The Effect of Ion-Implantation on the Resistive Switching Response of NiO Thin Films

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Resistive random access memory (RRAM) is based on the resistance of a dielectric thin film that can be switched between low and high resistance states by appropriate application of current-voltage pulses. However, the full realization of this technology is hampered by a lack of understanding of the resistance switching mechanism. Here we compare the resistive switching characteristics of thin NiO films before and after irradiation and show that ion-implantation is an ideal tool for exploring the resistive switching response of this technologically important material.

1. Introduction

Resistive random access memory (RRAM), a serious contender for the next-generation non-volatile memory (NVM), has attracted extensive attention due to its potential for overcoming future scaling limits [1]. Resistive switching is based on formation and rupture of a tiny conducting filament (CF) in metal oxides by appropriate application of current-voltage pulses. The CF is produced during a forming process in which a high electric field is applied across the dielectric layer to induce defects and promote conduction. This produces a conductive path (CF) with low device resistance (set state) that can be subsequently ruptured and reformed by the application of appropriate current-voltage pulses [2]. Resistive switching mechanism is considered to be a highly localized phenomenon within the dielectric layer [3]. Many models for resistive switching have been proposed, including trap charging in the dielectric [4], space-charge-limited conduction processes [5], ion conduction and electrodeposition [6], Mott transition [7], and Joule-heating effect [8].

Although several models have been proposed a clear understanding of the underlying physical mechanisms is still lacking. In this study, we compare the forming voltage and set (ON) and reset (OFF) characteristics of metal-insulator-metal (MIM) devices before and after implantation with Ni^- and O^- into NiO thin films of different thicknesses.

2. Experimental details

Metal-insulator-metal (MIM) structures were fabricated for device testing. The substrates consisted of 300nm thick thermally grown SiO_2 layers grown on boron-doped, p-type, (100) oriented silicon . The bottom electrode was fabricated on cleaned substrates by first depositing a 10nm thick Ti film to act as a wetting layer, then adding a 200nm thick Pt film. The Ti and Pt films were deposited by dc magnetron sputtering at room temperature. Following Pt deposition, NiO films of thicknesses 100nm and 195nm were reactively sputtered in an O_2 ambient on top of the Pt layer using a shadow mask. During this deposition process, the substrate was kept at room temperature and the working pressure was maintained at 4mTorr by a mixture of Ar and O_2 at mixing ratio of 9:1 with total flow rate of 20 sccm. Half the samples were annealed at 600^oC for 10 min in N_2, the remainders were left un-annealed. Portions of the as-deposited and annealed samples were subsequently implanted with Ni^- (260 keV for 195 nm and 75 keV for 100 nm)), O^- ions (80 keV for 195 nm and 25 keV for 100 nm), or both Ni and O ions, to fluences ranging from 5×10^{14} - 5×10^{15} ions.cm^{-2}. The current-voltage (I-V) characteristics of the samples were then measured at room temperature using an Agilent B1500A semiconductor parametric analyzer.

3. Results and Discussion

3.1 XRD Analysis

Grazing incident-angle X-ray diffraction (GIAXRD) was used to characterize the crystal structure of the as-deposited, annealed, and ion-implanted NiO films. Such analysis showed that the as-deposited NiO films were polycrystalline in nature and that they so after annealing and ion-implantation, as shown in Fig. 1. RBS spectra showed that the NiO film is approximately stoichiometric and has a thickness consistent with that measured during deposition, as shown in Fig. 1. Analysis also shows that the Pt contact layer contains ~15% oxygen as a contaminant.

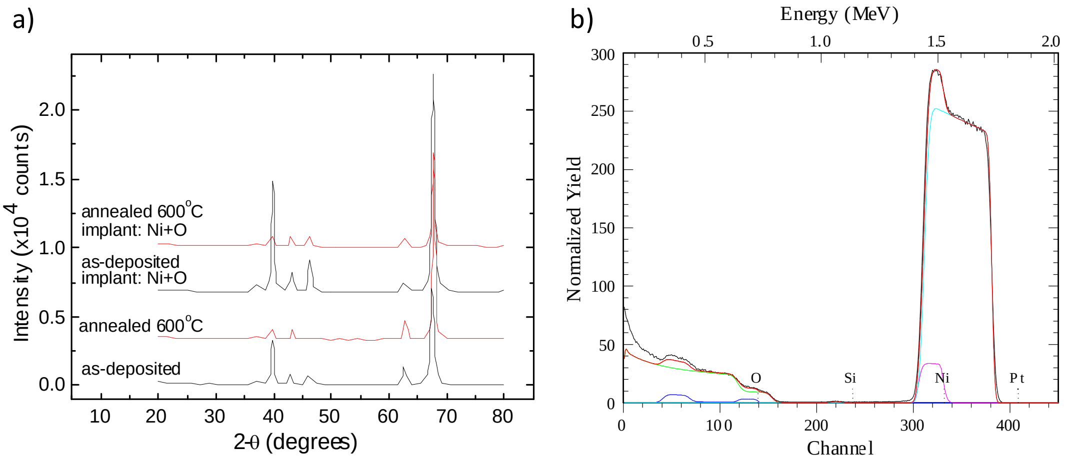

Fig. 1: (left) GIAXRD spectra of as-deposited, annealed and ion-implanted NiO films highlighting the polycrystalline nature of the films. (right) RBS spectrum of a 195 nm thick NiO layer on a 200 nm thick Pt contact layer.

