Depolarization process in ferroelectric HfO$_2$ probed by piezo-response force microscopy (PFM)

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Abstract

Depolarization process of ferroelectric HfO$_2$ was investigated with piezo-response force microscopy. Two kinds of depolarization process are reported. One is at the boundary between different polarized regions. The other is inside the polarized region. These processes are directly related to the ferroelectric film retention. Furthermore, the latter case suggests that both weakly and strongly polarized areas exists.

1. Introduction

Ferroelectric HfO$_2$ attracts much attention from the viewpoint of versatile applications using popular materials. The ferroelectricity of HfO$_2$ becomes evident by the cation doping and/or thickness control [1−5]. It is of vital importance to understand the depolarization process in terms of ferroelectric qualification as well as ferroelectric reliability [6,7]. Furthermore, since the ground state of HfO$_2$ is monoclinic, it is concerned that the ferroelectric phase may be due to the metastable one or may coexist with paraelectric one. To design the reliable ferroelectric HfO$_2$ devices, understanding of depolarization in the mesoscopic scale is mandatory.

In this study, with the piezo-response force microscopy (PFM), the time dependence of depolarization observed in ferroelectric HfO$_2$ film is discussed.

2. Sample fabrication

Y-doped HfO$_2$ film was prepared by rf co-sputtering of HfO$_2$ with Y$_2$O$_3$ on heavily doped p-type Ge substrate as the back electrode. HfO$_2$ thickness was estimated to be ~26 nm by GIXR. Y content in HfO$_2$ was ~3 at.% (metal ratio) estimated by XPS. PDA in N$_2$ at 600°C for 30 s was carried out. Au was deposited on HfO$_2$ for P-V and C-V measurements.

3. Results and discussions

Figure 1 shows both XRD pattern and P-V characteristics in Y-doped HfO$_2$. The highly symmetric phase is dominant and ferroelectric behavior is clearly observed in P-V curve with remanent polarization of ~20 μC/cm$^2$.

The contact resonant mode PFM measurement was performed. DC and AC biases ($V_{DC}$ and $V_{AC}$) were applied from the conductive cantilever to a sample surface, and both amplitude and phase of the tip response were detected. The amplitude and phase mean the deformation of surface height due to the piezo-response and the polarization direction with applied bias, respectively. In this study, $V_{AC}$ was set at -0.8 V and the resonance frequency was ~280 kHz.

Figure 2(a) shows the PFM phase and amplitude images scanned at the zero bias condition after the poling process. The poling process was the scan at $V_{DC}$=8.6 V in 1.5×1.5 μm$^2$ and $V_{DC}$=-6.4 V in 0.6×0.6 μm$^2$ in the center of 1.5×1.5 μm$^2$ area, subsequently. (b) Phase and amplitude images scanned at zero bias condition after poling at $V_{DC}$=-6.4 V in the mesoscopic scale.

Fig. 1 (a) Out of plane XRD 2θ pattern and (b) P-V curve measured at 100 Hz of Y-doped HfO$_2$ film. Highly symmetric denotes cubic, tetragonal and/or orthorhombic phases, because these diffraction peaks are too near to distinguish each of them.

Fig. 2 (a) PFM phase and amplitude images of 1.5×1.5 μm$^2$ area scanned at the zero bias condition after the poling process. The poling was carried out with $V_{DC}$=8.6 V in 1.5×1.5 μm$^2$, followed by $V_{DC}$=-6.4 V in 0.6×0.6 μm$^2$ in the center 1.5×1.5 μm$^2$ area. Just after the poling, the red and blue contrasts are clearly shown in the phase image. The amplitude at the boundary between red and blue areas in the phase image sharply decreases, while that in red or blue colored phase area does not change. Figure 2(b) also shows the phase and amplitude images of the red phase part in the mesoscopic scale. There are both mainly red and slightly white regions. Namely, this fact suggests that the red area in the phase very slightly includes phases different from the main polarization.

The above is the initial sample characterization for studying the time dependent depolarization of ferroelectric HfO$_2$. After a test for left in the ambient, the boundary between up
Phase boundary width should be affected by a finite size of the probing tip shown in Fig. 3. Increment of boundary width and the amplitude decrease in flat area are clearly shown. In the phase profile, it can be found that the edge roughness increases at the boundary. (c) The dependence of boundary width estimated from the amplitude images on the time left in the ambient. Orange region shows the measurement limit width caused by the finite tip size used in this study [8].

\[ f(r) = \frac{1}{2} \alpha (T - T_c) P(r)^2 + \frac{1}{4} \beta P(r)^4 + \frac{\sigma}{2} \nabla P(r)^2. \]  

Here, the third term indicates the additional boundary energy expressing the gradient of the polarization. Namely, the smooth boundary is favored to lower the free energy. Therefore, this is the direct evidence that the ferroelectric domain boundaries with differently polarized direction can work as the depolarization center.

Figure 5 shows the phase and amplitude images scanned at the zero bias condition in the mesoscopic scale after the poling at \( V_{DC} = 6.4 \) V and left in the ambient for ~40 min, which is the time dependent images of Fig. 2(b). Both amplitude and phase images were changed a lot in 40 min. Blue and white parts in the red significantly increase in the phase image, while the dark area substantially increases in the amplitude image. This fact indicates that even in the area with unidirectional polarization, polarization should change with the time in case that the surface is subject to the ambient.

4. Conclusions

The depolarization process in HfO\(_2\) has been studied from two aspects with PFM. One is the thermally accelerated retention in unidirectional polarized area. The other is at the boundary, which is driven by the polarization gradient term in TDGL. Both are of course quite important for estimating the ferroelectric retention. In case of HfO\(_2\), thermally accelerated retention might be potentially a big concern because the ferroelectric phase is not in the very stable ground state.

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References