

1-1-2013

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Jia, Ze; Wang, Linkai; Zhang, Naiwen; Ren, Tianling; and Liou, Juin J., "Effects of anode materials on resistive characteristics of NiO thin films" (2013). *Faculty Bibliography 2010s*. 4155.

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Cite as: Appl. Phys. Lett. **102**, 042901 (2013); <https://doi.org/10.1063/1.4789523>

Submitted: 04 November 2012 . Accepted: 14 January 2013 . Published Online: 28 January 2013

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Effects of anode materials on resistive characteristics of NiO thin films

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(Received 4 November 2012; accepted 14 January 2013; published online 28 January 2013)

This letter shows that the NiO-based structure with different anodes has different resistive switching properties. A conical conductive filament (CF) model is proposed for oxygen vacancies distributed in NiO films. Modeling analysis reveals much larger dissolution velocity of CF near anodes than near cathodes during the reset process. Different interfaces shown in Auger electron spectroscopy can be bound with the model to reveal that CF is dissolved in the structure with Pt or Au as anodes, while CF remains constant if the anode material is Ti or Al, which can explain whether switching properties occur in the specific NiO-based structures. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4789523>]

Resistive switching phenomena in metal/oxide/metal structures have been investigated for the application to resistive random access memory (RRAM) devices.^{1–4} Among various oxide films exhibiting resistive switching phenomena, NiO is one of the most promising materials because of its simple constituents, clear switching characteristics, and high on/off ratio.^{5,6} In the case of NiO-based RRAM devices, the switching mechanism has been recognized to be a highly localized phenomenon, where a conductive filament (CF) is alternatively formed and destroyed within the dielectric layer.^{7–9} Although the filament formation and rupture model describe unipolar resistive switching characteristics well, an understanding of microscopic details of the set and reset transitions is still important. Recent studies have reported that the filament formation and recovery may occur at metal/oxide interfaces.^{10,11} This suggests that electrode materials play an important role in the switching mechanism. If we can control the filaments and the regions where the formation and rupture occur, RRAM will be more stable and reliable for practical applications. In this study, switching behaviors of Pt (top)/NiO/Pt (bottom) and Au (top)/NiO/Pt (bottom) structures were carefully analyzed and compared to the I-V characteristics of Ti (top)/NiO/Pt (bottom) and Al (top)/NiO/Pt (bottom) structures. By means of the data analysis, a possible mechanism of resistive switching was given.

Devices were fabricated as a conventional metal/insulator/metal structure. A Pt bottom electrode was deposited on Ti/SiO₂/Si by sputtering. Then, a nickel oxide precursor was deposited by spin-coating at 3000 rounds per minute for 20 s on the Pt substrate. The nickel oxide precursor is available from Kojundo Chemical Company, Japan. After each coating, the wet film was baked at 260 °C for 5 min. Then, the spin-coated sample was annealed in a furnace at 450 °C in an oxygen atmosphere for 30 min. These coating, drying, and annealing processes were repeated several times to reach a

100-nm-thick NiO film. Various top metal electrodes with thickness of about 100 nm and area of 0.09 mm² were fabricated by sputtering through a shadow mask, just can be seen from Figure 1. All device characteristics were measured using an Agilent 4155C semiconductor parameter analyzer in dc sweep mode. An Auger electron spectroscopy (AES) analysis was also carried out for further investigation.

Figure 2 shows the measured current-voltage (I-V) curves of metal/NiO/Pt structures with Pt, Au, Ti, and Al top electrode, respectively. The positive bias voltage is applied to the top electrode while the bottom electrode is grounded. The bias voltage is swept from 0 to 3 V for the set process and high-to-low resistance switching is happened in all of the four structures. After the set process, the bias voltage is from 0 to 1.2 V for the reset process. It is obvious that Pt/NiO/Pt and Au/NiO/Pt structures show resistive switching characteristics, while the reset process does not occur in Ti/NiO/Pt and Al/NiO/Pt structures. These results show that I-V behaviors could be influenced by electrode materials. Interestingly, when the positive bias voltage is applied to the bottom electrode and the top electrode is grounded, resistive switching characteristics are observed in all devices with different top electrodes (as shown in Figure 3). However, when positive bias is applied to Ti electrode, the switching characteristics disappear again. Samples with Al electrode show a similar I-V characteristic. In brief, when positive bias is

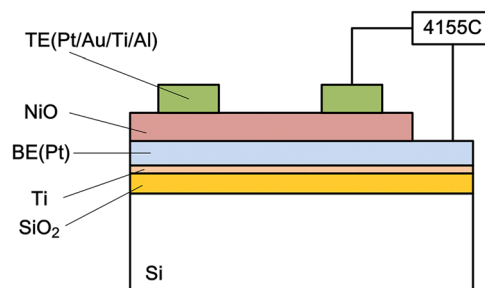


FIG. 1. Diagram of NiO-based device.

