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Citation: [Applied Physics Letters](#) **94**, 022906 (2009); doi: 10.1063/1.3072800

View online: <http://dx.doi.org/10.1063/1.3072800>

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# Interfacial reactions and resistive switching behaviors of metal/NiO/metal structures

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(Received 4 November 2008; accepted 27 December 2008; published online 15 January 2009)

Ag/NiO/Pt structures did (did not) exhibit reproducible resistive switching when a positive bias was applied to the Pt (Ag) electrode. X-ray photoemission spectra revealed that ultrathin NiO films on Pt (Ag) layers did (did not) undergo reversible chemical state change during heat treatment in a vacuum and oxygen ambient. Such differences in interfacial chemical interaction may affect filament formation and rupture processes near the electrode and hence alter the resistive switching behaviors. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072800]

Resistive switching (RS) phenomena in metal/oxide/metal (MOM) structures have been intensively investigated for nonvolatile memory applications.<sup>1–11</sup> Vacancy and off-stoichiometry are practically unavoidable in metal oxide thin films. The clustering of such defects is believed to cause local conducting paths or filaments.<sup>3–11</sup> Although the filament formation and rupture model describe unipolar RS characteristics well,<sup>3,4</sup> an understanding of the switching process on a microscopic level is still lacking.

The role of the electrode material in unipolar RS should be clarified for understanding the switching process, as well as for improving the device performance.<sup>5–7</sup> It is now accepted that high-to-low resistance switching (SET) corresponds to a local reduction in the metal oxide layer (filament formation), while low-to-high resistance switching (RESET) corresponds to reoxidation (filament rupture).<sup>4–11</sup> Recent studies have reported that filament formation and recovery may occur at metal/oxide interfaces.<sup>9–11</sup> This suggests that redox processes in the interface region should be explicitly investigated.

Here, we report the RS behaviors of Ag/NiO/Pt structures and reduction/oxidation processes at the metal/NiO interface. The Ag/NiO/Pt structures exhibited reproducible switching only when a positive bias was applied to the Pt electrode. Chemical analyses revealed that the NiO/Ag (NiO/Pt) interface underwent an irreversible (reversible) reaction during heat treatment in a vacuum and oxygen environment. Our results suggest that the metal-oxide interfacial reaction may play an important role in RS phenomena.

We prepared NiO thin films by the thermal oxidation of Ni films deposited on platinumized silicon substrates.<sup>7,8</sup> Ag electrodes (thickness: 10 nm) capped with Au layers (thickness: 30 nm) were evaporated onto the NiO surface, resulting in Ag/NiO/Pt structures. All electrical measurements were performed at room temperature (RT), using a probe station and an HP 4145B semiconductor parameter analyzer. For analysis of the chemical structures, *in situ* x-ray photoemission spectroscopy (XPS) was performed in an ultrahigh vacuum (UHV) system.

Figure 1 shows the RS characteristics of Ag/NiO/Pt structures. The data were obtained from different pads for each bias condition. The bias voltage was swept from 0 to  $\pm 3$  V for the SET process and from 0 to  $\pm 1.2$  V for the RESET process. The voltage sweep speed and compliance current (20 mA) were identical irrespective of the bias polarity. The first voltage sweep curves (denoted by “1” in Fig. 1) appeared similar for both bias conditions: the current increased abruptly for voltages  $\leq -2$  and  $\geq 2$  V. Repetitive RS was observed when a negative (positive) bias was applied to the Ag (Pt) electrode. RESET did not occur when Ag was anode (the curves, denoted by “2” and “3,” corresponding to the second and the third sweep results). Lee *et al.*<sup>5</sup> reported that an increase in the voltage sweep speed was required for RS of their Ag/NiO/Pt structures. These and our results showed that the Ag electrode could influence the RS behaviors.