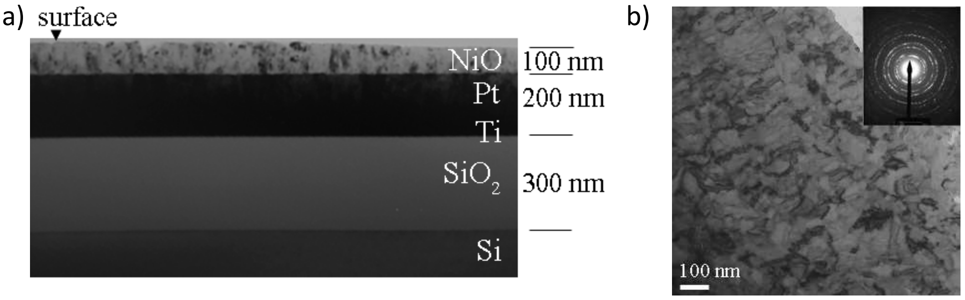

Fig. 2: TEM micrographs of a resistive switching test structure consisting of Si/SiO2/Ti/Pt/NiO layers (without top Pt). *(left)*: cross-section view; *(right)* plan view of the NiO thin film (inset showing the diffraction pattern).

Figure 2 shows cross-sectional and plan view TEM images of 100 nm Pt/NiO/Pt memory structure after implantation with Ni and after annealing, confirming the polycrystalline nature of the films, and showing the details of the sample structure.

The filament forming process is an essential prerequisite for resistive switching in metal-insulator-metal (MIM) devices. In the current study, forming was achieved by applying a positive dc voltage to the Pt top electrode using a current compliance of 30mA. Typical forming characteristics are shown for un-implanted structures in Fig. 3a. Results are shown for as-deposited samples and samples annealed at 600°C for 10 min. Each curve represents a separate device.

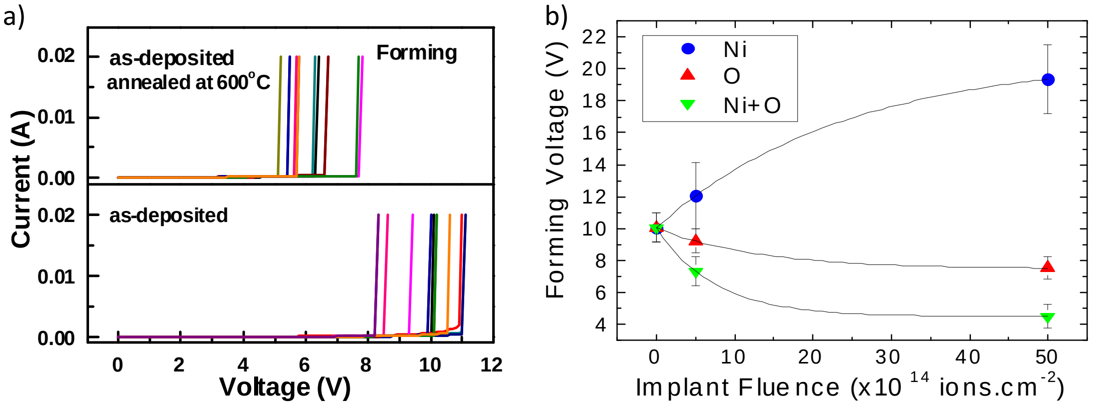

Fig. 3. a) I-V characteristics during forming, and b), mean forming voltage for 195 nm thin NiO samples implanted with Ni, O and Ni + O.

The effect of ion-implantation on the forming voltage is summarized in Fig. 3b. (NB: For the Ni + O implants the fluence scale represents the fluence of each Ion. i.e. the total fluence is twice that indicated). This shows that the forming voltage is influenced by ion implantation, increasing with Ni fluence and decreasing with O fluence. The resistivity of NiO is known to be a sensitive function of stoichiometry, controlled mainly by the presence of Ni vacancies. The concentration of such defects is expected to decrease/increase with Ni/O implantation, respectively, and likely accounts for the trends shown in Fig. 3b. However, a reduction in forming voltage is also observed for samples implanted with equal fluences of Ni and O, suggesting that radiation-induced defects can play a direct role in reducing the forming voltage.

