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Resistive switching in a $\text{GaO}_x\text{-NiO}_x$ p-n heterojunction

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We report a unidirectional bipolar resistive switching in an n-type GaO_x /p-type NiO_x heterojunction fabricated by magnetron sputtering at room temperature. The resistive switching behavior coincides with the switching between Ohmic conduction (low resistance) and rectifying behavior (high resistance) of the heterojunction diode. Under external electric field, electromigrated intrinsic defects, such as oxygen vacancies and oxygen ions, accumulate at the pn junction interface and modify the interface barrier, forming or rupturing the filamentary paths between n- GaO_x and p- NiO_x , leading to the switching between Ohmic and diode characteristics of the device. The device shows good endurance, retention performance, and scaling capability, signaling the potential of a diode-structured resistive switching device for non-volatile memory applications. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4757761>]

Resistive switching random access memory (RRAM) has attracted much interest with great potential in non-volatile data storage. Various RRAM devices have been reported thus far based on transition metal oxide (TMO) film sandwiched by two metal electrodes, such as TiO_2 ,¹ NiO ,² CuO ,³ ZrO_2 ,⁴ ZnO ,⁵ etc. Based on this basic metal/insulator/metal (MIM) structure, several mechanisms have been proposed to explain the origin of resistive switching (RS). To avoid the thermal disadvantages of unipolar RS (usually related with a filamentary path), recently more and more attention have focused on bipolar RS, which mainly attribute to the interface engineering in MIM structure. It is generally accepted that the RS occurs mainly at interface between oxide and electrode rather than in the bulk, and the interface-type RS usually originates from the redox process based on migration of oxygen vacancies (or oxygen ions) and change in Schottky barrier height or width by trapping/detrapping effects near interface region.⁶ As for the Schottky barrier mode of RS, the electrons pass through the thinner barrier in low resistive states (LRS) via a tunneling process, while the thicker barrier in high resistive states (HRS) prevents the electrons from tunneling.⁷ Similar as barrier engineering in MIM based RRAM device, adjusting the interface between p-type and n-type oxide films in metal/insulator/insulator/metal (MIIM) structure could also result in RS phenomenon. According to the initial rectifying characteristic of p-n junction (HRS under reverse bias, LRS under forward bias), the reproducible resistance change could be obtained by an opposite operation; the proper soft breakdown under reverse bias could turn the device from HRS to LRS, whereas the

forward bias will recover the device from LRS back to HRS (preferably in low voltage region).

Transition from stable rectifying behavior to RS behavior has been reported in MIM structure with a Schottky junction.^{8,9} However, there is little report on such transition for p-n junctions, although some early works had observed the resistance hysteresis in some perovskite oxide heterojunction.¹⁰ In this paper, we shall report a stable RS phenomenon in a p-n junction based on the $\text{GaO}_x/\text{NiO}_x$ heterostructure, which offers an alternative design of RRAM device. We shall show that migration of oxygen vacancies near interface of p-n junction play an important role in the switching process.

Commercial ITO glass was employed as the substrate with ITO as the bottom electrode in our device. A NiO_x and GaO_x film with a thickness of 90 nm and 70 nm respectively was deposited successively on the ITO substrate by rf magnetron sputtering. The sputtering process was carried out in an Ar ambient (6×10^{-3} Torr) at room temperature. Finally, indium shots were used as a simple top electrode for test. The schematic structure of device is shown in the inset of Fig. 1(a). The I-V characteristics were measured by a semiconductor parameter analyzer in a diode I-V sweeping mode at room temperature. During the test, the bottom ITO electrode was always grounded while different biases were applied on top electrode (In).

Fig. 1(a) shows the current-voltage (IV) characteristics of the as-fabricated stack of $\text{In}/\text{GaO}_x/\text{NiO}_x/\text{ITO}$ and stacks of $\text{In}/\text{GaO}_x/\text{In}$ and $\text{ITO}/\text{NiO}_x/\text{ITO}$ for comparison purpose. We can see a typical rectifying curve intrinsic to diode with a turn-on voltage of about -2 V for $\text{In}/\text{GaO}_x/\text{NiO}_x/\text{ITO}$ stack. It is worth mentioning that the positive voltage applied on In cannot be too high; otherwise, the diode will run into RS state. For our $\text{In}/\text{GaO}_x/\text{NiO}_x/\text{ITO}$ structure, the RS behavior

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FIG. 1. (a) I-V curve of initial behavior in In/GaO_x/NiO_x/ITO, In/GaO_x/In and ITO/NiO_x/ITO structure; inset is schematic of In/GaO_x/NiO_x/ITO device. (b) RS behavior in In/GaO_x/NiO_x/ITO structure; inset is RS performance in 50 cycles.