During the SET and RESET processes, Joule heating caused by the localized current distribution along the filamentary paths may have induced interfacial reactions. Thus, we performed an *in situ* XPS study to gain insight into the RS behavior. We prepared NiO thin films on Pt/TiO<sub>x</sub>/SiO<sub>2</sub>/Si (NiO/Pt) and Ag/TiO<sub>x</sub>/SiO<sub>2</sub>/Si (NiO/Ag) substrates by the reactive evaporation of Ni under an oxygen

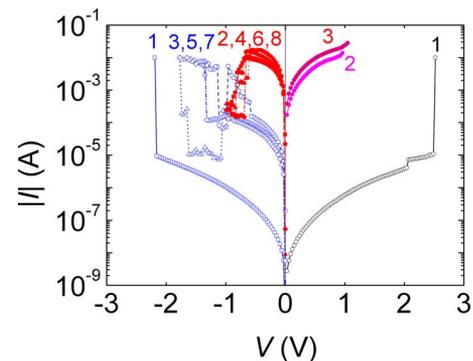


FIG. 1. (Color online) RS characteristics of Ag/NiO/Pt during repeated switching cycles. Reproducible RS occurred only when a negative bias was applied to Ag. The numbers indicate the sweep sequences for each bias polarity condition.

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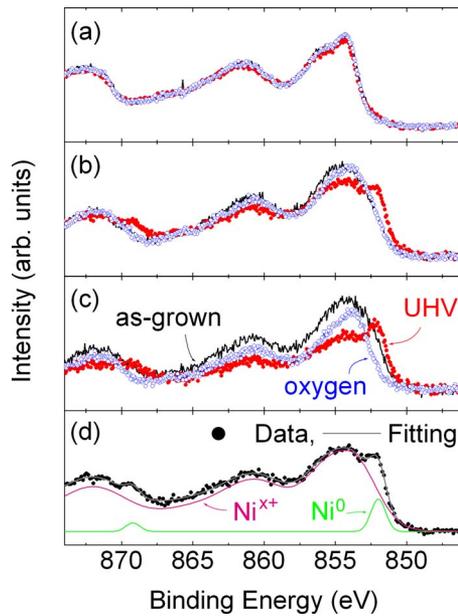


FIG. 2. (Color online) Variation in Ni  $2p$  core-level spectra obtained from (a) 50 ML NiO/Ag, (b) 5 ML NiO/Pt, and (c) 5 ML NiO/Ag for as-grown (solid lines), UHV-annealed (red and filled circles) and oxygen-annealed (blue and open circles) states. (d) Fitting result of the Ni  $2p$  spectrum obtained from the reduced 5 ML NiO/Pt sample. Curves of best fit (solid lines) corresponding to metallic Ni ( $\text{Ni}^0$ ) and ionized Ni ( $\text{Ni}^{x+}$ ) peaks are shown in green and pink, respectively. The spectra were obtained by a Shirley-type background subtraction process.

partial pressure ( $P_{\text{O}_2}$ ) of  $1 \times 10^{-6}$  Torr at RT. We caused reduction and oxidation by annealing the samples in UHV ( $P=2 \times 10^{-10}$  Torr) and in oxygen ambient ( $P_{\text{O}_2}=1 \times 10^{-5}$  Torr) at  $350^\circ\text{C}$  for 15 min. After each heat treatment, the XPS spectra were obtained after the samples cooled down to RT without breaking the vacuum.

Figures 2(a)–2(c) show Ni  $2p$  core-level spectra of the NiO thin films for as-grown and heat-treated states. A nominal Ni  $2p$  spectrum consists of several peaks depending on the Ni valence states, as demonstrated by the fitting result in Fig. 2(d).<sup>6</sup> After annealing in UHV, i.e., reduction, new peaks appeared at approximately 852 eV for 5 ML thick NiO samples [Figs. 2(b) and 2(c)]. These were metallic  $\text{Ni}^0$  states, formed by a reduction in the NiO phase.<sup>6</sup> Such metallic peaks were not seen in the 50 ML thick sample [Fig. 2(a)]. This indicates that the NiO reduction process could have been promoted at the interface region. Defects in the oxide layer and resulting low-coordination sites were likely to cause the unexpected chemical activity at the interface.<sup>12</sup> Such unusual chemical interactions may be relevant to the fact that the filament formation/rupture processes occur preferably at the interface rather than in the bulk interior.<sup>9–11</sup>

