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SPECTROSCOPIC CORRELATIONS TO RESISTIVE SWITCHING OF ION BEAM IRRADIATED FILMS*

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Abstract

Researchers concentrated on resistive random-access memories (RRAMs) due to excellent scalability, high integration density, quick switching, etc. Intrinsic physical phenomenon of RRAMs is resistive switching. In this work, ion beam irradiation was used as a tool to modify resistive switching of pulsed laser deposited (PLD) $Y_{0.95}Ca_{0.05}MnO_3$/Si films. Ion irradiation induced optimal resistive switching with spectroscopic correlations has been attributed to oxygen vacancy gradient. Resistive switching ratio is estimated to be increased for the film irradiated with fluence 1×10^{11} ions/cm^2 due to irradiation induced strain and oxygen vacancies verified by X–ray diffraction (XRD), Raman, atomic force microscopy (AFM), Rutherford backscattering spectrometry (RBS) and near–edge X–ray absorption fine structure (NEXAFS) measurements. Strain relaxation and oxygen vacancy annihilation have been realized for higher fluence (1×10^{12} and 1×10^{13} ions/cm^2) owing to local annealing effect. Present study suggests that the films understudy can be considered as emerging RRAMs.

INTRODUCTION

Hysteretic resistive switching (RS) based resistive random access memories (RRAMs) in the transition metal oxides have attracted considerable attention because of exceptional scalability, high integration density, fast switching, etc [1, 2]. Many metal oxide materials present a noteworthy part of promising memristive materials due to the presence of RS characteristics [3]. In recent times, it is reported that nanostructures containing manganites can also exhibit RS behavior [4, 5]. Trivial change in oxygen stoichiometry causes strong deviation in electrical conductivity and magnetic state [6]. Therefore, materials with non inherent RS may accomplish this feature with new findings.

RS is the phenomenon in which various resistance magnitudes can be executed such as write, read and erase by applying the suitable voltages. In general, two different resistance states such as high resistance state (HRS) and low resistance state (LRS) are observed per device. The device can be toggled between HRS and LRS by SET and RESET processes, respectively. For unbiased device, particular voltage is required to start the forming process which triggers the RS for the successive cycles. There are two switching modes broadly classified, namely, unipolar switching and bipolar switching. SET and RESET processes are obtained at the same polarity in unipolar switching. In the case of bipolar switching, reverse polarity of bias is required for SET and RESET processes.

Ion irradiation is the tool which can create controlled structural disorder as well as localized strain [7, 8]. Sensitive nature of manganites towards strain and structural disorder lead to significant modifications in transport and magnetic properties of ion irradiated hole doped manganites [8, 9]. In present study, we report the results on the effects of ion irradiation on resistive switching of $Y_{0.95}Ca_{0.05}MnO_3$ thin films.

EXPERIMENTAL

Thin film of $Y_{0.95}Ca_{0.05}MnO_3$ (YCMO) was grown on *a*-axis-oriented n-type single crystalline Si substrate by pulsed laser deposition (PLD) technique under effective conditions using pure target of YCMO (prepared by solid–state reaction method). After deposition process, the thin film of YCMO was cut into four identical pieces to maintain the uniform growth. One piece of PLD grown film was kept virgin, while other three pieces of films were irradiated with 100 MeV O^{7+} ion beam at 15 UD Tandem Pelletron Accelerator, IUAC, New Delhi, India. The pristine YCMO film is referred as PRI, while irradiated films with different ion fluences such as 1×10^{11}, 1×10^{12}, 1×10^{13} ions/cm^2 are denoted as 1E11, 1E12, 1E13, respectively. The irradiation was carried out under an elevated vacuum condition (~10^{-6} Torr). The thickness of all the films (~100 nm) was obtained by thickness profilometer. X–ray diffraction (XRD), Raman measurement, atomic force microscopy (AFM), Rutherford backscattering spectrometry (RBS) and near–edge X–ray absorption fine structure (NEXAFS) measurements (not shown here) and their outcomes have been discussed. Schematic diagram of the irradiated as well as the pristine films is displayed in Fig. 1. Silver paste was used to provide Ohmic contact with YCMO and Schottky contact with Si (as Ag ions diffuse through narrow SiO_x).

