Reset First Resistive Switching in Ni$_{1-x}$O Thin Films as Charge Transfer Insulator Deposited by Reactive RF Magnetron Sputtering

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Abstract: Reset-first resistive random access memory (RRAM) devices were demonstrated for off-stoichiometric Ni$_{1-x}$O thin films deposited using reactive sputtering with a high oxygen partial pressure. The Ni$_{1-x}$O based RRAM devices exhibited both unipolar and bipolar resistive switching characteristics without an electroforming step. Auger electron spectroscopy showed nickel deficiency in the Ni$_{1-x}$O films, and X-ray photoemission spectroscopy showed that the Ni$^{3+}$ valence state in the Ni$_{1-x}$O films increased with increasing oxygen partial pressure. Conductive atomic force microscopy showed that the conductivity of the Ni$_{1-x}$O films increased with increasing oxygen partial pressure during deposition, possibly contributing to the reset-first switching of the Ni$_{1-x}$O films.

Keywords: resistive random access memory; nickel oxide; nickel vacancy; reset-first resistive switching; oxygen partial pressure; conductivity; area dependence

1. Introduction

Resistive random access memory (RRAM) [1] has been widely studied as a candidate for next-generation non-volatile memory to overcome the limitations of conventional memories, such as flash memory and dynamic random access memory (DRAM). RRAM has a relatively low operation voltage with excellent program and erase speed [2]. In addition, the device could be fabricated in a simple metal–insulator–metal (MIM) [3] structure, enabling the high-density cell structure of a cross-bar array with 4F$^2$ [4,5]. It was reported that numerous transition metal oxides, including Al$_2$O$_3$ [6,7], HfO$_2$ [8–10], NiO$_x$ [11–14], TiO$_2$ [15,16], TaO$_x$ [17,18], Nb$_2$O$_5$ [19,20], and Pr$_{1-x}$Ca$_x$MnO$_3$ [21–23] show resistive switching (RS) characteristics. Moreover, various deposition techniques, such as sputtering [24–28], atomic layer deposition (ALD) [29] and pulsed laser deposition (PLD) [30] were used for the formation of such oxides. Notably, nickel oxide (NiO) film is one of the most widely studied oxides and is reported to have low operation power, a high on/off resistance ratio and is compatible with the CMOS fabrication process [31,32]. NiO has a rock salt structure composed of Ni$^{2+}$ and O$^{2-}$ and is a member of the strongly correlated 3d transition metal oxides that exhibit charge-transfer insulator behavior [33,34]. It is an insulating oxide with a wide bandgap (E$_g$ $\approx$ 4.3 eV) due to the charge transfer gap caused by “Hubbard U” between the 2p and 3d states [34,35]. Therefore, the pristine state of NiO is typically the insulating state in RRAM [36,37]. The RS phenomenon in NiO has been mainly described as the formation and rupture of conductive filaments. This reversible resistance transition between the high-resistance state (HRS) and low-resistance state (LRS) is caused by applying electrical stress after an “electroforming” step [38]. It was suggested that oxygen atoms are migrated by the electric field, leaving oxygen vacancies (Vo$^{2+}$) at the vacated sites during the electroforming step; the adjacent Ni$^{2+}$ atoms are changed to Ni$^{0}$ to compensate for the charge state, resulting in a Ni filament [39–41]. The electroforming...
process degrades the chemical and physical properties of devices of MIM structure, affecting their reliability. The characteristics of RS uniformity also deteriorate because of non-uniform filament formation among MIM devices [42]. Moreover, electroforming requires additional high-voltage circuits, significantly reducing the device density. Therefore, research on devices that can be operated without an electroforming step is essential for realizing RS memories [43–45].

This study investigated the RS characteristics of off-stoichiometric Ni$_{1-x}$O films for unipolar and bipolar RSs (URS and BRS, respectively). Particularly, it was demonstrated that nickel-deficient Ni$_{1-x}$O films deposited under excessive oxygen partial pressure exhibit a reset-first RS without an electroforming step. An RRAM device with a reset-first RS could be an alternative to overcome the limitations of RRAM requiring an electro-forming step.

