An understanding of the electronic bipolar resistance switching behavior in Cu/TiO₂/ITO structure

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Abstract: In this study, TiO_2 films and devices were prepared by sol-gel method. The bipolar resistive switching phenomena was observed in the Cu/TiO₂/ITO device. The conduction mechanism of devices were analyzed. It was found that the conduction mechanism is dominated by space charge limited current in high resistance state, and Schottky emission in low resistance state.

I. Introduction

Resistive random access memory (RRAM), a promising candidate for the next generation nonvolatile memory (NVM), is based on the switching of resistance (high and low) to record two logic states ('0'and'1')[1-4]. Because of its simple structure, high speed operation, low power consumption, high packing density, it has been widespread concern in the industry[2, 5]. However, before the realization of commercial product of the devices and systems, a design guide for RRAM based on switching mechanism is necessary[2, 6]. The RS phenomena can be catalogued into unipolar resistance switching (URS) and bipolar resistance switching (BRS), where the set/reset switching bias polarity is the same for URS and different for BRS[3, 4]. Although this classification is simple and clear, it barely gives any implications of the switching mechanism itself. Simple binary oxide materials, such as TiO_2 , ZnO and NiO[6-10], have advantage in microelectronics applications because of their simpler fabrication process and compatibility with standard semiconductor technology. In this letter, the resistive switching characteristics of Cu/TiO₂/ITO device was investigated.

II. Experimental

Three layers of TiO₂ films about 200nm were deposited onto glass and ITO using sol-gel spin coating technique at room temperature. The films were thermally annealed at 350 -500°C for 2 h. The Cu top electrodes were deposited on the thin films using thermal evaporation method. The diameters of the top electrodes about 50 μ m were defined by metal shadow masks. All devices were electrically characterized in the dark with computer controlled Keithley 2400. During the measurements of Cu/TiO₂/ITO device, the voltage bias was applied to the top electrode (TE), while maintaining the bottom electrode (BE) grounded. The current-voltage characteristics were studied by voltage sweeping measurements.

III. Results & discussion

The surface of thin films was characterized by Atomic Force Microscopy (AFM). As is shown in Fig.1, the roughness of TiO_2 thin films increases with annealing temperature. The texture observed in high temperature annealed thin films may come from the formation of domain boundary. B. Samuneva et. al showed that TiO_2 films are amorphous while the annealing temperature was less than 400 °C, and become polycrystal after annealing at 500 °C[11]. The observation of domain structure is consistent with this. And the resistance of TiO_2 film was measured using Keithley 2635, and we found that, as annealing temperature increases, the resistivity decrease dramatically first and nearly do not change at higher annealing temperature (Fig.2).



Figure 1 (a) AFM images (annealing @350-500°C); (b) The roughness of TiO₂ thin films increases with annealing temperature.



Figure 2 the resistivity of films

All Cu/TiO₂ /ITO devices with different annealing temperature showed bipolar resistive switching behavior (not showed here). In order to clarify the origin of the switching characteristics, the conduction mechanisms of the high resistance state (HRS) and low resistance state (LRS) of samples annealing at 350°C were analyzed. The current-voltage (I-V) characteristics of the Cu/TiO₂/ITO devices were studied by DC sweep measurements and a typical result was shown in Fig. 3, where the arrows indicate the switching direction. The voltage was swept in steps of 0.04 V, within $\pm 2V$ range. During the measurements, a current compliance of 0.01 mA was set to avoid any hard-breakdown of the devices. The investigated device exhibits bipolar switching behavior.



Figure 3 bipolar RS phenomena of Cu/TiO₂ /ITO devices

In order to clarify the origin of the switching characteristics of RRAM, the conduction mechanisms of the HRS and LRS were analyzed in details. The classical nonlinear conduction mechanisms including Schottky emission, Poole-Frenkel(PF) emission, space charge limited current (SCLC), and Fowler–Nordheim were adopted to fit the nonlinearity of the measured I–V relation. It was found that the conduction mechanism of HRS fit well to the space-charge-limited conduction (SCLC) mechanism. Other conduction mechanisms such as Schottky, Poole–Frenkel and Fowler–Nordheim were investigated but they did not fit the I–V curves at all. According to the mechanism of SCLC, the I–V relation can be expressed as[12]:

$$\mathbf{J} = qn\mu \frac{\mathbf{v}}{d} \qquad \mathbf{V} < \mathbf{V}_{\Omega} \tag{1}$$

$$I \propto \frac{9}{8} \varepsilon_r \varepsilon_0 \mu S \frac{v^2}{d^3} \qquad V > V_\Omega \tag{2}$$

$$LnI \propto lnV \qquad V < V_{\Omega} \tag{3}$$

$$LnI \propto 2lnV \qquad V > V_{\Omega} \tag{4}$$

in which q is the electric charge, S is the area of the Cu Electrode, ε_r is dynamic dielectric constant, ε_o is the permittivity of free space, d is the thickness of the film, n is the thermally produced free carrier density, μ is the electron mobility in the TiO2 film.

