

Ferroelectric HfO₂ Formation by Annealing of HfO₂/Hf/HfO₂/Si(100) Stacked Structure

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Abstract

In this research, ferroelectric characteristics of HfO₂ formed by annealing of HfO₂/Hf/HfO₂/Si(100) stacked structure were investigated. It was found that the stacked structure enhanced the formation of metastable orthorhombic phase on Si(100) substrate. 2P_r of 20 $\mu\text{C}/\text{cm}^2$ was obtained, which is larger than that induced by HfO₂ without Hf layer.

1. Introduction

Ferroelectric materials are receiving much attention to realize the 1-transistor-type ferroelectric random access memory (1T-FeRAM). In 2011, it was revealed that orthorhombic phase of HfO₂ exhibits ferroelectricity [1], which is suitable for 1T-FeRAM. Although the transformation to metastable orthorhombic phase of HfO₂ is reported by various kinds of dopants, doped HfO₂ requires high crystallization temperature especially on Si(100) substrates [2,3,4]. High temperature anneal would form thicker interfacial layer between Si and HfO₂, which leads to the degradation of retention characteristics caused by the depolarization field.

In this research, we investigated ferroelectric HfO₂ formation by low temperature annealing of HfO₂/Hf/HfO₂/Si(100) stacked structure.

2. Experimental Procedure

Metal/ferroelectric/p⁺-Si(100) (MFS) diodes were fabricated as shown in Fig. 1. Heavily-doped p⁺-Si(100) substrates were cleaned by SPM and DHF solutions. Then, HfO₂ (12 nm)/Hf (1 nm)/HfO₂ (12 nm) was in-situ deposited by RF magnetron sputtering at room temperature. Next, 25-nm-thick HfO₂ was also deposited as a comparison. Sputtering gas flow rate was Ar/O₂ = 3.4/0.7 sccm for HfO₂ and

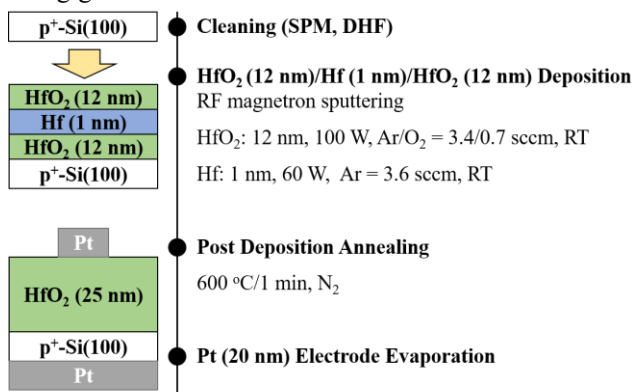


Fig. 1 Fabrication process and schematic cross-sections of the metal/HfO₂/p⁺-Si(100) diode.

Ar = 3.6 sccm for Hf layer. The gas pressure was 0.58 Pa. Then, post deposition annealing at 600°C for 1 min was carried out. Finally, Pt electrodes were deposited by e-beam evaporation through a stencil mask.

The ferroelectric characteristics were measured by a ferroelectric tester (Toyo FCE fast). Out-of-plane x-ray diffraction (XRD) measurement was performed by PANalytical X'pert MRD with θ -2 θ scan. J-V characteristics was measured by Agilent 4156C.

3. Results and Discussion

Figure 2 shows out-of-plane XRD characteristics of the MFS diodes (a) with and (b) without a Hf layer. Figure 2(a) shows the clear peak of orthorhombic (O)/tetragonal (T)/cubic (C) phase (111) at 30.5° with that of monoclinic (M) phase (-111) at 28.4°. However, the peak intensity of O/T/C phase (111) was reduced in case of HfO₂ formed without Hf layer. Therefore, 1-nm-thick Hf layer is effective to induce orthorhombic phase.

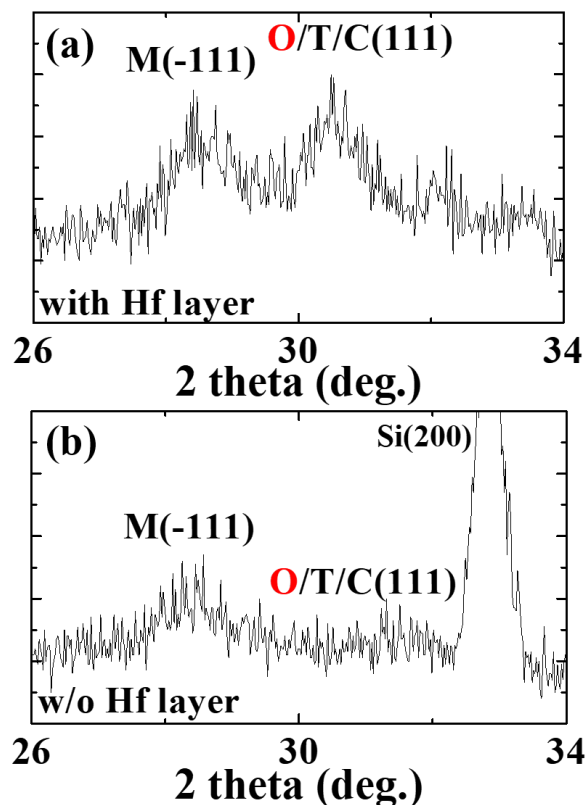


Fig. 2 X-ray diffraction pattern of HfO₂ on Si(100) formed from (a) HfO₂/Hf/HfO₂ stacked structure and (b) HfO₂ single layer.