2. Experimental

MIM devices with Pt/NiO/Pt and Pt/NiO/TiN stacks were fabricated for electrical characterization. First, Ti/TiN adhesive layers with thicknesses of 10–50 nm were deposited onto SiO$_2$ on a Si substrate using DC magnetron sputtering. Pt or TiN films were then deposited as bottom electrodes (BE). BE with various areas of 0.18~4.0 $\mu$m$^2$ were formed to investigate the area-dependence of the electrical characteristics. After BE formation, off-stoichiometric Ni$_{1-x}$O films with a thickness of 10 nm were deposited via reactive RF magnetron sputtering using a Ni target under various O$_2$ partial pressures. During sputtering, the base and working pressures were less than $3 \times 10^{-3}$ and 3 mTorr, respectively. During deposition, the RF power and temperature of the substrate were maintained at 100 W and 400 °C, respectively. The fraction of the O$_2$ partial pressure in the mixture of Ar and O$_2$ varied from 10% to 50% for deposition. Finally, Pt top electrodes (TEs) with a thickness of 100 nm were formed using DC magnetron sputtering and a lift-off process. The electrical characteristics of the device were characterized using a Keysight B1500A analyzer at 21~23 °C. RS under DC bias was measured with a compliance current of 10 mA to avoid hard breakdown of the Ni$_{1-x}$O films. The spatial distribution of conductivity in the pristine state was investigated using conductive atomic force microscopy (C-AFM) (Park Systems, XE-100) with a measurement bias of 3 V [46,47]. Grazing incidence X-ray diffraction (GI-XRD, Rigaku SmartLab), Auger electron spectroscopy (AES, PHI-700, ULVAC-PHI), and X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo U. K.) analyses were conducted to investigate the crystallinity, composition, and valence states of Ni in the Ni$_{1-x}$O films, respectively.

3. Results and Discussion

XRD analysis was conducted to investigate the crystallinity of Ni$_{1-x}$O films. The XRD patterns of Ni$_{1-x}$O films deposited under various O$_2$ fractions are illustrated in Figure 1a. The peaks of NiO (111), NiO (200), NiO (220), and NiO (311) imply a polycrystalline structure [48]. NiO films, deposited with an O$_2$ partial pressure fraction of 50% showed lower intensity with a more comprehensive full-width half maximum (FWHM), implying poorer crystallinity of NiO films. The XRD peak of the (111) plane shifted to lower diffraction with increasing O$_2$ partial pressure, indicating an increase in the lattice constant with increasing O$_2$ partial pressure, as shown in Figure 1b. The increase in the lattice constant could be ascribed to the increased strain effect as Ni vacancies increase with excessive O$_2$ partial pressure [48–50]. Figure 1c shows the composition of Ni and O, estimated from AES analysis of the Ni$_{1-x}$O films with various O$_2$ partial pressures during deposition. The volume of Ni is gradually reduced with increasing O$_2$ partial pressure, resulting in a Ni-deficient Ni$_{1-x}$O film. The compositions of nickel oxide at 10% and 50% O$_2$ partial pressures were estimated to be Ni$_{0.89}$O and Ni$_{0.86}$O, respectively.
Figure 1. (a) XRD patterns of Ni$_{1-x}$O films deposited with various oxygen partial pressures. (b) Lattice constant of Ni$_{1-x}$O, estimated from (111) peak position, as a function of oxygen partial pressures. (c) Nickel and oxygen composition in Ni$_{1-x}$O by AES.

Figure 2a shows the typical behavior of Pt/Ni$_{1-x}$O/Pt stacks. The pristine Ni$_{1-x}$O films deposited under an O$_2$ partial pressure fraction of 10% offered an initial high resistance [51] at an applied voltage of 1.77 V (1.4 MV/cm) on the TE. The film resistance changed from HRS to LRS during the forming step. The resistance state was changed back to HRS at 0.64 V (0.5 MV/cm) during the subsequent bias application, exhibiting reversible switching for the positive bias on TE. The difference between the forming voltage ($V_{\text{form}}$) and set voltage ($V_{\text{set}}$) was approximately 0.57 V. In contrast, pristine Ni$_{1-x}$O films deposited under the 30% or 50% O$_2$ ratio showed low resistance in the pristine state without the electroforming step and reset-first RS behavior, where the initial LRS state was changed to the HRS state, as shown in Figure 2b,c. While $V_{\text{set}}$ is similar to that of Ni$_{1-x}$O films for the O$_2$ partial pressure fraction of 10%, the $I_{\text{HRS}}/I_{\text{LRS}}$ ratio decreased because of the overall high current level in the HRS state. In particular, the $I_{\text{HRS}}$ between these oxygen partial pressure fractions showed that the 50% O$_2$ ratio was 10 times higher than that of 30% O$_2$. The I-V curves of TiN/Ni$_{1-x}$O/Pt stacks are plotted in Figure 2d–f. The Ni$_{1-x}$O film deposited under a 10% O$_2$ partial pressure fraction shows BRS [52] characteristics, as shown in Figure 2d. The pristine Ni$_{1-x}$O film showed high resistivity, and the resistance state changed to LRS after the electroforming step with a negative bias on TE. The difference between $V_{\text{form}}$ (~4.0 V) and $V_{\text{set}}$ (~0.7 V) was approximately 3.3 V. On the contrary, the Ni$_{1-x}$O film deposited under the 30% or 50% O$_2$ partial pressure fraction showed reset-first BRS behavior for a positive voltage on the TE, as shown in Figure 2e,f.