could happen in the following regions: the GaO_x layer, the NiO_x layer, the interface between GaO_x and NiO_x, and the interfaces of In/GaO_x and NiO_x/ITO. As shown in Fig. 1(a), the In/GaO_x/In and ITO/NiO_x/ITO structures show Ohmic behavior, and no resistive switching are triggered by applying bias with any polarity or intensity. Thus, we can exclude the possibility of RS in the semiconductor layer and their interfaces with electrodes. As reported previously, non-stoichiometric NiO_x ($x > 1$) is a p-type semiconductor due to the excess oxygen ions (Ni-deficient) as acceptors for generating holes,¹¹ and non-stoichiometric GaO_x ($x < 1.5$) is an n-type semiconductor due to the oxygen vacancies (oxygen-deficient) as donors for generating electrons.¹² With Hall Effect measurement, we confirmed the carrier type for GaO_x and NiO_x and the sheet carrier concentration of GaO_x and NiO_x is $-8.603 \times 10^{11}/\text{cm}^2$ and $+2.012 \times 10^{14}/\text{cm}^2$, respectively. Accordingly, the as-prepared GaO_x and NiO_x layers in Ar ambient at room temperature were relatively conductive due to the existence of intrinsic defects (oxygen vacancies/oxygen ions). On the other hand, from the curves in Fig. 1(a), the contact of NiO_x/ITO and GaO_x/In are close to ideal Ohmic; thus, there exist no Schottky barrier between the semiconductor and electrode. Concluded from the analysis above, the rectifying and RS behaviors should come from the p-n junction formed by GaO_x and NiO_x; under external excitation, the alteration of the potential barrier at the junction between n-type GaO_x and p-type NiO_x should be responsible.

Fig. 1(b) demonstrates a typical resistive switching behavior of the In/GaO_x/NiO_x/ITO stack. When a positive

bias on In sweeps to a critical value of about 3 V, the current suddenly increases due to a restorable breakdown and the device is set from HRS to LRS. An Ohmic behavior is detected as the bias sweeps back to negative (within -1 V). When the negative voltage increases further, an abrupt decrease of current occurs and the device is reset from LRS to HRS. With further increase of the negative voltage, the current increases again, but it is not an Ohmic behavior. In fact, after reset process, the device returns to rectifying behavior again, and the HRS state just exists in a narrow negative voltage range. It is worth mentioning that the device could only be set by applying positive voltage and reset by applying negative voltage on In, which also provides the evidence that RS behavior originates from the n-p interface in metal/n-type semiconductor/p-type semiconductor/metal structure. Supposing the RS occurs from either the interface between In and n-type GaO_x or p-type NiO_x and ITO, the device should be set from HRS to LRS when negative voltage was applied on the In (reverse bias on In/n-type GaO_x) or when positive voltage was applied on ITO (reverse bias on p-type NiO_x/ITO). The inset of Fig. 1(b) shows the I-V curves of RS performance in 50 cycles, from which we can see that the set voltages distribute in a larger range compared to reset and the was randomly distributed for the 50 cycles below 5 V. As is widely accepted, the forming process and compliance current (CC) are two important factors for RS operation. In our measurement, there exists no apparent forming process. A CC of 5 mA was applied to the set operation to prevent the device from permanent breakdown. When the CC exceeds 15 mA, the repeatable RS behavior disappears and is replaced by permanent Ohmic behavior.

Fig. 2(a) shows the endurance characteristics of the In/GaO_x/NiO_x/ITO memory cell in DC sweep mode at room temperature. We can see that although there is a relatively larger fluctuation in HRS resistance in the first 30 cycles, the resistance ratio of HRS/LRS is $\sim 10^2$ with little degradation, which is suitable for practical applications. After 30 cycles, the resistance of HRS becomes stable. The retention performance of our device under room temperature is shown in Fig. 3(b). Both resistance in HRS and LRS display little decay in 10^5 s, showing very good non-volatility for RRAM applications.

To study the switching behavior of p-n heterojunction, the conduction property during whole resistive switching were investigated. As illustrated in Fig. 3, typical I-V curve of both set and reset were both redrawn in positive log-log scale. The device exhibits Ohmic behavior in LRS and represents the existing filamentary path as widely accepted.¹³ However, the case is more complicated in HRS region. Under low electric field, the device obeys the Ohmic behavior, while the I-V curve shows nonlinearity under higher electric field. Three main conduction models, including space charge limited conduction (SCLC), Schottky emission, and Poole-Frenkel emission (PF emission) were employed respectively to fit the nonlinear region. The slope in log-log curves was 3.18 in set process and 3.09 in reset process, which exclude the SCLC mechanism (slope should be around 2 according to Child's Law) in our case. For Schottky emission, the relationship between current and voltage could be expressed as follows:¹⁴

FIG. 2. (a) Endurance performance in 100 repeating cycles; (b) retention characteristic at room temperature.

$$I \propto T^2 \exp \left[\frac{e\sqrt{(eV)/(4\pi\epsilon_i\epsilon_0 d)}}{kT} \right]. \quad (1)$$

And PF emission can be depicted as¹⁴

$$I/V \propto \exp \left[\frac{e\sqrt{(eV)/(\pi\epsilon_i\epsilon_0 d)}}{kT} \right], \quad (2)$$

where I is the current, V is the voltage, e is the electron charge, ϵ_0 is the permittivity of free space, ϵ_i is the dielectric constant, d is the thickness of film, k is the Boltzmann's constant, and T is the temperature. After comparison, the PF emission better fit the nonlinear curve than Schottky emission as shown in the inset of Figs. 3(a) and 3(b). The Schottky emission usually refers to electric-field-enhanced thermal excitation of electrons from defect-related trapped states into conduction band, and according to previous reports, it usually occurs at higher electric field region compared with Schottky emission in RS behavior.^{15,16} The PF model was also been modified by Ieda *et al.* that at low electric field the current can follow the Ohm's law, while at high field it will obey the usual PF equation.¹⁷ Therefore, the transport characterization corresponds to filamentary property in LRS while it is dominated by PF emission in HRS in our device.

