強誘電性 HfO_2 の Waking-up 過程において電界印加で駆動される相変態の XRD による直接観察

Direct Evidence of Electric Field driven Phase Transformation in the Waking-up Process of Ferroelectric HfO_2 Characterized by Conventional X-ray Diffraction

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[Introduction] One of the remaining issues of ferroelectric (FE) HfO_2 technologies is the waking-up effect. This effect has been observed in ferroelectric HfO_2 with various dopants, and it is considered to be the result of the phase transformation, driven by an electric field, to increase the amount of the orthorhombic (O-) phase [1]. The change in the lattice structure has been locally observed by TEM [2] and a synchrotron XRD on a microscopically small area under the top electrode [3]. In this study, we would like to provide direct evidence of the phase transformation driven by voltage cycling in FE-HfO_2 thin films using conventional XRD techniques.

[Experimental] Two types of MFM capacitors with ~30 nm-thick HfO_2 were fabricated: 1.5 cat% Y-doped HfO_2 (Y-HfO_2) and pure HfO_2 on Ge substrate. To evaluate the crystal structure by conventional XRD, the signal intensity of the 'woke-up' HfO_2 has to be amplified. Hence, an array of 144 Au top electrodes with the size 400×400 μm was patterned on a 5×5 mm HfO_2/Ge stacks using photolithography. After that, 10^3 cycles of voltage cycling were individually applied to the 144 capacitors at 12 V and the frequency of 10 kHz. The woke-up ratio [$r_{woke} = (P_{max} - P_{initial})/P_{amx}$] was used to quantify the amount of the waking-up effect. Finally, the Au top electrodes were physically removed before the XRD measurement. We estimated the volume ratio of the higher symmetric (o/t/c) phase ($r_{o/t/c}$) before and after the waking-up cycles, as the ratio of o/t/c peak intensity to the total intensities of o/t/c, m(111), and m($11\bar{1}$) peaks.

[Results and Discussions] The average r_{woke} of all 144 Au/Y-HfO_2Ge and Au/HfO_2/Ge capacitors was calculated to be 0.25 and 0.14 (data not shown), respectively. Fig.1 shows the in-plane XRD of Y-HfO_2 before and after 10^3 cycles of voltage cycling. The increase in the estimated r_{otc} with the number of voltage cycling is shown in Fig. 2. It is clear that the phase transformation, driven by voltage cycling, increased the amount of $r_{o/t/c}$. We also found that the increase in the $r_{o/t/c}$ correlates with the r_{woke}, as shown in Fig. 3. For the first time, we have provided direct evidence that the phase transformation that increases the $r_{o/t/c}$ is driven by an electric field. One might notice the shift in the peak positions in Fig. 1. It is important to note that the amount of structural distortion (defined as the difference between the in-plane and the out-of-plane interplanar spacing) is the driving force that determines the r_{woke} [4]. The observed shift in XRD peak positions shown in Fig. 1 would be explained by the partial release of such structural distortion during the waking-up process.

References: [1] M. Pešić, *et.al.*, Adv. Funct. Mater. 26, 4601 (2016). [2] E.D. Grimley, *et.al.*, Adv. Electron. Mater. **2**, 1600173 (2016) [3]. S.S. Fields, *et.al.*, ACS Appl. Mater. Interfaces 12, 26577 (2020). [4] S. Nittakayasetwat and K. Kita, SSDM 2020.

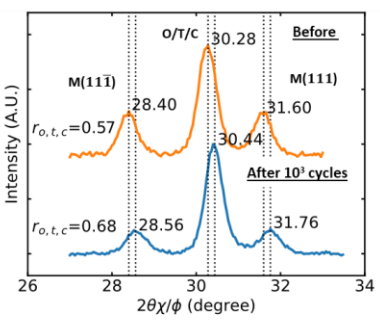

Fig1. In-plane XRD of Y-HfO_2 before and after 10^3 cycles of electrical pulses

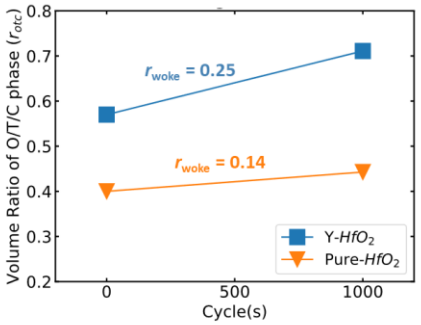

Fig.2 The change in $r_{o.t.c}$ of Y-HfO_2 and pure-HfO_2 with the number of cycles during volage cycling

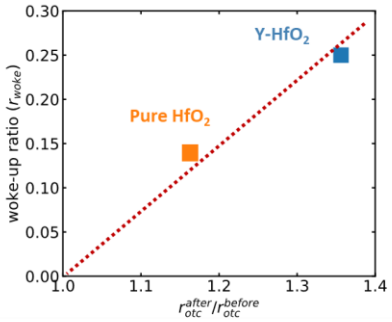

Fig.3 The relationship between r_{woke} and increase in $r_{o.t.c}$ (shown by the ratio of $r_{o.t.c}$ before and after 10^3 cycles of voltage cycling.)