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Ru-Al codoping to mediate resistive switching of NiO:SnO$_2$ nanocomposite films

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The Ru-Al codoped NiO:SnO$_2$ nanocomposite films are revealed to exhibit bipolar resistive switching. The switching mechanism is well explained by the formation/rupture of filamentary paths due to the field-induced migration of oxygen vacancies and oxygen ions. Compared with that of the undoped NiO:SnO$_2$ film, the ON/OFF ratio of Ru-Al codoped samples is largely improved. This is ascribed to the increased content of oxygen vacancies and trapped states between the equilibrium Fermi level and conduction band induced by the interstitial defects of Ru and Al. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4869231]

Resistive random access memory device is considered one of the potential candidates for future non-volatile memory application due to its low power consumption, high speed, and simple device structure.\(^1\) NiO has been intensively explored because of its simple constituent, clear switching characteristics, and high ON/OFF ratio.\(^2,^3\) Excess Ni atoms and O vacancies are considered to play key roles in the formation of conductive filaments in the NiO$_x$ films. Through controlling defects by doping impurities such as Ti, Al, Li, or Nb, resistive switching (RS) property can be improved.\(^4,^5\) Constructing oxide heterostructures or multi-layer structures is another effective way to modulate RS performance via interfacial effects.\(^6,^7\) For example, the Pt/NiO/Mg$_x$Zn$_{1-x}$O/Pt and In/GaO$_x$/NiO$_x$/ITO devices have displayed good endurance with the ratio of high resistance state (HRS) to low resistance state (LRS) about $10^6$ and $10^2$, respectively.\(^8\) Kinoshita et al.\(^8\) indicated that heterojunction structure may be useful to avoid filament formation owing to interfacial defects. The interfacial barrier height or work function engineered by the migration of oxygen vacancies or oxygen ions controls the formation and rupture of filaments at interface. Therefore, effects of interfacial defects on carriers transport and RS properties need to be further investigated.

Intrinsic NiO is a p-type semiconductor, while SnO$_2$ is n-type with excess oxygen vacancies.\(^9\) It is possible to constitute nanoscale p-n junctions using NiO and SnO$_2$. On the other hand, Ru and Al may effectively generate nonstoichiometry in NiO:SnO$_2$ (NTO) system considering their different valence state (+3) with those of Ni and Sn. Moreover, doping Ru and Al may increase the density of metallic Ni$^{0}$/Sn$^{0}$ by substituting Ni$^{2+}$/Sn$^{4+}$ in lattice or improve oxygen vacancies content by occupying the interstitial sites. Thus, it is of much interest to investigate if p-n heterostructures of Ru-Al codoped NiO:SnO$_2$ (RANTO) nanocomposite films exhibit good RS properties. In this Letter, we report on the RS observations in GaIn/RANTO films/ITO heterostructures. The effects of the impurity doping and interface modification on the RS performance were discussed.

The RANTO nanocomposite films were prepared by sol-gel spin-coating. As starting materials and dopant sources, nickel acetate tetrahydrate [Ni(CH$_3$COOH)$_2$·4H$_2$O] and tin dichloride dihydrate [SnCl$_2$·2H$_2$O], aluminium nitrate nonahydrate [Al(NO$_3$)$_3$·9H$_2$O] and ruthenium trichloride trihydrate [RuCl$_3$·3H$_2$O] were used, respectively. Details of sol-gel synthesis and film fabrication were previously described elsewhere.\(^6,^9\) The Ni/Sn and Al/Ni molar ratios of the RANTO sols were kept at 3:1 and 1:100, respectively. While the Ru/Al molar ratios were kept at 0, 3, 5, 7, 9, and 15, as named the ANTO, RANTO3, RANTO5, RANTO7, RANTO9, and RANTO15, respectively. To make film samples, the sols were spin-coated onto clean ITO and Si (100) substrates, and then calcined in a muffle furnace at 400°C for 1 h with a heating rate of 6°C/min. The films on silicon were subjected to the X-ray diffraction (XRD) analysis, while the samples on ITO were used for electrical characterizations. The film thickness is about 100 nm. The XRD patterns were collected on a X’ Pert Pro diffractometer with Cu K$_\alpha$ radiation wavelength of 0.154056 nm. Current–Voltage ($I$–$V$) curves were measured using a LK2005A potentiostat with device structure of GaIn/RANTO films/ITO. The GaIn top electrode was grounded, while the bias was applied to the ITO electrode. All the tests were carried out in ambient conditions.

