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Direct Evidence of 3-nm-thick Ferroelectric HfO$_2$

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Abstract

Direct evidence of ferroelectric properties in 3- nm-thick HfO$_2$ is undoubtedly demonstrated through conventional P-V and I-V measurements at room temperature. Besides, the remanent polarization in ultrathin HfO$_2$ films is demonstrated to be proportional to the symmetric portion of crystalline phases in HfO$_2$. This fact indicates that ferroelectric HfO$_2$ will be very usable for scaled devices.

1. Introduction

Ferroelectric devices are promising candidates for the next-generation nonvolatile devices [1]. Ultrathin ferroelectric HfO$_2$, which shows moderate remanent polarization will in particular have high potential in the application of scaled devices such as nonvolatile FETs or ferroelectric tunnel junctions. However, to our knowledge, 5 nm is the minimum thickness in ferroelectric HfO$_2$ so far reported in the literatures [2]. Although the ferroelectricity in ultrathin HfO$_2$ has been reported with piezoelectric force microscopy (PFM) [3], PFM results and interpretation are still under the debate [4]. Therefore, undoubted demonstration of HfO$_2$ ferroelectricity in the ultrathin region is very important. In this work, the ferroelectricity in Y$_2$O$_3$-doped HfO$_2$ films with thickness varying from 3nm~30nm is clearly demonstrated by conventional charge and displacement current measurement techniques.

2. Experiment

Heavily doped p-type Ge ($\rho \approx 5 \times 10^{-3}$ $\Omega \cdot$cm) was used for the bottom electrode. 30~3nm Y-doped HfO$_2$ films were prepared by co-sputtering of Y$_2$O$_3$ and HfO$_2$ on Ge substrate, followed by post deposition annealing at 600°C in N$_2$ for 30 s (700°C for below 4 nm films). Film thickness was inspected by X-ray reflectivity (XRR). Cation ratio of Y to Hf was estimated to be around 2.1% by XPS. Top Au electrode pad (radius=40 μm) was deposited through a shadow mask. Ferroelectric properties of all films were measured by ferroelectric analyzer with Q-V and I-V mode at 10 kHz, and the pulse-measurements.

3. Results and Discussion

The device structure is shown in the **Fig. 1(a)**. **Figure 1(b)** shows a typical polarization-electric field (P-E) and current-electric field (I-E) measurement results for 30 nm Y-doped HfO$_2$ film. Considering the voltage drop in the potential interface layer (IL) and the depletion region, the remanent polarization (P$_r$) was obtained by gradually increasing the bias to saturate the hysteresis. The result shows P$_r$ is around 11 μC/cm^2. Concerning the coercive field (E$_c$), it was estimated by both P-E and I-E measurements, and to be around 1.7 MV/cm for 30 nm Y-doped HfO$_2$ film. It is noted that I-E measurement is more appropriate for determining E$_c$ more accurately, because of the tilting of P-E hysteresis to some extent, especially in ultrathin films.
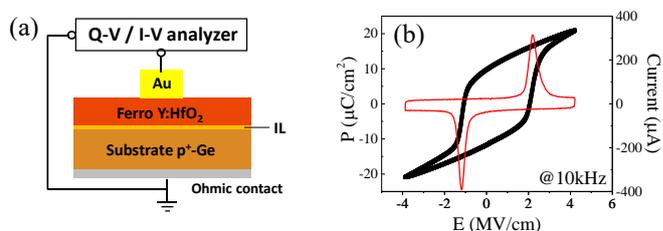

Fig. 1 (a) Schematic image of device structure and measurement circuit. **(b)** P-E and I-E measurement of 30-nm-thick Y-doped HfO$_2$.
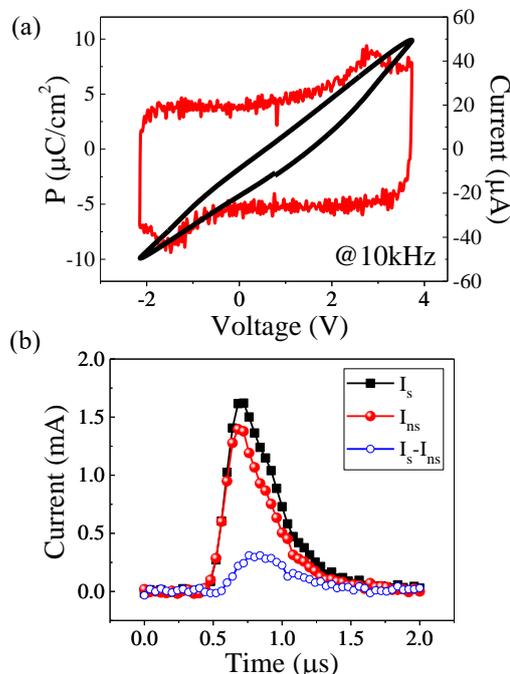

Fig. 2 Ferroelectric characterization of 3-nm-thick Y-doped HfO$_2$ film. **(a)** P-V measurement (black) and I-V measurement (red) at 10kHz. **(b)** double pulse measurement in which the ferroelectric switching current (blue open symbol) is measured as the difference between the first switching current peak (black symbol) and the second non-switching current peak (red symbol) [5].