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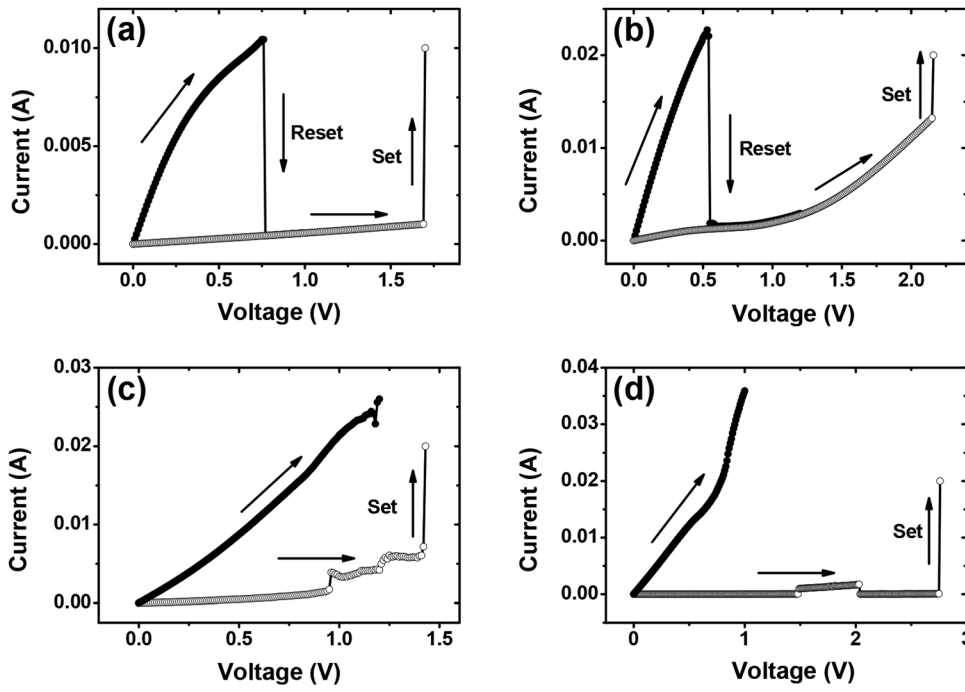


FIG. 2. I-V characteristics of metal/NiO/Pt structures with bottom electrodes grounded (a)Pt/NiO/Pt, (b) Au/NiO/Pt, (c) Ti/NiO/Pt, and (d) Al/NiO/Pt.

applied to the Pt or Au electrode, switching characteristics are observed. In contrast, switching characteristics disappear when positive bias is applied to the Ti or Al top electrode. The measured I-V characteristics show that anode materials that anodic electrode materials play an important role in the switching mechanism.

The switching mechanism of NiO-based devices has been recognized that CF is alternatively formed (set process) and destroyed (reset process) under the certain electric field within the NiO film.^{12,13} The transition of the device is from high resistive to low resistive when the CF is built and from low resistive to high resistive when the CF is dissolved. In this experiment, a positive bias is first applied to the metal/NiO/Pt structures, then CF is built thus set process is finished

in all four structures. Besides, the oxygen vacancies in transition metal oxides have great influences on the CF.^{5,14} So the movement and distribution of oxygen vacancies can influence the formation and the shape of CF. Due to the bias, many oxygen vacancies with positive charge will be attracted to the cathode. Therefore, the filament is strong in the region near the cathode and weak in the region near the anode. For the sake of simplicity, we consider a conical CF of height equal to the thickness of the oxide film ($t = \text{NiO}$). As shown in Figure 4, the CF is surrounded by the oxide and contacted by the anode and the cathode. The characteristics of temperature in the CF is computed by the Fourier heat-flow equation