The overall Ni  $2p$  peak intensities for the reduced 5 ML NiO layers [red lines in Figs. 2(b) and 2(c)] were smaller than those of the as-grown ones [black lines in Figs. 2(b) and 2(c)]. Because the annealing temperature ( $350^\circ\text{C}$ ) was well below the Ni desorption temperature, the decrease in the peak intensity indicated that some of the Ni elements diffused into the underlying electrode layers below the XPS probing depth. The peak intensity decrease was larger in the 5 ML NiO/Ag sample than in the 5 ML NiO/Pt sample. On the Ag layer, Ag–Ni alloy formation was very unlikely because Ag and Ni are immiscible over a wide temperature

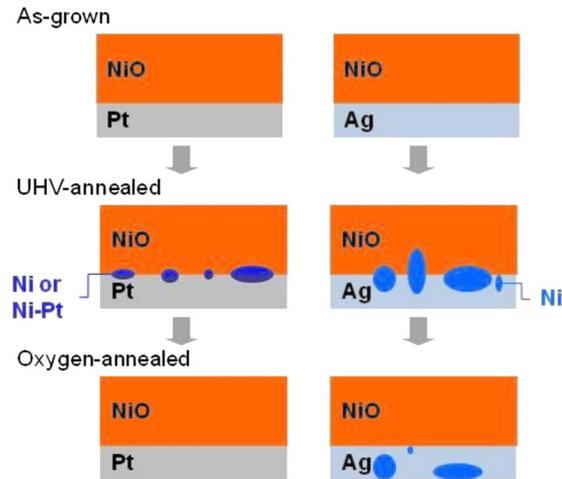


FIG. 3. (Color online) Schematic of the reduction/oxidation processes in NiO/Pt and NiO/Ag samples.

range.<sup>13</sup> The Ni elements most likely formed clusters and embedded in the Ag electrodes.<sup>13,14</sup> In the Pt case, however, Ni can form an alloy phase and remained at the interface.<sup>8,15</sup> Such a difference in interfacial reactions can explain the electrode dependence of the XPS spectra after the reduction.

Another difference in the XPS spectra may be noted after oxidation: the Ni  $2p$  intensity for NiO/Pt was nearly the same as that of the as-grown sample [Fig. 2(b)], while that for NiO/Ag was far smaller [Fig. 2(c)]. During oxidation, Ni elements diffuse out from the Ni–Pt alloy and are oxidized to form the NiO phase.<sup>8</sup> In contrast, the Ni clusters embedded in the Ag layer may hardly escape, instead remain in the electrode interior.<sup>13</sup> All these results reveal that the interfacial redox process can be significantly influenced by the electrode materials. The interface microstructures during the redox processes are illustrated in Fig. 3.

The unipolar RS in MOM structures seems to be caused by the local reduction and oxidation of defect clusters, i.e., filaments.<sup>4–11</sup> Because the NiO/Pt interface exhibited reversible redox processes, reproducible switching can be expected for Pt/NiO/Pt structures.<sup>4–8</sup> At the NiO/Ag interface, however, the metallic Ni clusters embedded in the Ag layer were difficult to reoxidize, as depicted in Fig. 3. This implies that the bases of the conducting filaments are hard to be ruptured during RESET. This is consistent with the switching characteristics in Fig. 1.

There is one remaining question: why did the anodic electrode interface play a greater role in the RS than in the cathode electrode? The answer may be related to the electromigration of oxygen ions. During oxidation (RESET), oxygen must be supplied to the filament region. In metal/NiO/metal structures, oxygen ions can be present at the interstitial sites and grain boundaries in the oxide layers and/or in the electrodes.<sup>9–11</sup> Negatively charged oxygen ions move toward the anode side, which promotes oxidation near the anode interface.<sup>11</sup>

In summary, we investigated the unipolar RS behaviors of Ag/NiO/Pt structures and the oxidation/reduction processes at the metal/NiO interface. The chemical reaction between Ni and the electrode materials appeared to play a crucial role in determining the RS characteristics. This result can give insight into the microscopic level switching pro-

cesses and may help us to optimize the electrode materials for device fabrication.

This work was supported by the KRF Grant (Grant No. KRF-2008-314-C00094) and Nano R&D program through KOSEF funded by MEST (Grant No. 2008-02557). S.H.P. and T.W.N. were supported by the Creative Research Initiatives of KOSEF. R.J. was supported by the Research Grant of Kwangwoon University in 2008.

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