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Effects of metal electrodes on the resistive memory switching property of NiO thin films

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The effects of various metal electrodes on the resistive switching of NiO thin films were investigated. Contrary to the belief that Pt is used for its high work function, which enables Ohmic contact to *p*-type NiO, resistive switching was observed in films with Ta or Al electrodes with a low work function in the as-deposited state. The resistive switching of films with a Ag or Cu top electrode with a low work function and high free energy of oxidation shows the importance of the formation of an oxide layer at the metal/NiO interface. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2967194]

Currently, one of the subjects facing the semiconductor industry involves the scaling limit of conventional nonvolatile memory (NVM). Among the several candidates for next-generation NVMs to solve this problem, resistive random access memory (RRAM) based on a simple binary metal oxide such as NiO has the potential to serve as a replacement for conventional NVM owing to its good retention, high endurance properties, rapid operation, low power consumption, and especially due to its three dimensional multistack structures that enable it to realize ultrahigh density memory.[1] Most scientific research related to NiO has focused on the resistive switching mechanism of the NiO thin film itself. The main issues are related to how resistive switching occurs and wide distribution controls.[2–4] Many experimental results have explained the resistive switching mechanism of NiO or TiO_2 in terms of the formation and rupture of the conducting path at the localized anodic site in thin film bulk.[5,6] However, if the conducting path ruptures in bulk, the role of the metal electrode would simply involve the carrying of the current. Few papers exist regarding the role of metal electrodes and the interface between NiO and the metal electrode.[7,8] For NiO, a *p*-type semiconductor, Pt with a high work function has generally been used as an electrode, as resistive switching is induced in films with Ohmic contacts to the electrodes, whereas well-defined Schottky contact has been shown to hinder switching. However, many results exist that are not easily explained solely in terms of the work function and contacts. For example, Pt is also widely used for resistive switching materials of *n*-type semiconductors prone to form a Schottky contact with Pt.[6] Furthermore, considering the relatively high cost of the widely used Pt, reducing the manufacturing cost is essential before RRAM can be commercialized as a type of next-generation NVM. Therefore, the effects of electrodes on the switching properties must be considered as an important factor in pursuit of a proper substitute for metal electrodes.

This study details a systematic investigation of the effects of various metal electrodes on the resistive switching properties of NiO thin films. The importance of the reaction at the metal/NiO interface is demonstrated in relation to the free energy of oxide formation of electrode metals and Ni.

A Pt bottom electrode was deposited on $Ti/SiO_2/Si$ by dc magnetron reactive sputtering. Polycrystalline NiO thin film with a thickness of approximately 40 nm was deposited onto the Pt bottom electrode at a substrate temperature of 360 °C under a mixed gas atmosphere with a partial pressure of $P(Ar):P(O_2)=19:1$. The base pressure was 5×10^{-7} Torr and the pressure during the deposition process was 5 m Torr. Various top metal electrodes with thickness of about 50 nm and area of 30×30 μm^2 were fabricated by successive of sputtering, photolithography, and lift-off processes. To prevent damage from the W probe tip, Pt (~50 nm) was coated on top of the metal electrodes of Cu and Ta. Pt_xTi_{1-x} metals were cosputtered from Pt and Ti targets, and the composition was analyzed using an inductively coupled plasma atomic emission spectrometer. All of the device characteristics were measured using an Agilent 4156B semiconductor parameter analyzer in dc sweep mode. The valence states at the interface of the metal oxides were analyzed by x-ray photoelectron spectroscopy (XPS) high-resolution spectra.