$$-\nabla \kappa \nabla T = \rho J^2, \quad (1)$$

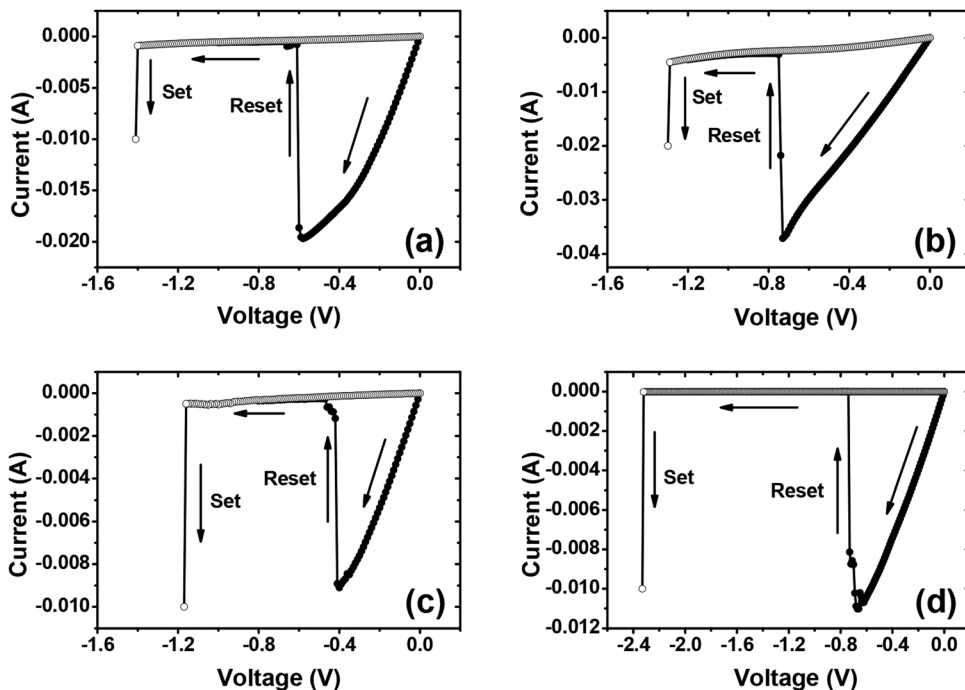


FIG. 3. I-V characteristics of metal/NiO/Pt structures with top electrodes grounded (a)Pt/NiO/Pt, (b) Au/NiO/Pt, (c) Ti/NiO/Pt, and (d) Al/NiO/Pt.

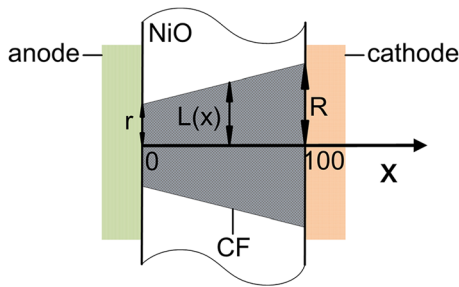


FIG. 4. Schematic diagram for CF.

where κ is the material thermal conductivity, ρ is the material resistivity, and J is the current density in the CF, thus the right-hand side represents the dissipated Joule power density.¹⁵ For the further calculation, the uniformity of transversal temperature is assumed then only x -direction is considered. Equation (1) is simplified as

$$\frac{d^2T}{dx^2} = -\frac{\rho J^2}{\kappa}. \quad (2)$$

The radius of the CF is r ($r=40$ nm) near the anode ($x=0$) and R ($R=200$ nm) near the cathode ($x=t_{\text{NiO}}$), then the radius of any point along x -direction is

$$L(x) = r + \frac{R-r}{t_{\text{NiO}}}x. \quad (3)$$

The current in the CF is set as I , thus

$$J = \frac{I}{S} = \frac{I}{\pi L(x)^2} = \frac{I}{\pi \left(r + \frac{R-r}{t_{\text{NiO}}}x \right)^2}. \quad (4)$$

Then, the heat flow equation (2) can be written as

$$\frac{d^2T}{dx^2} = -\frac{\rho I^2}{\kappa \pi^2 \left(r + \frac{R-r}{t_{\text{NiO}}}x \right)^4}. \quad (5)$$

Boundaries conditions are taken into consideration, the temperature in the anode and cathode is in accordance with Eq. (2), the current is the same with that in the CF. For the sake of simplicity, the temperatures in the upper surface of anode and the under surface of cathode are equal to room temperature. Equations (2) and (5) are coupled to simulate the temperature along the x -direction to describe the thermal dissolution of the CF. The values of parameters used for simulation are reported in Table I. We assume that the dissolution was resulted from the diffusion of conductive elements out of the filament.¹⁵ As a consequence, filament dissolution

TABLE I. Parameters used in the electrothermal simulations.