As shown in Fig. 1, XRD measurements present clear (111) peaks of the rutile phase SnO$_2$ (PDF 00-050-1429), while there is only a weak peak corresponding to the NiO (200). So, irrespective of Ru concentration, NiO is just short-range ordered with cubic phase.\(^10\) No other crystal phases can be noted, suggesting that all the films are a mixture of NiO/SnO$_2$ hybrids. As the secondary phase, SnO$_2$ can highly disperse in the NiO nanocrystals and inhibits the grain growth of NiO.\(^11\) With Al incorporation, there is no change in the peak position of NiO (200), while the SnO$_2$ (111) peak shifts to smaller 2θ value. After Ru doping, SnO$_2$ (111) peak further moves to the left (see the inset of Fig. 1). The impurities of Ru and Al are expected to occupy the

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interstitial positions (Ru\(^{3+}\) and Al\(^{3+}\)) in ANTO and RANTO films due to the smaller ionic radii of Al\(^{3+}\) (0.051 nm) and Ru\(^{3+}\) (0.068 nm) than that of Sn\(^{4+}\) (0.071 nm). The Ru\(^{3+}\) and Al\(^{3+}\) interstitial defects may increase the content of oxygen vacancies in SnO\(_2\) crystal and affect the RS performance.\(^{15}\)

A typical \(I-V\) curve of the GaIn/RANTO film/ITO device is given as Fig. 2(a), which shows reversible bipolar resistance switching without any forming process. The forming-free behavior can be attributed to the high-density oxygen-deficient defects. Hsiung et al.\(^{16}\) previously observed similar phenomenon in studying TiO\(_2\) film. As shown in Fig. 2(a), a set voltage \(V_{\text{set}}\) is required to turn on the device, while a reset voltage \(V_{\text{reset}}\) switches the device back to the OFF state. By introducing Al, the ON/OFF ratio only shows a slight increase. As the increase of Ru codoping ratio, the ratio largely increases with the maximum value of about 430 (see Fig. 2(b)). At the same time, the \(V_{\text{set}}\) increases from 0.95 to 1.90 V, while \(V_{\text{reset}}\) fluctuates between 0.67 and 1.91 V. As detailed later, such observation can be attributed to the increased interfacial defects due to Ru-Al codopants, which largely modify the charge transport and switching properties.

When \(I-V\) data are continuously measured at the same sample point for multiple cycles, the local Joule heating has no time to dissipate. The effective local temperature \(T_{\text{eff}}\) as a function of bias can be obtained (see the inset of Fig. 3(a)).\(^{17}\) The current values at \(-0.5\) V of HRS and LRS both increase as \(T_{\text{eff}}\) increases. The HRS and LRS thus behave thermally activated transport.\(^{18}\) The switching confirms to filamentary conduction caused by the generation/recombination of oxygen vacancies.\(^{19,20}\) Such temperature dependent behaviors may be controlled by the filling status of traps in the initial switching process and the Joule heating accumulation in the continuous measurement.\(^{21}\)

The device endurance was tested on NTO, ANTO, and RANTO samples for 9 measuring cycles. As shown in Fig. 3(b), the threshold voltages of all the samples gradually enhance as the scanning cycles increase. The reason may be that the oxidation of oxygen-deficient defects induced by Joule heating can weaken the as-formed filaments.\(^{22}\) Moreover, Jiang et al.\(^{21}\) proposed that there is a threshold filling level dominating the RS behavior. The capture and release of carriers by traps are two dynamic processes occurring simultaneously. The increased local temperature may make the probability of release exceed that of capture, resulting in downshift of the filling level. Consequently, the set and reset voltages are increased. Switching failure is noticed in the NTO and ANTO samples after 6 sweep cycles due to hard dielectric breakdown of the active layer because of the accumulative Joule heating.\(^{23}\) Ru-Al codoping can

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**FIG. 1.** XRD patterns of the NTO, ANTO, and RANTO nanocomposite films. The inset shows the peak position of SnO\(_2\) (111) plane versus the content of Ru dopant.

**FIG. 2.** (a) Typical \(I-V\) curves of the RANTO5 with arrows and numbers indicating the bias sweeping directions. The inset shows the schematic device configuration. (b) The set and reset voltages, and ON/OFF ratio at \(-0.5\) V of the NTO, ANTO, and RANTO films.