Similarly, the conduction mechanism of LRS can be fitted with the Schottky emission mechanism. According to the mechanism of Schottky emission, the I-V relation can be expressed as [13]:

$$\ln I \propto \frac{\sqrt{\frac{e^3}{4\pi\varepsilon_0\varepsilon_r}}}{kT}\sqrt{V} \tag{5}$$

in which k is the Boltzmann's constant.

Curves 3 and 4 also showed similar behavior. The mechanisms for resistive switching of the transition metal oxides are interesting but still controversial. We believe that device in the HRS containing high density of defects exists at TiO₂/ITO interface, where the high density of surface states is induced by the positively charge. The dense interface defects act as trap centers of carriers and dominate the I-V characteristics with SCLC conduction mode. A large current increase occurs when trapping sites are fully occupied at a threshold voltage. The meanwhile the Schottky barrier exist at TiO₂/Cu interface. The Schottky-like I-V characteristic becomes dominant in the LRS. When the voltage was swept to the reset voltage, the resistance increased suddenly. Because carriers escape from the traps, curves 4 showed SCLC conduction mechanism.

IV. Conclusion

In this paper, an electronic type BRS behavior observed in the $Cu/TiO_2/ITO$ structure was analyzed. The fitting of I –V curves showed that SCLC controlled the conduction of HRS and Schottky emission controlled the conduction of LRS, respectively.

References

- [1] Meijer GI. Materials science. Who wins the nonvolatile memory race? Science. 2008;319:1625-6.
- [2] Sawa A. Resistive switching in transition metal oxides. Materials Today. 2008;11:28-36.

- [3] Tang MH, Zeng ZQ, Li JC, Wang ZP, Xu XL, Wang GY, et al. Resistive switching behavior of La-doped ZnO films for nonvolatile memory applications. Solid-State Electronics. 2011;63:100-4.
- [4] Waser R, Dittmann R, Staikov G, Szot K. Redox-Based Resistive Switching Memories Nanoionic Mechanisms, Prospects, and Challenges. Advanced Materials. 2009;21:2632-63.
- [5] Li H, Niu B, Mao Q, Xi J, Ke W, Ji Z. Resistive switching characteristics of ZnO based ReRAMs with different annealing temperatures. Solid-State Electronics. 2012;75:28-32.
- [6] Fan Y-S, Liu P-T, Hsu C-H. Investigation on amorphous InGaZnO based resistive switching memory with low-power, high-speed, high reliability. Thin Solid Films. 2013;549:54-8.
- [7] Bae YC, Lee AR, Kwak JS, Im H, Hong JP. Dependence of resistive switching behaviors on oxygen content of the Pt/TiO2–x/Pt matrix. Current Applied Physics. 2011;11:e66-e9.
- [8] Ma G, Tang X, Zhong Z, Zhang H, Su H. Effect of Ni3+ concentration on the resistive switching behaviors of NiO memory devices. Microelectronic Engineering. 2013;108:8-10.
- [9] Senthilkumar V, Kathalingam A, Kannan V, Senthil K, Rhee J-K. Reproducible resistive switching in hydrothermal processed TiO2 nanorod film for non-volatile memory applications. Sensors and Actuators A: Physical. 2013;194:135-9.
- [10] Zhang J, Yang H, Zhang Q-l, Dong S, Luo JK. Structural, optical, electrical and resistive switching properties of ZnO thin films deposited by thermal and plasma-enhanced atomic layer deposition. Applied Surface Science. 2013;282:390-5.
- [11] B. Samuneva VK, Ch. Trapalis, R. Kranold. Sol-gel processing of titanium-containing thin coatings. Journal of Materials Science. 1993;28.
- [12] Lampert M. Simplified Theory of Space-Charge-Limited Currents in an Insulator with Traps. Physical Review. 1956;103:1648-56.
- [13] Chang W-Y, Lai Y-C, Wu T-B, Wang S-F, Chen F, Tsai M-J. Unipolar resistive switching characteristics of ZnO thin films for nonvolatile memory applications. Applied Physics Letters. 2008;92:022110.