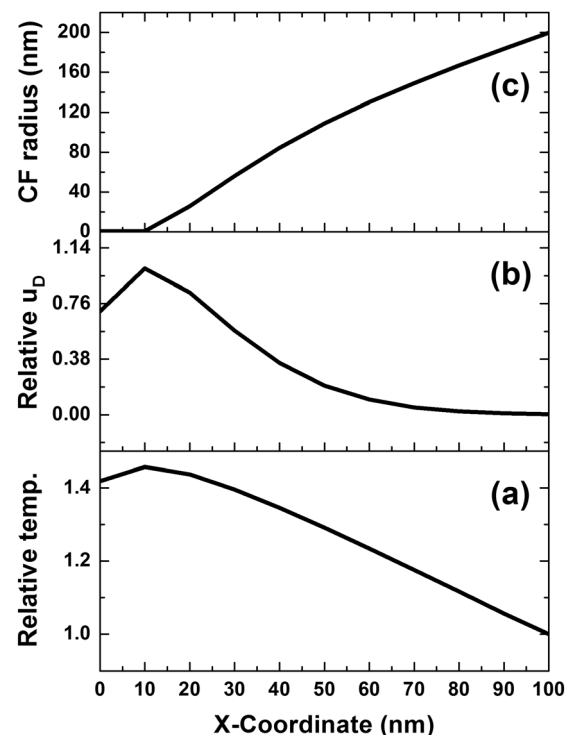
Parameter	Value	Reference
$\rho_{\text{CF}} (\mu\Omega\text{cm})$	810	15
$\kappa_{\text{CF}} [\text{W}/(\text{K m})]$	21.4	15
$\rho_{\text{NiO}} (\mu\Omega\text{cm})$	80×10^6	15
$\kappa_{\text{NiO}} [\text{W}/(\text{K m})]$	20	16
E_a (eV)	1.2	17
V_{D0} (m/s)	200	15

velocity v_D can be used to describe the velocity of the decreasing of the CF diameter in a simplified way. Also, filament dissolution velocity v_D is assumed to obey an Arrhenius dependence on temperature, i.e.,

$$v_D = v_{D0} e^{-\frac{E_a}{k_B T}}, \quad (6)$$

where E_a is an activation energy and k_B is the Boltzmann constant¹⁵ in Table I. As can be deduced from Eq. (6), the higher the temperature is, the larger the v_D is, thus the thinner the CF diameter is. Pt/NiO/Pt structure is adopted in the simulation and the results are shown in Figure 5. As can be seen from Figures 5(a) and 5(b), temperature and dissolution velocity near the anode are much larger than that near the cathode. When the CF radius near the anode decreased to zero, there was little change about the CF radius near the cathode, just as shown in Figure 5(c), thus the filament rupture will occur at the region near the anode during the reset process.

An AES analysis is carried out to find why the devices with Ti or Al top electrode lose their switching characteristics. Figure 6 shows the scanned atom profiling between TE and BE by the AES analysis. The AES analysis reveals that the Ti (and Al) is served as an oxygen getting material, as reported in Refs. 1 and 12, which would modify the oxygen vacancies distribution within the NiO film. As shown in Eq. (6), the filament dissolution velocity v_D is affected by the activation energy, E_a , which is characterized by the oxygen vacancies. The less the vacancies are, the larger the E_a is and the smaller the v_D is.¹⁸ Therefore, it is obvious that the switching characteristics are influenced by the oxygen vacancies distribution at the interface between the NiO film and the anode. This change did not occur at the interface when Pt or

FIG. 5. Simulation results on the CF (a) relative temperature distribution, (b) relative v_D distribution, and (c) the shape of CF after reset process.

