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Transport mechanism in $Hf_{0.5}Zr_{0.5}O_2$-based ferroelectric diodes

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Doped HfO_2, as an emerging ferroelectric material, could overcome the shortcomings of traditional ferroelectrics [1]. $Hf_{0.5}Zr_{0.5}O_2$ (HZO) is a good choice for Hf-doped materials because of its excellent ferroelectric properties and mature preparation process. In our previous studies, we proposed a new HZO switchable ferroelectric diode (FE diode) with several advantages, such as high operating speed, 3D stackability, and built-in nonlinearity [2]. From other work, the transport model of devices is complicated because of different structures and preparation processes. HZO ferroelectric devices, such as FE capacitors, ferroelectric transistors (FeFETs), and ferroelectric tunneling junctions (FTJs), could obey the Schottky model [3], Poole-Frankel model [4], or tunneling [5]. Since FE diodes have the characteristics of programmable and bidirectional operation, etc., which are different from other HZO devices, the physical origin of their electron transport must be studied.

To investigate the transport mechanism, electrical characteristics of HZO-based FE diodes were measured in a dark and open atmosphere environment at various temperatures (303–363 K). By fitting the measured *I-V* curves with various existing models, a qualitative analysis was given to explain the transport mechanism in the HZO-based FE diode. The TiN/HZO/TiN/W-structured FE diode had been fabricated (Figure 1(a)). The *I-V* curves of the FE diode at the on-state and off-state are shown in Figure 1(b). Typical ferroelectric *P-V* curves are found in Figure S1(a) of metal-insulator-metal (MIM) capacitor devices under the same annealing conditions. The on and off directions could be exchanged when applying a voltage to switch the polarization of the FE diode (Figure S1(b)). Additionally, we could control the polarization of the device by providing a large program voltage. However, the read voltage should be significantly smaller than the program voltage to avoid ferroelectric switching [2].

At the on-direction, the current of the FE diodes is fitted and plotted in Figure 1(c). Figure 1(d) shows the verification of the current conduction mechanism for 7 nm thickness at different temperatures. The relationship between the current and voltage follows the equation $\ln(I) \propto \sqrt{V}$ and the relationship between current and temperature at an operating voltage of 1.54 V could be described as $\ln(\frac{I}{T^2}) \propto \frac{1}{T}$. It showed that when the FE diode was turned on, the current transport profile could be fitted by the Schottky model [6]. This relationship well fitted the Richardson-Schottky equation:

$$I = AST\exp\frac{e\beta_{\mathrm{RS}}E^{\frac{1}{2}} - \phi_0}{kT} \tag{1}$$

where $\beta_{\mathrm{RS}} = (e/4\pi\varepsilon_\infty\varepsilon_0)^{(1/2)}$, which is the R-S constant, A is the effective Richardson constant, and S is the area of device. More details and calculations about Schottky model could be found in Tables SI–SIII.

At the off-direction, the current transport mechanisms followed the hopping conduction model. Figures 1(e) and (f) indicated that the *I-V* relationship at a low voltage of the device follows $I \propto V$ and the *I-T* relationship at the voltage of 1.5 V followed $\ln(\frac{I}{V}) \propto \frac{1}{T}$. The mechanism fitted well with the electron hopping model [6]. More details about the fitting could be found in Table SIV.

$$I = \frac{s}{d}V\sigma_0\exp\frac{-E_a}{kT}, \tag{2}$$

where E_a is the electron activation energy.

The reasons for the change in the transport mechanism of FE diodes need to be analyzed. Here a possible explanation for the change in the transport mechanism of FE diodes is given as follows. The energy band of the HZO layer would yield a corresponding bending with respect to the polarization direction after the ferroelectric polarization operation, as shown in Figure 1(g). When the applied voltage