Figure 3 shows the electric currents at 0.64 V of the Pt/Ni$_{1-x}$O/TiN stacks in the HRS and LRS states, where Ni$_{1-x}$O films were deposited at various O$_2$ partial pressures. The mean values of $I_{\text{HRS}}$ and $I_{\text{LRS}}$ (red line) increased with the O$_2$ ratio, suggesting that the Ni$_{1-x}$O film conductivity depends on the O$_2$ partial pressure, as shown in Figure 3a. The Ni$_{1-x}$O films with a 10% O$_2$ fraction required electroforming for resistive switching, but the Ni$_{1-x}$O films with a 30% O$_2$ fraction or higher showed reset-first RS behavior without electroforming. Figure 3b shows the electrical currents at 0.64 V in the LRS states, which has a similar tendency to the $I_{\text{HRS}}$ with O$_2$ partial pressure, but the slope was lower than that of the $I_{\text{HRS}}$ state. The $I_{\text{HRS}}$ and $I_{\text{LRS}}$ showed the highest values for Ni$_{1-x}$O films deposited under the 50% O$_2$ partial pressure fraction.

To understand the nature of resistance switching, HRS and LRS resistances were measured from devices with BE of 0.18, 0.38, 2.00, and 3.69 μm$^2$ at a bias of ±0.48 V. Figure 4a shows the area dependence for BRS device with Ni$_{1-x}$O films deposited by 10% O$_2$ partial pressure fraction. The resistance of the HRS remained almost constant with decreasing geometric device area, where that of the LRS is almost independent of the device area. These area-independent characteristics imply that resistance switching through the device occurs in local regions, such as filamentary paths, rather than homogeneously distributed switching paths [53–57]. Meanwhile, the resistances of reset-first RS devices with Ni$_{1-x}$O films deposited at 50% O$_2$ partial pressure showed increased dependence on the device area, as shown in Figure 4b. Because the area dependence of the LRS for Ni$_{1-x}$O films with 50% O$_2$ partial pressure is close to that of Ni$_{1-x}$O films with 10% O$_2$ partial pressure, the nature of the RS is filamentary in the local area. The significant dependence
of HRS on the Ni$_{1-x}$O films with 50% O$_2$ partial pressure is attributed to the reduced resistance of the Ni$_{1-x}$O films, as shown in Figure 4b.

![Figure 2](image1.png)

**Figure 2.** I–V characteristics of Ni$_{1-x}$O devices with a bottom electrode of $2 \times 2$ $\mu$m$^2$. URS characteristics of Ni$_{1-x}$O films deposited with partial oxygen pressure of (a) 10%, (b) 30% and (c) 50%. BRS characteristics of Ni$_{1-x}$O films deposited with oxygen partial pressure fraction of (d) 10%, (e) 30% and (f) 50%.

![Figure 3](image2.png)

**Figure 3.** Influence of oxygen partial pressure on (a) $I_{HRS}$ of Ni$_{1-x}$O films and (b) $I_{LRS}$ of Ni$_{1-x}$O films.

The DC, and AC endurance characteristics of the Ni$_{1-x}$O device are shown in Figure S1. DC endurance in Figure S1a was measured at a read voltage ($V_{\text{read}}$) of $\pm0.25$ V under a compliance current of 10 mA. The measured $I_{HRS}/I_{LRS}$ ratio is higher than $10^4$ even after $10^3$ cycles. Figure S1b shows the AC endurance under pulse, which is measured with a set pulse of $-0.95$ V with 180 ns, a reset pulse of 1.2 V with 180 ns, and a $V_{\text{read}}$ of 0.3 V conditions. The device has a uniform $I_{HRS}/I_{LRS}$ ratio even after $10^5$ cycles, which results in a stable RS property.
It was reported that nickel deficiency could promote the further oxidation of Ni
2+
ions, which can be expressed with Kröger–Vink notation, as follows [48,49]:
\[
2\text{Ni}_{\text{Ni}}^{2+} + \frac{1}{2}\text{O}_2(g) \rightarrow 2\text{Ni}_{\text{Ni}}^{3+} + \text{O}_6^0 + \text{V}_{\text{Ni}}^0
\]
(1)
where \(\text{Ni}_{\text{Ni}}^{2+}\), \(\text{Ni}_{\text{Ni}}^{3+}\), \(\text{O}_6^0\), and \(\text{V}_{\text{Ni}}^0\) represent Ni2+, Ni3+, O2−, and ionized Ni vacancies, respectively. Ni2+ ions react with oxygen to generate ionized nickel vacancies and two Ni3+ ions, which affect the conductivity of the nickel oxide films. Therefore, it is shown that the increase

Figure 4. Area dependence of HRS and LRS resistances for Pt/Ni1−xO/TiN stacks (a) with Ni1−xO films, deposited with oxygen partial pressure fraction of 10%, with electroforming (b) with Ni1−xO films that are deposited with oxygen partial pressure fraction of 50%, with reset-first BRS without electroforming.

