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Enhanced Electroresistance in HfZrO based Metal/ferroelectric/Semiconductor Tunnel Junction

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Abstract

We achived greatly improved ferroelectricity with a large remanent polarization of 30 μC/cm² and enhanced tunneling electroresistance of 200 for TiN/HZO/Ge ferroelectric tunnel junctions (FTJs) formed by high pressure annealing (30-200 atm). By process optimization, we found key parameters to control the effective barrier height, thereby leading to modulate electrically space charge limited region formed at the ferroelectric/semiconductor interface. In this presentation, we will demonstrate the effect of atomospheric pressure (30-200 atm) and ambient (forming gas, oxygen, nitrogen and air) on the TER and remanent polarization value of FTJ devices.

1. Introduction

Ferroelectric materials with two spontaneous polarization states have recently received tremendous attention as various electrical applications due to their fast switching speed and non-volatility, which offer important power consumption benefits.[1]-[2] Among the electronic devices using HfO_2-based ferroelectric materials, HfO_2-based ferroelectric tunnel junctions (FTJs) have emerged as capable applicants for next-generation memory.[3] However, a comparatively low on/off ratio of HfO_2-based FTJs has remained a key issue for actual device applications.

In this paper, to improve the tunneling electroresistance, we fabricated HfZrO(HZO)-based FTJ with Ge semiconductor bottom electrode. Compare to Metal/Ferroelectric/Metal (MFM) structure, Metal/Ferroelectric/Semiconductor(MFS) junction has depletion region in the semiconductor according to the polarization direction resulting increase the effective barrier width and improve the TER effect.[4]

2. Experimental

We fabricated FTJ devices with a TiN metal electrode and highly doped p-type (ρ=0.005Ω) Ge semiconductor electrodes. Films of 6nm-thick HZO were grown on each bottom substrates using atomic layer deposition. Then, 25nm-thick TiN was deposited as the top electrode of devices by using DC sputtering. A Ti(10nm)/ Pt(20nm) were formed as a contact pad through a shadow mask with a 70um-hole diameter. After forming the contact pad, the TiN which was not covered by Ti/Pt was wet etched using SC-1 etchant at 40°C. After device fabrication, rapid thermal annealing and high pressure annealing (200atm.) in N_2 atmosphere was formed at 500°C for HZO film crystallization.

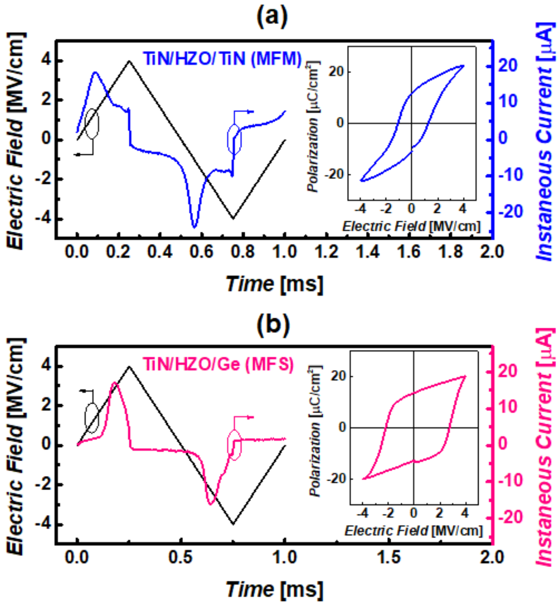

Fig. 1 Time-transient current and P-E hysteresis loops of (a) MFM-type capacitor and (b) MFS-type capacitor

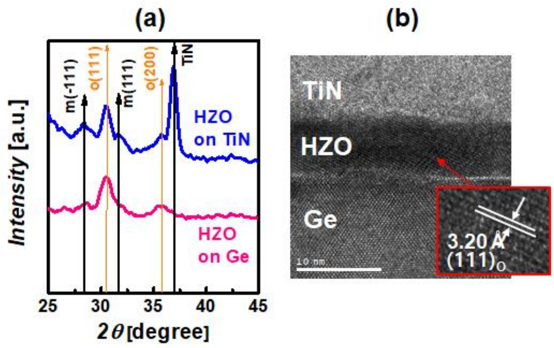

Fig. 2 (a) GIXRD patterns of HZO film on TiN and Ge substrate. (b) The cross-section TEM image of TiN/HZO/Ge stack.

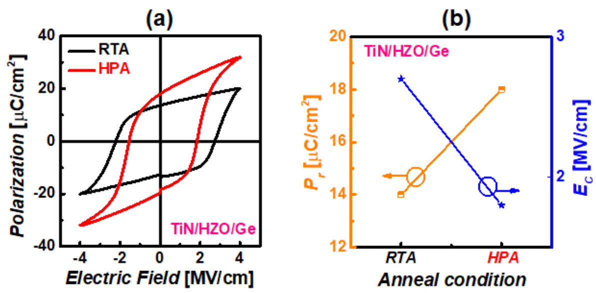

Fig. 3 (a) P-E curve of MFS capacitors. (b) comparison P_r value and E_c value according to the annealing method.