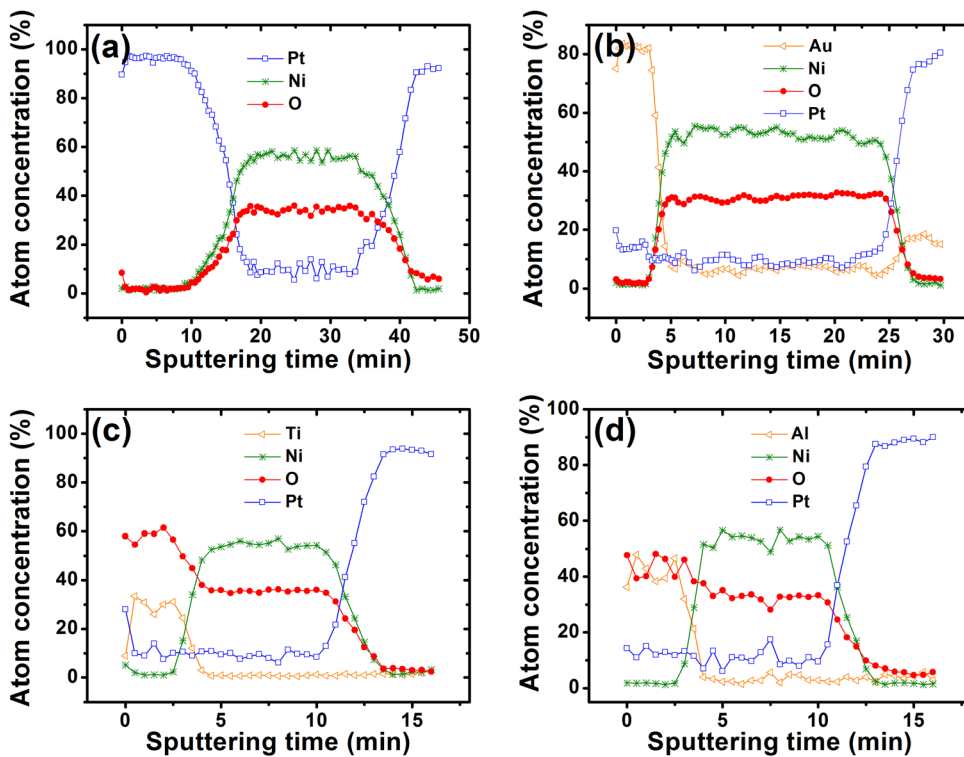


FIG. 6. AES vertical profiles of metal/NiO/metal structures (a) Pt/NiO/Pt, (b) Au/NiO/Pt, (c) Ti/NiO/Pt, and (d) Al/NiO/Pt.

Au was adopted as anode. As can be seen from Figure 7, simulation results also show that the shape of CF in the four structures is different from each other. If the anode is Pt or Au, the interface within the NiO film contains many oxygen vacancies then generating a relatively smaller E_z and a larger filament dissolution velocity. The filament near the anode fuses during the reset process and the CF radius is near zero in this region. On the contrary, when Ti or Al is used as anode, a larger E_z and a smaller filament dissolution velocity are resulted from the less oxygen vacancies near the interface. Then, the filament cannot be fused during the reset process and the CF radius is unchanged thus the resistive switching characteristics is disappeared, just as shown in Figures 2(c) and 2(d).

In this work, NiO thin films were fabricated by a spin-coating process followed by thermal annealing. Switching characteristics were observed when positive bias was applied to the Pt or Au electrode in NiO-based devices. When positive bias was applied to the Ti or Al electrode, switching

characteristics disappeared. The formation and the shape of CF can be influenced by the oxygen vacancies in the NiO film thus CF near anode is thinner than that near cathode. A conical model of CF is proposed and adopted in the simulation and analysis. The results show that CF near anode is easily fused in the Pt/NiO/Pt and Au/NiO/Pt structure thus the reset process can be achieved, while CF cannot be dissolved when Ti or Al is served as anode material due to decreased obviously dissolution velocity of CF near the anode of the oxygen-getting materials, such as Ti and Al, which is verified in the AES analysis and results in no reset process and no resistive switching.

The authors would like to acknowledge the National High Technology Research and Development Program of China for the support under Grant No. 2009AA01Z115.

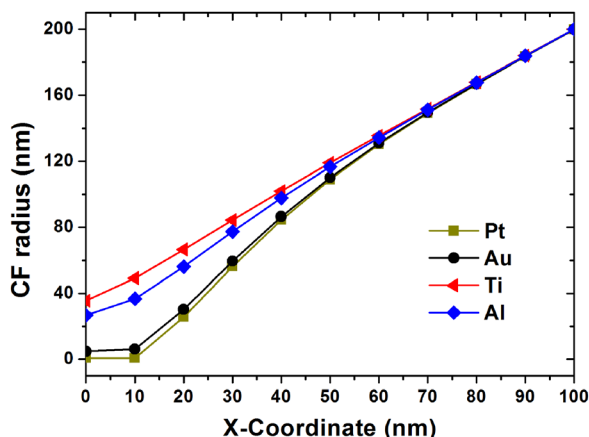


FIG. 7. The shape of CF with different anodes after reset process.

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