Figure 1(a) shows the current versus voltage (*I-V*) characteristics of metal/NiO/Pt sandwiches with Pt, Ta, and Al top electrodes. Positive bias voltage was applied to the top electrode while the bottom electrode was grounded. All of the as-deposited samples showed resistive memory switching, although the switching voltages and the current levels varied. In particular, the sample of Al top electrode did not show similar resistive switching characteristics as reported previously.[7] This phenomenon cannot be explained in terms of previous report,[7] as the work function of Al (~4.28 eV) or Ta (~4.25 eV) is lower than that of NiO and because the metal/NiO interface is supposed to form an Ohmic contact. However, in 24 h, Al/NiO/Pt and Ta/NiO/Pt films lose their switching characteristics. The abrupt decrease in the resistance directly results in an irreversible breakdown of Ta/NiO/Pt and Al/NiO/Pt films, while Pt/NiO/Pt continues to exhibit repetitive resistive switching, as shown in Fig. 1(b). Interestingly, when Al, Mo, or Ta metal electrodes are used as a bottom electrode, resistive switching characteristics similar to that in a Pt/NiO/Pt structure are observed. However, resistive switching properties disappear when positive

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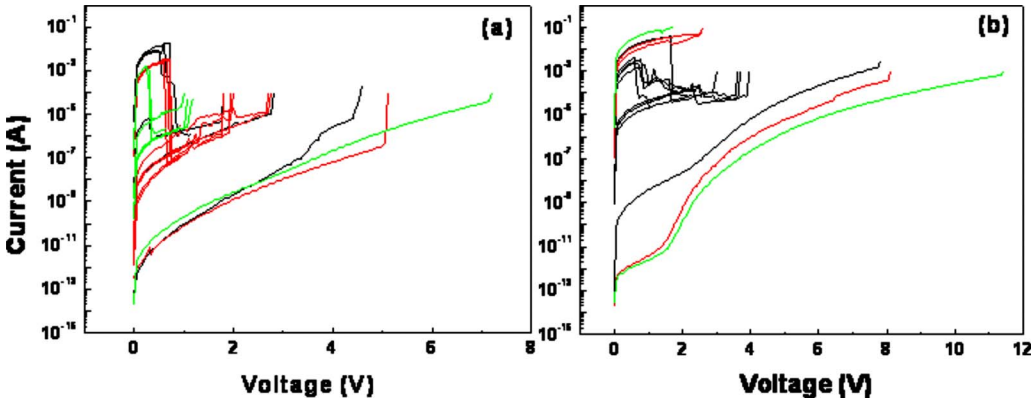

FIG. 1. (Color online) The *I-V* characteristics of NiO films using Pt (black), Ta (red), and (green) top metal electrode (a) at the as-deposition state (b) after one day. All samples have a Pt bottom electrode.

bias is applied to Al, Mo, or Ta bottom electrode.

From these time-dependent phenomena at the interfaces, it is inferred that the interface reaction between the top metal electrode and NiO likely plays an important role in resistive switching. After a forming or set process, various conducting paths form in bulk. Through a subsequent reset process, the paths are ruptured by local oxidation at the anodic site. During these processes, if oxygen atoms that are usually involved in the oxidation of Ni react with the top metal, a metal oxide can be created at the interface without local oxidation of the Ni conducting path. Generally, the oxidation of Al or Ta occurs more easily than that of Ni in a comparison of the standard free energy of the formation of oxides shown in the Ellingham diagram in Fig. 2.[9,10] Upon applied voltage, the created thin metal oxide can undergo permanent breakdown. As a result, the film maintains a low resistance state instead of reset process to a high resistance state (HRS), as in the Ta/NiO/Pt and Al/NiO/Pt shown in Fig. 1(b).

In order to elucidate the effects of the oxide layer at the interface, the switching properties of $Pt_{1-x}Ti_x/NiO/Pt$ films are shown in Fig. 3(a) with varying proportions of Ti. The Pt top electrode sample shows typical resistive switching, whereas the Ti top electrode sample does not. As the proportion of Ti increases, the resistance level of the HRS after reset process becomes lower to the point that all initial off state resistances and forming voltages are nearly identical. Some of the Ti atoms of the top electrode at the interface possibly form a metal oxide. During switching processes, the breakdown occurs at titanium oxide, as in the case of the Al or Ta top electrodes, whereas resistive switching normally occurs at the Pt interface. Therefore, an increased proportion of titanium oxide lowers the resistance level. Furthermore, the switching property completely disappears over a critical proportion of Ti (~33 mol %).