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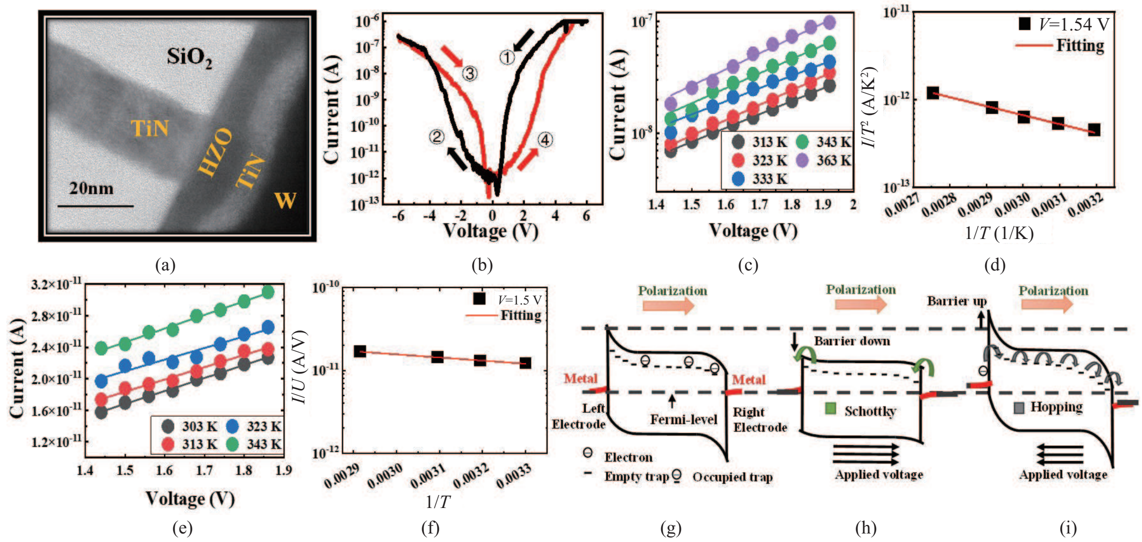

Figure 1 (Color online) (a) Cross-sectional TEM image of an FE diode. (b) Typical I-V loop of the TiN/HZO/TiN/W device marked with arrows. The thickness of HZO is 7 nm. The area of the device is 19 nm × 1.31 μm [2]. (c) and (d) I, V, and T relationships at various temperatures for the device when the FE diode is opened. The transport mechanism follows the Schottky model. (e) and (f) the FE diode is closed. The transport mechanism follows the hopping model. (g) Band bending caused by polarization. (h) Band bending profile for the FE diode at the on-state with the Schottky model. (i) Off-state transport mechanism with the hopping conduction model.

was 0, fewer electrons gathered on the polarization direction side (left electrode) while more electrons accumulated on the other side (right electrode). When the applied voltage direction was identical to the polarization direction (the FE diode is turned on, Figure 1(h)), electrons entered HZO near the right electrode more easily because the applied voltage reduced the band bending, making the trap level and the conduction band edge closer to the Fermi level near the right electrode. Simultaneously, the barrier near the left electrode side was reduced, which made entering TiN easier for electrons. A large FE-diode current could therefore be obtained, which exactly followed the Schottky model.

When the applied voltage was in the opposite direction to the polarization direction, the energy band was further bent, causing the trapping level and conduction band edge to move further from the Fermi level. Under the low voltage operation mode in Figure 1(i), only a few electrons could continuously jump or tunnel to the trapping sites and hop within these sites, as the energy was insufficient to excite the electrons to the conduction band. In the polarized ferroelectric materials, the number of electrons that could be reversely conducted was inherently small, so the reverse current was always smaller than the forward current.

This study showed that the defect distribution affects the FE-diode transport mechanism. This result shows options in the direction of the device performance optimization. For example, defect engineering based on the proposed mechanism could be used to optimize the on/off current ratio. In addition, polarization switching has certainly been influenced by the distribution of traps, the mechanism of which is not yet clear, and further work needs to be done to carefully explore this topic.

In summary, a series of temperature-variant electrical measurements were performed to study the transport mechanism. The current transport mechanism of the programmable FE diode is related to the polarization of the FE diode. If the applied voltage and the polarization of the FE diode are in opposite directions, the carrier transport is dominated by the Schottky model; if the directions are the same, the hopping conduction mechanism dominates. A clearer understanding of the FE-diode transport mechanism is crucial for optimizing the FE diode.

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Supporting information Figure S1, Tables SI–SIV. The supporting information is available online at info.scichina.com and link.springer.com. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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