wake} and $\Delta d_{\text{spacing, in-out}}$ of o/t/c phases. The dotted line is the modelling of the relationship.

To explain the anomalous shrinkage of the out-of-plane d_{spacing} and how it affects the waking up phenomenon in FE-HfO$_2$, we consider the relationship between the r_{wake}, and the difference between the in-plane and out-of-plane d_{spacing} of o/t/c phases ($\Delta d_{\text{spacing, in-out}}$), as shown in Fig. 3(a). By assuming that the formation of the polar o-phase is facilitated by the lattice distortion of its parental t-phase,[9] we speculate that the pristine difference in the in-plane and out-of-plane d_{spacing} (induced by the annealing process) is one of the driving forces on the waking-up effect in FE-HfO$_2$. This would infer that FE-HfO$_2$ with a large $\Delta d_{\text{spacing, in-out}}$ would have a larger r_{wake} by the phase transformation of the provisional polar t-phase to polar o-phase during cycling. So far, our experimental finding is in good agreement with our consideration.

4. Conclusion

From bipolar cycling, a significant amount of waking-up effect was observed in Y-HfO$_2$; whereas, a small waking-up effect was found on pure-HfO$_2$. By analyzing the lattice structure of HfO$_2$, it was found that there is a remarkable difference in the in-plane and out-of-plane d_{spacing} of FE-HfO$_2$. The in-plane d_{spacing} was slightly expanded, whereas the out-of-plane d_{spacing} was significantly shrunk when comparing to the reported values of the relaxed d_{spacing}. Although the mechanism is still under investigation, the relationship between the $\Delta d_{\text{spacing, in-out}}$ and the observed r_{wake} of FE-HfO$_2$ can be explained by our proposed model that the significant distortion (expressed as $\Delta d_{\text{spacing, in-out}}$) in HfO$_2$ film is one of the factors that drive the waking-up effect of FE-HfO$_2$.
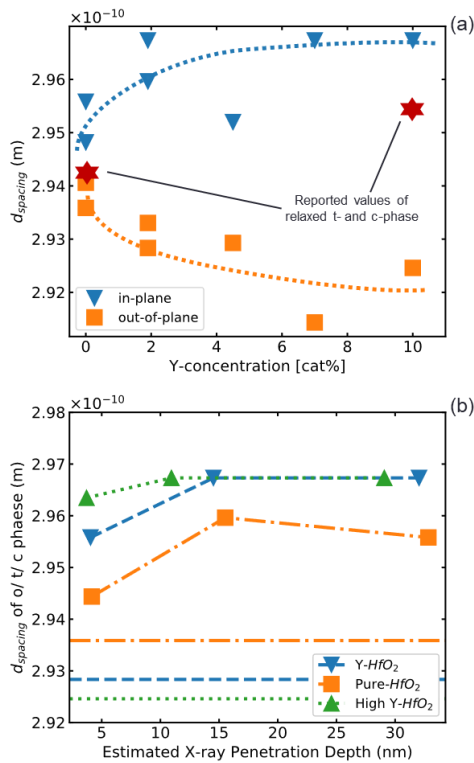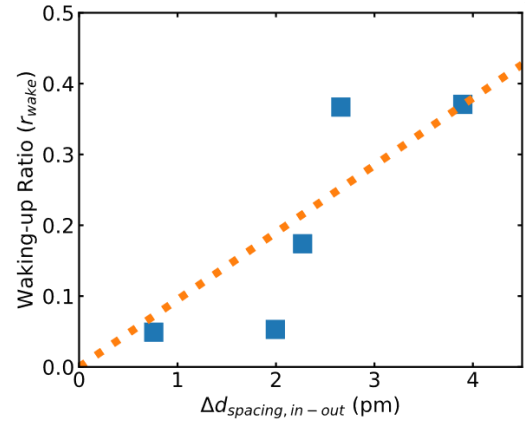

Fig. 2 (a)The d_{spacing} of o/t/c phases at different Y-doping concentrations in the in-plane and out-of-plane directions. The reported value of relaxed d_{spacing} of the t-phase and c-phase are indicated by the red stars. (b) The depth dependence of the in-plane d_{spacing} of o/t/c phases of pure-HfO$_2$, Y-HfO$_2$, and high Y-HfO$_2$. The horizontal lines are indicating d_{spacing} determined from the $2\theta/\theta$ scan.

5. References

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