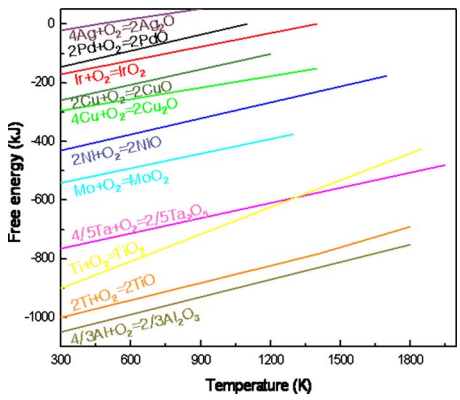

FIG. 2. (Color online) Ellingham diagram plotting the standard free energies of the formation of oxides (ΔG^o) of the metals mentioned in manuscript.

It is interesting to investigate the effect of the Ag electrode, as the free energy of the oxidation of Ag (positive value over 462 K) is higher than that of Ni while the work function of Ag (~4.26 eV) is lower than that of NiO. Figure 3(b) shows the resistive switching characteristic of Ag/NiO/Pt film, showing that the free energy of oxidation is the more important factor. XPS spectra at the interface between the top metal and NiO explain the difference between the Ag/NiO/Pt and Ta/NiO/Pt, as shown in Fig. 4. Both samples were analyzed directly after a reset voltage was applied. The resistance state of Ag/NiO/Pt film changes to HRS but that of Ta/NiO/Pt does not. Figure 4(a) corresponds to O $2s$ and the Ta $4f$ core peak region. The Ta $4f_{7/2-5/2}$ doublet located at 26.8–28.3 eV is assigned to Ta ions in the +5 formal oxidation state from Ta_2O_5. The presence of a shoulder (26.0–27.8 eV) corresponding to a further reduced Ta ion, "$Ta^{\delta+}$" ($\delta < 5$) was also observed. On the low binding energy side, the presence of a main peak centered at 22.5 eV corresponding to the specific ionization of the oxygen $2s$ orbitals was noted, as was a doublet at 22.0–23.9 eV associated with Ta metal. From the Ta $4f$ core peaks, tantalum oxide generated during aging or switching processes exists at the interface between NiO and the top Ta metal. However, the Ag $3d_{5/2-3/2}$ XPS spectra show core peaks at 368.1–374.1 eV [Fig. 4(b)] that was identified as Ag^0.

The Cu top electrode was also investigated, as Cu has higher free energy of oxidation than that of Ni. The Cu/NiO/Pt film showed a resistive switching property that was similar to that of the Ag top electrode, although Cu has a lower work function (~4.65 eV). This demonstrates the importance of the free energy of oxidation. However, the switching properties of the Ag and Cu top electrode samples differ slightly from that of the Pt top electrode sample. The resistive switching, especially the reset process, at a slower sweep speed is more stable when the other conditions are identical. This may result from the higher energy that is required in the reset of Ag/NiO/Pt and Cu/NiO/Pt. Ag and Cu are highly diffusive elements in semiconductor materials due to their high diffusion coefficient, $D=D_0\exp(-Q/kT)$.[11]

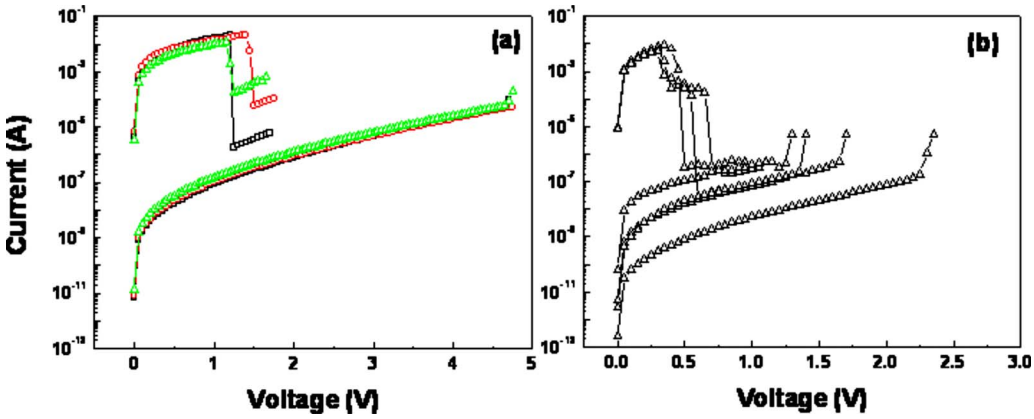

FIG. 3. (Color online) (a) Comparison of the resistance values after a reset process and the *I-V* characteristics of $Ti_{0.10}Pt_{0.90}$ (black square), $Ti_{0.21}Pt_{0.79}$ (red circle), and $Ti_{0.31}Pt_{0.69}$ (green triangle). (b) *I-V* characteristics of a NiO film with a Ag top electrode.