Next, the ferroelectricity in 3-nm-thick HfO_2 film is unequivocally displayed in **Fig. 2**. The film thickness estimated by XRR was around 3.2 nm. A significant alternation of the hysteresis loop is not observed in the P-V measurement in **Fig. 2 (a)**, which is still identified to be ferroelectric. The leakage current was well suppressed in the 3 nm HfO_2, which is in striking contrast to conventional perovskite type of ferroelectrics. Switchable polarization (P_{sw}) obtained from the P-V hysteresis is around 3 $\mu C/cm^2$ for 3-nm-thick HfO_2. Besides, the displacement current peak associated to the polarization switching is clearly observed in the I-V measurement in **Fig. 2 (a)**, in which the current peak supports that the displacement current overwhelmed the leakage current in the device. This is the direct confirmation of maintaining the ferroelectricity in 3-nm-thick ferroelectric HfO_2. The E_c of the 3 nm HfO_2 film is around 2 MV/cm by considering the voltage drop on the IL and depletion region, which is consistent with other report [3]. Furthermore, the double pulse measurement which directly reveals the ferroelectric switching was carried out to characterize the ferroelectricity in the ultrathin HfO_2. The pulse width was 1 μs, which was below the RC constant of the measurement circuit. Both transient currents show the same charging current peak, whereas the displacement current due to the polarization switching added the current composition of the first peak, which is differentiated from the second non-switching current peak, as shown in **Fig. 2(b)**. The integration of I_s-I_{ns} gives P_{sw} to be around 3 $\mu C/cm^2$ as well, which further supports the quantitative accuracy in the P-V measurement. Thus, the ferroelectricity in 3-nm-thick HfO_2 film was proved without any doubt.

Ferroelectricity in polycrystalline HfO_2 is considered to be due to the polar orthorhombic phase formation in HfO_2. Because the strongest diffraction peaks are located around 27°~33° for monoclinic and orthorhombic/ tetragonal/ cubic (o/t/c) phases in HfO_2, the high symmetric phase ratio (r_H) is defined by eq. (1), where I represent the intensity of the corresponding diffraction peaks. In the ultrathin films, the broadened diffraction peak due to a smaller grain size was decomposed to three peaks as shown in **Fig. 3(a)**. The r_H vs. thickness is summarized in **Fig. 3(b)**, which shows that r_H behaves flat from 8 to 30 nm, while it gradually dropped below 8 nm.

$$ r_H = \frac{I_{o/t/c\ phase}}{I_{m(111)} + I_{m(11\bar{1})} + I_{o/t/c\ phase}} \quad (1) $$

P_{sw} obtained from P-E measurement for 30~3nm films is shown in **Fig. 3(c)**. By thinning HfO_2 from 30nm to around 8nm, P_{sw} progressively increased, whereas r_H is almost stable within this range. This sheds light on the potential process that non-ferroelectric phase (t/c) transitions to ferroelectric phase. After that, P_{sw} gradually declined, which shows similar behavior with the phase transition. In order to figure out the influence of phase transition on P_{sw}, the relationship between them is drawn in **Fig. 3(d)**. P_{sw} shows a monotone increasing

with r_H, especially in the ultrathin region below 8nm, which indicates a dominant role of crystalline structure in the ferroelectricity of ultrathin HfO_2. On the other hand, it suggests the depolarization field effect which is severe for the ultrathin single crystalline ferroelectrics, is not playing a critical role during this process.
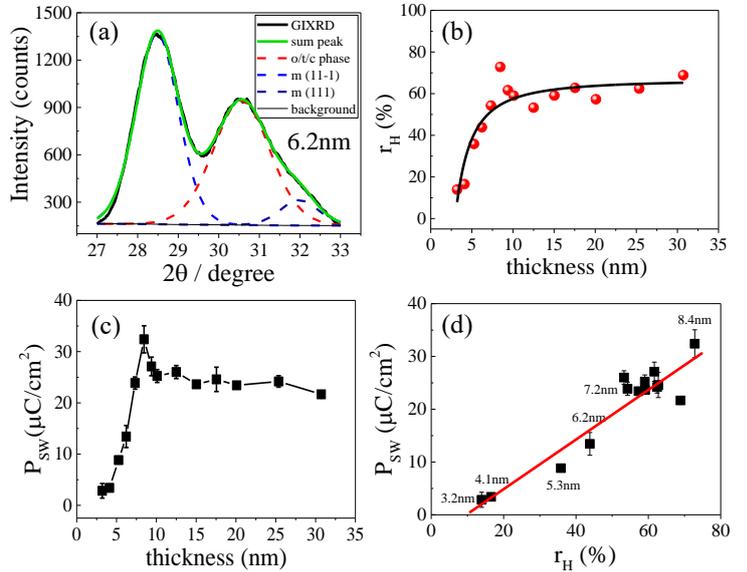

Fig. 3 (a) Peak separation of o/t/c phase and monoclinic phase in 6-nm-thick HfO_2. **(b)** High symmetric phase ratio obtained by eq. (1) vs. thickness. **(c)** P_{sw} obtained by P-E measurement vs. thickness. **(d)** The relationship between P_{sw} and r_H.

The proportional relationship between P_{sw} and r_H enlightens us that, the ferroelectricity in the ultrathin HfO_2 is controllable through manipulating the crystalline phases of films by means of controlling annealing conditions or device structures. In that sense, ferroelectric HfO_2 is quite promising for the nano-scale memory devices.

4. Conclusions

Ferroelectricity is undoubtedly demonstrated for 3-nm-thick HfO_2 for the first time. The strong suppression of leakage current in the ultrathin film indicates its high potential for nano-scale ferroelectric devices. The switchable polarization value in the ultrathin HfO_2 is demonstrated to relate to the crystalline phases of the film, and to be fitted for scaled device application.

References
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