強誘電 HfO_2 の分極繰り返しに伴う劣化に対する電荷注入の効果に関する考察
Consideration of Charge Injection Effect on the Degradation of Ferroelectric HfO_2 during Bipolar Voltage Cycling

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[Introduction] It is commonly observed that the switchable polarization (P_{sw}) of ferroelectric (FE) HfO_2 degraded during bipolar voltage cycling, which can be a major issue that leads to the instability of the device operations. Despite the well know fabrication process of FE-HfO_2, the mechanism for the fatigue effect, whether it is due to atomic re-orientation or the increase in defect density, is still remains unclarified. Hence, in this study, we investigate the possible factors contributing to the degradation of FE-HfO_2 during dipolar voltage cycling.

[Experimental] Two types of MFM capacitors with ~30 nm-thick of HfO_2 were fabricated: 1.5 cat% Y-doped HfO_2 (Y-HfO_2) and pure HfO_2. Both samples were fabricated by sputtering HfO_2 on heavily doped Ge substrates, where the Y-dopant was introduced by co-sputtering HfO_2 and Y_2O_3. Then, the stacks were annealed at 600°C in N_2 ambient for 30 s, followed by the deposition of Au top electrodes. The degradation of FE-properties was characterized by 12 V bipolar voltage cycling at the frequency of 10 kHz and constant DC-bias stress.

[Results and Discussions] Figure 1 shows the P-V hysteresis of Y-HfO_2 at a different number of cycles during the bipolar cycling. The change in P_{sw} during cycling is summarized in Fig. 2. There was a noticeable increase in the P_{sw} at the beginning of the cycling. After 10^3 cycles, P_{sw} gradually decreased, and rapidly dropped after 10^4 cycles. From the P-V hysteresis, the dielectric constant of HfO_2 (ε_{HfO2}) can be roughly estimated from the slop (dP/dV) as indicated in Fig.1. By assuming that there was no reaction at HfO_2/Ge interface during voltage cycling, the ε_{HfO2} decreased constantly with the number of voltage cycling, as shown in Fig. 2 This could suggest a phase transformation during the voltage cycling, regarding that the ferroelectricity of HfO_2 originates from the *o*-phase, and the ε_{HfO2} is strongly dependent on its crystal phases [1]. To evaluate the dominant factors that determine the degradation mechanism, DC-bias stress of +9 V and +12 V were applied on Y-HfO_2 before making P-V measurement. The injected charges (Q_{inj}) were calculated and are plotted as the horizontal axis of Fig.3 At a certain amount of Q_{inj}, both the P_{sw} of Y-HfO_2 and pure-HfO_2 (data not shown) stressed at 9 V and 12 V began to drop. Also, the ε_{HfO2} was also estimated after the DC-bias stress (shown in Fig. 3). Both the estimated ε_{HfO2} during the voltage cycling and after DC-bias stress monotonically in a similar trend along with the reduction in P_{sw}. Thus, it is reasonable to consider that Q_{inj} is one of the crucial factors that determine the degradation of FE-HfO_2 during bipolar voltage cycling.

References: [1] K. Kita, *et.al.*, APL. **86**, 102906 (2005)

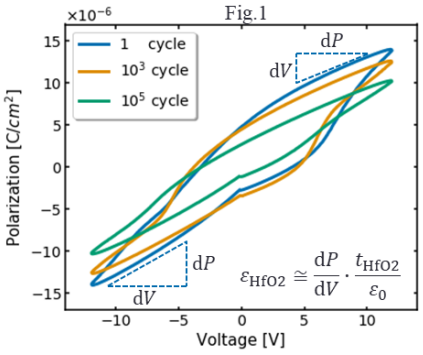

Fig1. The P-V hysteresis of Y-HfO_2 at its pristine, 10^3, and 10^5 cycles. The ε_{HfO2} was estimated from the slope of the fitting above the coercive field.

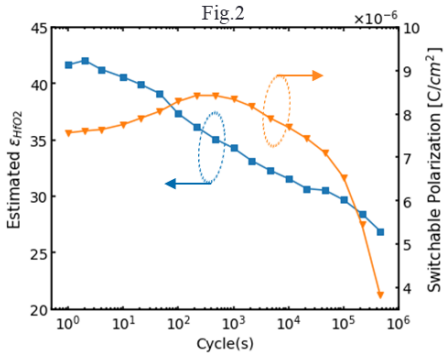

Fig.2 The change in P_{sw} (right) and ε_{HfO2} (left) during bipolar voltage cycling at 12 V and 10 kHz.

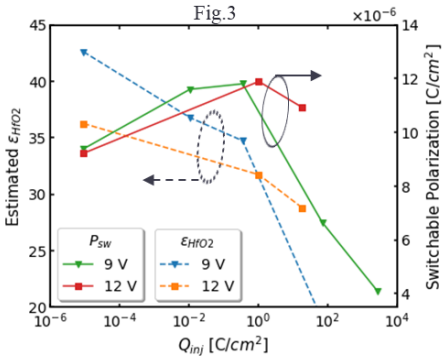

Fig.3 The change in P_{sw} (right) and ε_{HfO2} (left) after stressed at 9 V and 12 V for a certain time. The Q_{inj} were calculated and are shown above.