They can migrate into the NiO bulk from the top electrode and affect the resistive switching characteristics. The migrated atoms can connect to metallic Ni in the conducting path after the set or forming process. From these reasons, the length of the Ni conduction path is shorter due to the migrated portion. According to a recent simulation, the shape of the conducting path is like a cone rather than a cylinder.[12] In this case with a Ag or Cu electrode, the end of the cone can be thicker than that in Pt/NiO/Pt due to the migrated metal atoms; additional energy is required to rupture the end of the conduction path during the reset process.

In summary, the electrode dependence on resistive switching does not result from the work function or from the metal electrode/NiO contact but instead is a result of the free energy of formation of metal oxide compared to Ni oxidation. The metal oxide created at the interface between NiO and the metal electrode affects the resistive switching characteristics due to the metal oxide breakdown that occurs at the anodic site. Additionally, it was found that migrated atoms have an effect on the resistive switching properties. This study demonstrates the mechanism of the metal electrodes and the reset process in NiO-based RRAM in an effort to elucidate the criterion for selecting the metal electrode.

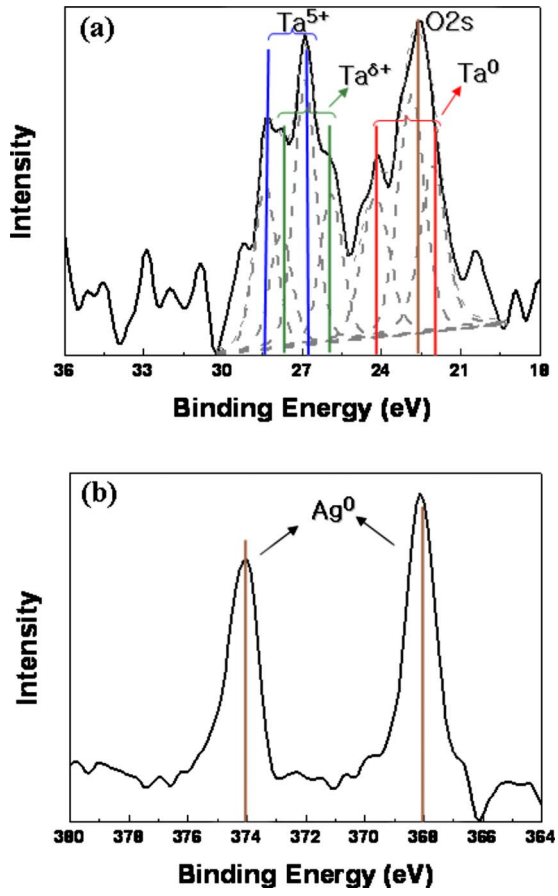

FIG. 4. (Color online) X-ray photoelectron spectra of (a) Ta $4f_{5/2}$ and Ta $4f_{7/2}$, and (b) Ag $3d_{3/2}$ and Ag $3d_{5/2}$. Ta^{5+}, $Ta^{\delta+}$, Ta^0, and O $2s$ in (a) correspond to the blue, green, red, brown lines, respectively. For confirming clear peak position, the XPS spectrum was fitted by using a combination of Gaussian (70%) and Lorentzian (30%) distributions (gray dashed lines). The curves fit for Ta $4f$ peaks were obtained using a fixed amplitude ratio $I_{7/2}/I_{5/2} \sim 4/3$ with a minimum number of doublets in order to fit the experimental curves. In (b), Ag $3d_{3/2}$ and Ag $3d_{5/2}$ peaks at 374.1 and 368.1 eV indicate Ag^0.

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