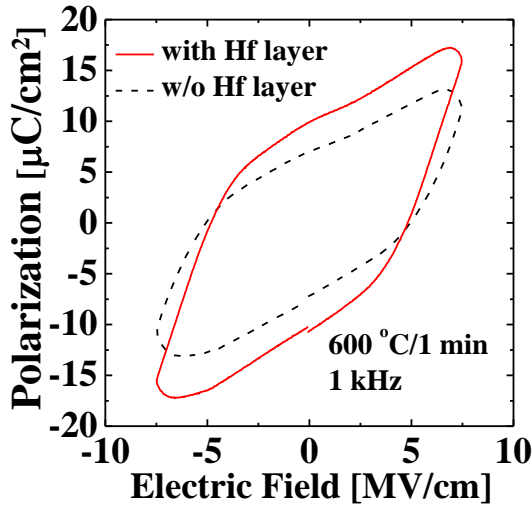


Fig. 3 P-E characteristics for HfO₂ formed on p⁺-Si(100) from HfO₂/Hf/HfO₂/p⁺-Si(100) stacked structure compared with single HfO₂ layer.

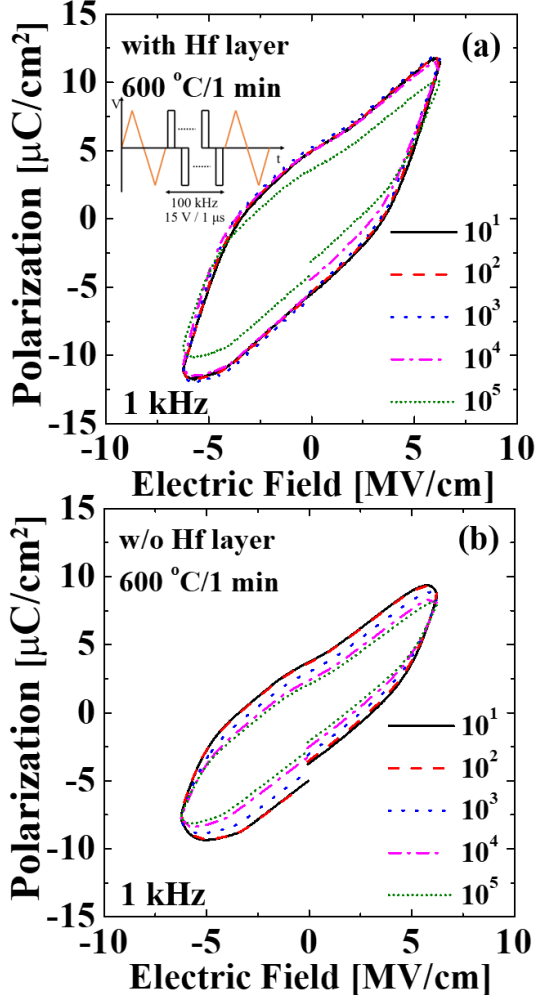


Fig. 4 Switching characteristics of HfO₂ on p⁺-Si (100) (a) without and (b) with Hf layer.

Figure 3 shows the comparison of P-E characteristics of the MFS diodes. The HfO₂ formed without Hf layer showed $2P_r$ of 14 $\mu\text{C}/\text{cm}^2$. It was increased to 20 $\mu\text{C}/\text{cm}^2$ in case of HfO₂ formed from HfO₂/Hf/HfO₂/Si(100) stacked structure. It corresponds to its XRD pattern with peak of O phase. As

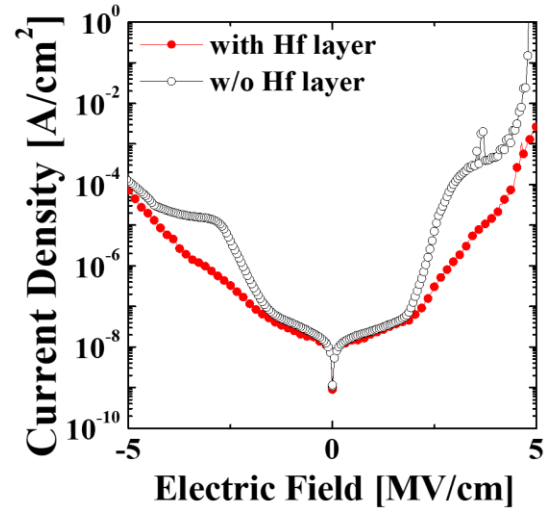


Fig. 5 Comparison of J-V characteristics for Pt/HfO₂/p⁺-Si(100).

the peak intensity of O phase was increased, ferroelectric characteristic was enhanced. However, they show large $2E_c$ of 10 MV/cm and 9.6 MV/cm, respectively, which are much larger than reported $2E_c$ (1~2 MV/cm) in metal-ferroelectric-metal (MFM) structure [5].

Figure 4 shows endurance characteristics of HfO₂ after applying bipolar switching pulse. The amplitude, frequency, and pulse width was ± 15 V, 100 kHz, and 1 μs , respectively. In Fig. 4(a), the degradation did not occur until 10^5 cycles in HfO₂ formed from HfO₂/Hf/HfO₂/p⁺-Si(100) stacked structure. On the other hand, it was found that the polarization characteristics was degraded after 10^3 cycles in case of HfO₂ formed with Hf layer.

J-V characteristics is shown in Fig. 5. Breakdown voltage was increased for HfO₂ formed from HfO₂/Hf/HfO₂/p⁺-Si(100) stacked structure.

3. Conclusions

In this research, the ferroelectric characteristics of undoped HfO₂ was investigated. The undoped HfO₂ formed from HfO₂/Hf/HfO₂/p⁺-Si(100) stacked structure was found to improve the ferroelectric characteristics. Therefore, precise control of the crystallinity would further improve the ferroelectric characteristics of undoped HfO₂.

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