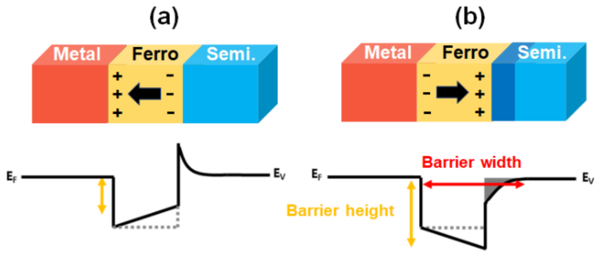

Fig. 4 Electron band diagram of an MFS-type FTJ with (a) R_{on} state and (b) R_{off} state according to the polarization direction.

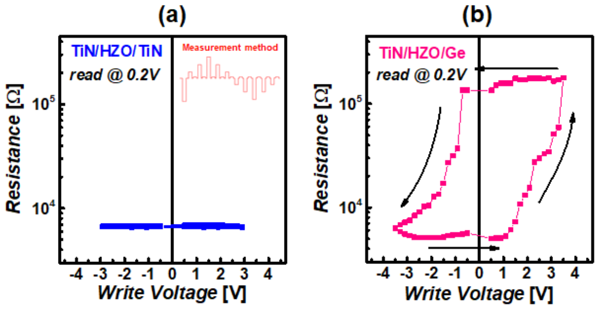

Fig. 5 Resistance-voltage hysteresis loops for (a) [TiN/HZO/TiN] FTJ and (b) [TiN/HZO/Ge] FTJ

3. Result and Discussion

Fig. 1(a) and (b) presents the P-E and transient current data of [TiN/HZO/TiN] and [TiN/HZO/Ge] capacitors which can directly verify the ferroelectric properties. The HZO film with Ge and TiN substrates exhibited clear P-E hysteresis curves, showing the maximum remnant polarization (P_r) value of 14 μC/cm^2 and 12 μC/cm^{2}at an applied electric field of 4MV/cm. The GIXRD peaks from the non-centrosymmetric o-phase, (111) and (200) planes which is origin of ferroelectricity, were detected in the HZO film with both substrates as shown in Fig. 2(a). It can be verified by cross-section TEM image as shown in Fig. 2(b). In order to form high quality o-phase thin film, high pressure annealing (HPA) is introduced. As shown in Fig. 3(a) and (b), HZO films suffer in-plane tensile stress during HPA process resulting improved remnant polarization and reduced coercieve field value.

In FTJs, binary electrical resistance conditions are constructed by switching in the effective potential barrier according to the polarization directions, caused by asymmetric screening lengths at the barrier/electrode interface. For that reason, in the case of HZO with the same top and bottom TiN electrode no TER effect was found because the height of the tunneling barrier was identical, and consequently, the tunneling probability was also the same even when the polarization was changed. On the other hand, in MFS-type FTJs, when the polarization direction of HZO was pointing to the metal side, the hole in the semiconductor, which is the majority carrier in the p-type semiconductor, piled up at the ferroelectric/semiconductor interface and the accumulated semiconductor could play a role as a metal, resulting in a lower barrier height and higher the tunneling probability, consequently increasing resistance (ON state) as presented in Fig. 4(a). On the other hand, when the polarization was switched (pointing to the semiconductor), as presented in Fig. 4(b), the depletion region could be formed on the semiconductor surface due to the ferroelectric bound charge, which causes the creation of an extra Schottky barrier and increased tunneling barrier width, consequently significantly increased the resistance (OFF state). Fig. 5(a) and(d) show the resistance-write voltage (R-V) curve of [TiN/HZO/TiN], [TiN/HZO/Ge] junctions at the 0.2V read voltage, respectively. The largest ON/OFF ratio of 25 was achieved with MFS-type FTJ device.

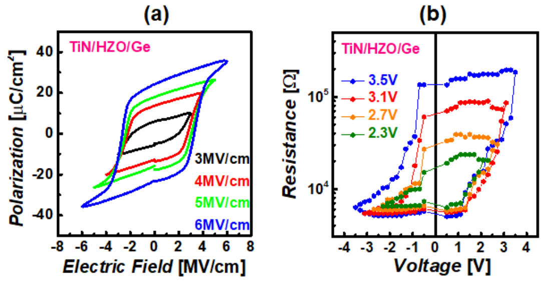

Fig. 6 (a) P-E characteristics of the [TiN/HZO/Ge] capacitors according to maximum electric field. (b) R-V hysteresis curves according to maximum amplitude of write pulse.

Fig. 6(b) shows a properties of multi-level junction resistance as we applied different pulse amplitude. The polarization state can be changed gradually according to applied voltage as shown in Fig. 6(a); that is, intermediate resistance states can be modulated by changing the maximum applied voltage.

3. Conclusions

Compared to MFM-type FTJ device, the TER effect of the MFS-type FTJs could be extensively improved, due to the improvement of ferroelectricity of HZO and formation of the depletion region. By using HPA, HZO film with Ge bottom substrate goes through effective in-plane tensile stress resulting in superb crystallinity and high o-phase ratio with an excellent remnant polarization of 18 μC/cm^2. Additionally, not only the barrier height but also the width can be electrically controlled as a result of the formation of a space charge limited region in Ge substrate improving tunneling properties with a TER value of 25. It also contains 4 different level which provide tremendous potential for next generation nonvolatile memory devices.

Acknowledgements

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