**FIG. 3.** (a) The HRS and LRS current values at \(-0.5\) V with \(T_{\text{eff}}\) ranging from 300 to 510 K. The inset shows the fitting curves of \(T_{\text{eff}} - \gamma\) with \(T_0 = 298\) K, \(\gamma_{e-p} = 230\) K/V\(^{1/2}\) and \(\gamma_{e-e} = 100\) K/V, respectively. (b) Distributions of the \(V_{\text{set}}\) and \(V_{\text{reset}}\) of RANTO7 in multiple sweeping cycles with inset showing those of NTO and ANTO.
obviously control the dispersion of set and reset voltages.\(^7\),\(^{24}\) This is because the traps induced by Ru\(^{3+}\) and Al\(^{3+}\) defects are distributed in an energy range rather than located at a single discrete level. Meanwhile, Ru\(^{3+}\) and Al\(^{3+}\) defects may provide additional carriers and further enhance the probability of carrier capture by the traps. And these effects are stronger in RANTO owing to the more defects resulted from Ru dopant.

To understand the conduction mechanisms of the GaIn/RANTO film/ITO memory devices, carrier transport was analyzed via isothermal \(I–V\) correlations. For the LRS, the NTO, ANTO, and RANTO samples follow the Ohmic law (data not shown). For the HRS NTO, Poole–Frenkel model conforming to enhanced thermionic emission dominates the current from 0 to 1 V. While the device is governed by trap-free space-charge-limited conduction (SCLC) from 1 to 3 V. When the bias is over 3 V, the Schottky emission is dominated (data not shown). As for the HRS of ANTO and RANTO, the P–F emission is dominant at 0–0.5 V (see Fig. 4(a)). This may be because the adsorbed oxygen or Ru and Al defects at the grain boundary capture carriers and produce a potential barrier.\(^25\) Under electrical field, the barrier height is reduced and the trapped electrons are thermally excited; thus, the conductivity through the grain boundary is increased.\(^26\) In bias range from 0.5 to 1 V, the dominant conduction in HRS is Schottky emission (see the linear plots in Fig. 4(b)), which refers to electric-field-enhanced thermal excitation of electrons from defect-related trap states into conduction band.\(^7\),\(^{18}\) As the voltage increases from 1 to 3 V, the injected electrons rapidly increase and the SCLC becomes dominated. The slopes \(\alpha\) of the \(\log(I)–\log(V)\) plots change from about 2.19 to 3.99 (see Fig. 4(c)). We thus indicate that the traps induced by Ru\(^{3+}\) and Al\(^{3+}\) defects are located between the equilibrium Fermi level and conduction band.\(^27\) For bias over 3 V, the \(I–V\) curves correspond to trap-free SCLC (Fig. 4(d)), suggesting that the traps are all filled.\(^28\) In addition, it can be seen that the current of RANTO largely enhances compared with that of ANTO, which is because Ru\(^{3+}\) defects provide lots of additional carriers.

As for the switching mechanism, the filament and interface models contribute simultaneously to RS behavior. At equilibrium condition, a barrier or depletion region is initially formed at the NiO/SnO\(_2\) interfaces, leading to the HRS.\(^3\) According to Ref. 7, the migration of oxygen vacancies and oxygen ions under applied bias can alter the junction barrier and thus control filamentary paths passing through the interface, resulting in the switching behavior.\(^3\) The SnO\(_2\) nanocrystals dispersed in less-crystallized NiO as a sink or reservoir for oxygen vacancies, can affect the formation of filamentary paths. The local enhancement of electric field may cause the connection of filaments preferentially around the SnO\(_2\) crystals.\(^24\) Moreover, a variety of defects aggregated at the interface can form space charge region, modifying the switching properties too. In our RANTO films, the Ru\(^{3+}\) and Al\(^{3+}\) impurities may gather at the SnO\(_2\) grain boundary and increase the boundary barrier. Consequently, it is difficult for the filamentary paths to get through the grain boundary. This is consistent with the observations that \(V_{\text{set}}\) is enhanced with the incorporation of Al and Ru dopants.

Figure 5(a) shows the dependence of LRS and HRS current on the Ru doping ratios. The HRS current is independent of Ru content, while the LRS one increases with Al incorporation and Ru codoping, which agrees well with the larger ON/OFF ratio of ANTO and RANTO than that of NTO. Because of the co-presence of NiO and SnO\(_2\) phases without any alloys formed, it is difficult to say that only one gap existing in such materials. Ynineb \(\text{et al.}\)^29 proposed an effective band gap \(E_{\text{eff}}\): \[ E_{\text{eff}} = xE_g(SnO_2) + (1 − x)E_g(NiO), \] where \(x\) is the SnO\(_2\) phase ratio. The \(E_{\text{eff}}\) parameters for NTO, ANTO, and RANTO films are estimated from the

![Figure 4](http://scitation.aip.org/termsconditions)
The Ru and Al dopants can increase the oxygen vacancies and induce trap states between the equilibrium Fermi level and conduction band. Our work may provide some useful information for optimizing heterostructured memory devices.

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