C-AFM measurements investigated the two-dimensional (2D) variation of the Ni1−xO film conductivity. Figure 5a illustrates the scheme of the C-AFM measurement. NiO/Pt and NiO/SiO2/Pt stacks were simultaneously formed on a sample to compare the differences during the current image mapping. Cross-sectional TEM images of the Ni1−xO films are shown in Figure 5b. The sample-to-sample variation in the Ni1−xO thickness on the SiO2/Pt stacks was estimated to be within 15%. Therefore, we ignore the difference in conductivity due to thickness variation. Figure 5c–e show the current mapping images at a bias of 3 V from Ni1−xO films deposited under various O2 partial pressures. The left region of each mapping image represents the reference of the insulating SiO2 between the BEs and Ni1−xO films. The regions on the right represent the Ni1−xO films on the Pt BEs in their pristine state. Similar to the I-V characteristics of MIM devices, C-AFM shows an increased current through the Ni1−xO films with increasing O2 partial pressure. The conductive regions in the Ni1−xO film regions increased with increasing O2 partial pressure fraction, as shown in Figure 5d,e. In particular, the current distribution is relatively uniform in Ni1−xO film with a 50% O2 fraction. In contrast, films deposited under 10% O2 partial pressure fraction showed improved resistivity, as shown in Figure 5c.

The effect of the O2 partial pressure on the chemical bonding states in the Ni1−xO films is investigated through XPS analysis. Figure 6a–c show the Ni 2p3/2 peaks of Ni1−xO films deposited with various O2 partial pressures. Ni0, Ni2+ and Ni3+ states with binding energies of 852.5, 853.7, and 855.5 eV, respectively, are used for deconvolution of Ni 2p3/2 peaks [58,59].

The proportion of the Ni3+ state was estimated from the ratio of the Ni3+ peak area to the Ni2+ peak area. The Ni3+ valence state increased while the fraction of Ni2+ ions decreased with increasing O2 partial pressure (Figure 6a–c). The Ni3+ ratio in the film grown under 10% and 50% O2 partial pressure was estimated at 14.0% and 23.9%, respectively. Meanwhile, the Ni0 state at the 852.5 eV peak was not observed in our Ni 2p2/3 peak analysis, although it was considered a conductive path in previous studies [39–41]. Conventionally, Ni vacancies form in Ni-deficient NiO films with relatively excessive oxygen. It was reported that nickel deficiency could promote the further oxidation of Ni2+ ions, which affect the conductivity of the nickel oxide films. Therefore, it is shown that the increase
in Ni$^{3+}$ in Ni$_{1-x}$O films is related to the increase in the current in the HRS state of MIM devices and C-AFM. It is expected that Ni deficiency in Ni$_{1-x}$O films grown under high O$_2$ partial pressure causes a high Ni$^{3+}$ concentration, leading to a highly conductive state and possibly the reset-first RS behavior with reinforced localized conductive paths [39,60,61]. Further investigation is required to understand how excess Ni$^{3+}$ ions produce the reset-first resistive switching behavior in Ni$_{1-x}$O films.

Figure 5. (a) Schematic diagram of the C-AFM measurement. (b) Cross-sectional TEM image of Ni$_{1-x}$O films deposited at various oxygen partial pressure. C-AFM current mapping images of the pristine Ni$_{1-x}$O films under oxygen partial pressure fraction of (c) 10%, (d) 30%, and (e) 50%.

Figure 6. XPS peaks of Ni 2p$_{3/2}$ of Ni$_{1-x}$O films with oxygen partial pressure fraction of (a) 10% (b) 30% (c) 50%.

4. Conclusions

In this study, the reset-first RS characteristics of off-stoichiometric Ni$_{1-x}$O films were investigated. The RS behavior without the electroforming step was observed in the unipolar
and bipolar off-stoichiometric Ni$_{1-x}$O films. Ni$^{3+}$ distribution contributes significantly to the conductivity of the pristine Ni$_{1-x}$O films. The conductivity and Ni deficiency of pristine Ni$_{1-x}$O films increased as the O$_2$ partial pressure increased during a deposition as revealed by the C-AFM and AES results. Moreover, Ni$^{2+}$ was further oxidized to Ni$^{3+}$ as the O$_2$ partial pressure increased, as revealed by the XPS results.

The NiO$_2$ bonding by Ni$^{3+}$ ions is related to the reset-first RS behavior without the electroforming step. This is advantageous in terms of device scale-down, making Ni$_{1-x}$O films promising candidates for memory applications by overcoming the limitations of the electroforming step in RRAM.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12132231/s1, Figure S1: Endurance characteristics of Ni$_{1-x}$O bipolar RS device.

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