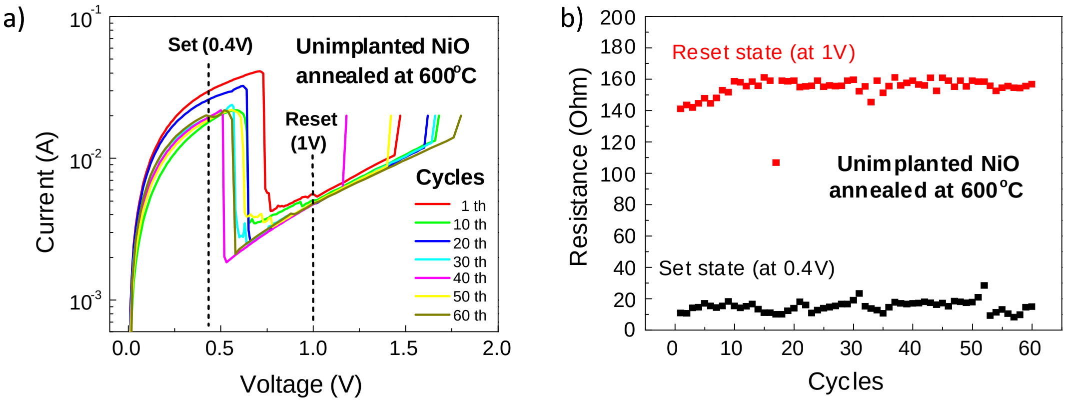

Fig. 4. Current-voltage response of a device annealed at 600°C and the extracted resistance during repeated measurements.

After forming process, the devices were tested by sweeping voltage over a certain range. Filaments can be "set" and "reset" via the application of appropriate current-voltage pulses. Both ON (set) and OFF (reset) states are nonvolatile and reversible and quite stable [1]. Fig. 4 shows set/reset behaviour for an individual sample and its resistance state during repeated measurements.

The effect of ion-implantation of the set/reset response of devices is summarized in Fig. 5. No significant change in response is observed for any of the implants. Because the set/reset process occurs over short distances (~ nm) it is likely to be less sensitive to the bulk properties of the NiO film.

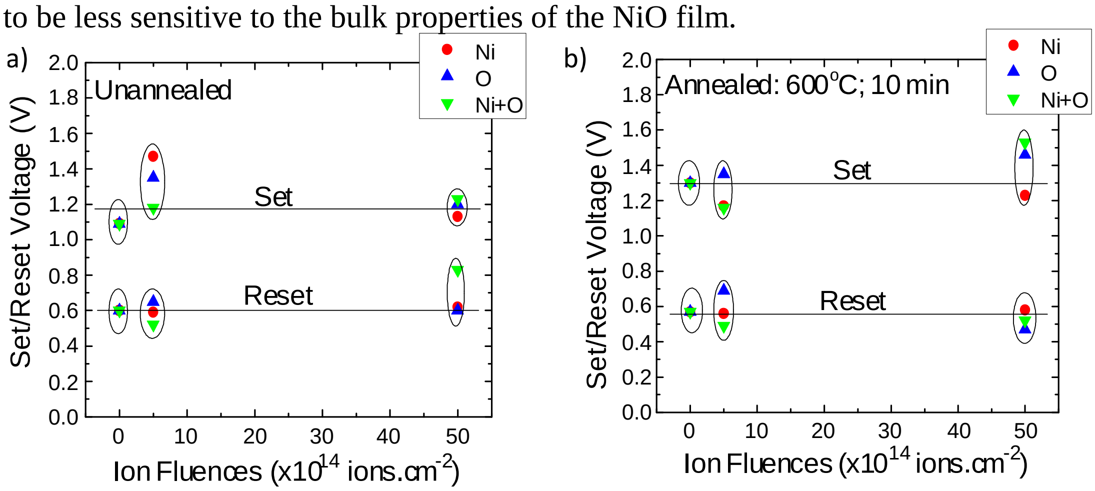

Fig. 5. Set/Reset voltage for devices implanted with Ni, O and Ni+O ions.

5. Conclusion

It has been demonstrated reproducible and stable resistive switching behaviour in as-deposited, annealed and ion-implanted Pt/NiO/Pt devices. Ion-implantation of Ni and O ions is shown to affect the voltage required to form conductive filaments in NiO thin films, with Ni increasing the forming voltage and O reducing it. The fact that co-implants of Ni and O also reduce the forming voltage suggests that these effects are not simply due to stoichiometry but also to defects caused by the irradiation. This study also reveals that ion-implantation has little or no effect on the set/reset voltage of NiO RRAM devices.

Acknowledgement

The authors are grateful to David J Llewellyn for TEM analysis.

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