As for the RS mechanism, a controversy between the filament and interface models has lasted for a long period.

FIG. 3. The I-V curve of (a) set and (b) reset process drawn in log-log scale; the insets in both images show the PF emission fitting with $\ln(I/V)-V^{1/2}$ axis.

Unlike the irreconcilable discussion in early time, recently more people would like to believe that these two mechanisms can exist simultaneously and affect each other in some types of RS behaviors. Akinaga *et al.* also offered a unified model of RS based on such combination.¹⁸ Considering the conduction analysis above, the RS process in the p-n heterojunction could be illustrated with the energy band diagram as Fig. 4 shows. The process can be divided into four steps: (a)

FIG. 4. The illustration of RS behavior in p-n heterojunction: (a) low current due to the barrier, (b) high current due to the soft breakdown of barrier, (c) low current due to the recovery of barrier, (d) increasing current under forward bias of diode.

FIG. 5. (a) The schematic of 1- μm testing cell and corresponding SEM image. (b) The comparison of RS behavior between previous device and 1- μm testing cell.

When a positive bias is applied on the In top electrode, the p-n junction is reversely biased, external electric field will enlarge the depletion region and elevate the interface barrier, which suppresses the diffusion current passing through the junction as a usual diode behaves. The conductive paths at both sides were blocked by the interface barrier and the device is in HRS. (b) Oxygen vacancies (V_{O}^{+}) are known to be positively charged and mobile.¹⁹ Further increasing the positive bias leads to accumulation of positive oxygen vacancies (from inside GaO_x) at the p-n junction on GaO_x side, forming a high-doping region. At the same time, there also forms a negatively charged high-doping region on NiO_x side near the interface due to the accumulation of negative oxygen ions (O^{2-}). Thus, a significant reduction of effective barrier height and depletion region width could be expected.^{19,20} Beyond a critical value, large amount of electrons tunnel through the narrower barrier between two high-doping regions and the filamentary paths are able to pass through the interface,²¹ which bring the device to LRS. The process corresponds to the so-called soft breakdown of insulator. (c) Due to the high density of defects (oxygen vacancies/oxygen ions) near the interface, the junction behaves like a resistor with high current and the LRS is non-volatile. Until a high enough negative bias on In electrode to repel these defects away from interface region, the barrier recovers back, cutting off the connected filaments. The device returns to HRS and the small drift current mainly due to the electron transport over the p-n barrier (like diode). (d) With further increase of negative bias, the height of barrier reduces and an increasing current could pass through the interface, tracing back the rectifying behavior of heterojunction. Summarizing from above description, the RS can be interpreted as a switching between

rectifying and Ohmic behavior. The filaments in both NiO_x and GaO_x away from interface just serve as virtual cathode and anode, while the junction barrier engineered by defects migration controls the connection and rupture of filaments near interface, resulting in the RS behavior. There exists only a unidirectional bipolar RS in p-n heterojunction (set in reverse bias, reset in forward bias) due to the rectifying characteristics. And the HRS of the RRAM device exists at low voltage region when the p-n junction is in forward bias.

We also fabricate a 1- μm testing cell with the same thickness of GaO_x and NiO_x to investigate the scaling property of p-n heterojunction RRAM. As presented in Fig. 5(a), the whole device was deposit by magnetron sputtering on silicon wafer and patterned by photolithography. Ti/W alloy instead of indium spots is employed as n-contact top electrode on GaO_x film. Compared with previous device, an apparent decreasing of current (increasing of resistance) in both LRS and HRS was observed in the 1- μm testing cell as Fig. 5(b) shows. According to the resistance dependence on cell area reported by many other works,⁶ the interface factor should play a significant role in the RS in the GaO_x - NiO_x heterojunction. The reducing cell area directly decreases the amount of conductive paths crossing over the interface and further increases the resistance.

In conclusion, a unidirectional bipolar RS was observed in the GaO_x - NiO_x heterostructure fabricated by magnetron sputtering at room temperature. The RS behavior could be concluded as the switching between rectifying and Ohmic behavior of the diode. The alteration of junction barrier due to the electric field and the migration of intrinsic defects (oxygen vacancies in GaO_x and oxygen ions in NiO_x) control the filamentary paths passing through the interface, which accounts for the RS behavior observed. The device shows good endurance and retention performance, manifesting the potential application of p-n junction structure in non-volatile memory.

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