# Ferroelectric HfO<sub>2</sub> Formation by Annealing of HfO<sub>2</sub>/Hf/HfO<sub>2</sub>/Si(100) Stacked Structure

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### Abstract

In this research, ferroelectric characteristics of HfO<sub>2</sub> formed by annealing of HfO<sub>2</sub>/Hf/HfO<sub>2</sub>/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  $\mu$ C/cm<sup>2</sup> was obtained, which is larger than that induced by HfO<sub>2</sub> 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 HfO<sub>2</sub> exhibits ferroelectricity [1], which is suitable for 1T-FeRAM. Although the transformation to metastable orthorhombic phase of HfO<sub>2</sub> is reported by various kinds of dopants, doped HfO<sub>2</sub> requires high crystallization temperature especially on Si(100) substrates [2,3,4]. High temperature anneal would form thicker interfacial layer between Si and HfO<sub>2</sub>, which leads to the degradation of retention characteristics caused by the depolarization field.

In this research, we investigated ferroelectric  $HfO_2$  formation by low temperature annealing of  $HfO_2/Hf/HfO_2/Si(100)$  stacked structure.

## 2. Experimental Procedure

Metal/ferroelectric/p<sup>+</sup>-Si(100) (MFS) diodes were fabricated as shown in Fig. 1. Heavily-doped p<sup>+</sup>-Si(100) substrates were cleaned by SPM and DHF solutions. Then, HfO<sub>2</sub> (12 nm)/Hf (1 nm)/HfO<sub>2</sub> (12 nm) was in-situ deposited by RF magnetron sputtering at room temperature. Next, 25nm-thick HfO<sub>2</sub> was also deposited as a comparison. Sputtering gas flow rate was  $Ar/O_2 = 3.4/0.7$  sccm for HfO<sub>2</sub> and



Fig. 1 Fabrication process and schematic cross-sections of the metal/HfO<sub>2</sub>/ $p^+$ -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  $\theta$ -2 $\theta$  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  $30.5^{\circ}$  with that of monoclinic (M) phase (-111) at  $28.4^{\circ}$ . However, the peak intensity of O/T/C phase (111) was reduced in case of HfO<sub>2</sub> formed without Hf layer. Therefore, 1-nm-thick Hf layer is effective to induce orthorhombic phase.



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



Fig. 3 P-E characteristics for  $HfO_2$  formed on  $p^+$ -Si(100) from  $HfO_2/Hf/HfO_2/p^+$ -Si(100) stacked structure compared with single  $HfO_2$  layer.



Fig. 4 Switching characteristics of  $HfO_2$  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 HfO<sub>2</sub> formed without Hf layer showed 2P<sub>r</sub> of 14  $\mu$ C/cm<sup>2</sup>. It was increased to 20  $\mu$ C/cm<sup>2</sup> in case of HfO<sub>2</sub> formed from HfO<sub>2</sub>/Hf/HfO<sub>2</sub>/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/HfO<sub>2</sub>/p<sup>+</sup>-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 HfO<sub>2</sub> after applying bipolar switching pulse. The amplitude, frequency, and pulse width was  $\pm 15$  V, 100 kHz, and 1  $\mu$ s, respectively. In Fig. 4(a), the degradation did not occur until 10<sup>5</sup> cycles in HfO<sub>2</sub> formed from HfO<sub>2</sub>/Hf/HfO<sub>2</sub>/p<sup>+</sup>-Si(100) stacked structure. On the other hand, it was found that the polarization characteristics was degraded after 10<sup>3</sup> cycles in case of HfO<sub>2</sub> formed with Hf layer.

J-V characteristics is shown in Fig. 5. Breakdown voltage was increased for  $HfO_2$  formed from  $HfO_2/Hf/HfO_2/p^+$ -Si(100) stacked structure.

#### 3. Conclusions

In this research, the ferroelectric characteristics of undoped HfO<sub>2</sub> was investigated. The undoped HfO<sub>2</sub> formed from HfO<sub>2</sub>/Hf/HfO<sub>2</sub>/p<sup>+</sup>-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 HfO<sub>2</sub>.

#### Acknowledgements

The authors would like to thank Prof. H. Funakubo of Tokyo Institute of Technology for useful discussion for this research. This research is based on the Cooperative Research Project of Research Center for Biomedical Engineering, Ministry of Education, Culture, Sports, Science and Technology. M. G. Kim acknowledges Honjo International Scholarship Foundation (HISF) for financial support.

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