RESULTS & DISCUSSION

X–ray diffraction (XRD), Raman spectroscopy, Atomic force microscopy (AFM), Rutherford backscattering spec-

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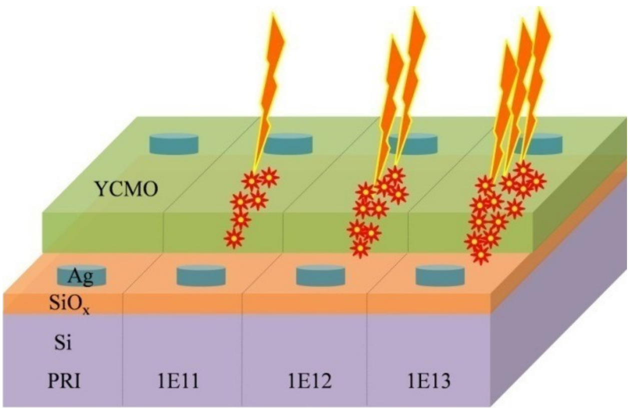

Figure 1: Schematic diagram of all YCMO films.

trometry (RBS) and near–edge X–ray absorption fine structure (NEXAFS) measurements (not shown here) suggest the strain/stress and oxygen vacancy modifications with ion irradiation in $Y_{0.95}Ca_{0.05}MnO_3$ (YCMO) films. XRD results of all films indicate orientation of all the peaks in a-axis direction with Si substrate. Film and substrate peak separation gets varied due to lattice mismatch and indicates maximum compressive strain in 1E11 film. These results are supported by Raman measurements which also show maximum irradiation effect on 1E11 film. From AFM measurement, it is evident that the maximum hillock like defects (in number) is present in 1E11 which gets reduced for high doses of ion beam fluence due to annihilation process. Oxygen content variation has been verified by RBS analysis. Results of RBS measurements reveal minimal content of oxygen in 1E11 film for both YCMO film and SiO_x layer. NEXAFS results show Mn^{4+} to Mn^{3+} valance change for 1E11 film as a result of most number of oxygen vacancies which is relaxed for 1E12 and 1E13 films.

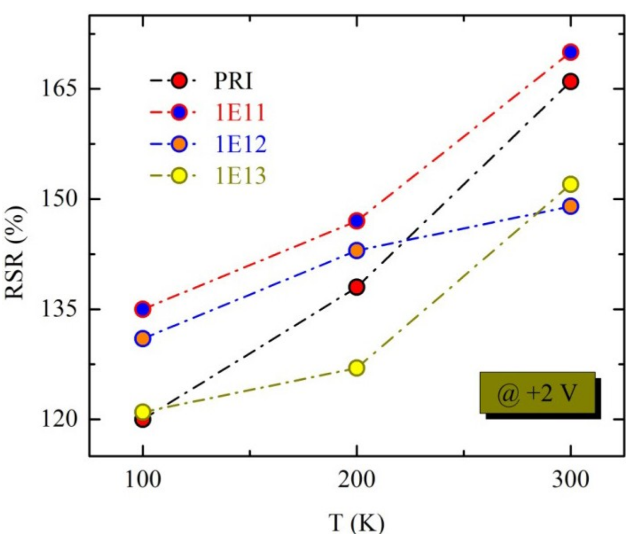

Figure 2: RSR of YCMO films performed at +2 V.

Resistive switching ratio (RSR) of pristine and irradiated films as a function of temperature at reading voltage +2 V is displayed in Fig. 2 and estimated from high to low resistance states. It is vivid from Fig. 2 that the RSR increases as temperature increases for all the films. It is reported that the oxygen vacancy migration time decreases as a function of temperature [10]. Oxygen vacancies with high mobility are expected with small migration time for highest temperature (300 K). This leads to better RSR at 300 K than the lower temperatures (200 K & 100 K). With ion irradiation, RSR is found to be increased for lowest temperature which gets reduced at highest temperature studied for higher fluences (1E12 and 1E13). Although in 1E11 film, the RSR remains at higher magnitude for all the temperatures under study. This deviation in RSR clearly indicates the dependence of RSR on ion beam irradiation. Presence of large number of oxygen vacancies is responsible for better RSR in 1E11 through easy conduction path for oxygen vacancies. This conduction path becomes weak in 1E12 and 1E13 films resulting in decreased RSR.

From Fig. 2, it is observed that highest RSR is observed at 300 K due to which we have selected 300 K for fluence dependence analysis. Figure 3 illustrates a model that represents the RSR with defects and ion dose at room temperature (300 K). By keeping in mind that the defects are lowest in PRI film as compared to the irradiated films, the model has been prepared. Lower defects and ion dose point out lower RSR in percentage. With increase in defects and ion dose, the RSR also increases up to certain defects and ion dose level i.e. optimal ion dose range or critical ion dose. After optimal ion dose, the RSR decreases and, then, slightly increases. Experimental confirmation of this model with ion dose (fluence) is shown in Fig. 4. From PRI to 1E11, the RSR is increased due to more number of oxygen vacancies present in 1E11 film. For higher irradiated films (1E12 and 1E13), RSR is reduced as a result of decrease in oxygen vacancies. Experimental confirmation of this deviation in oxygen vacancies is given by RBS and NEXAFS measurements whereas indirect support to this discrepancy is provided by XRD, AFM and Raman analysis.

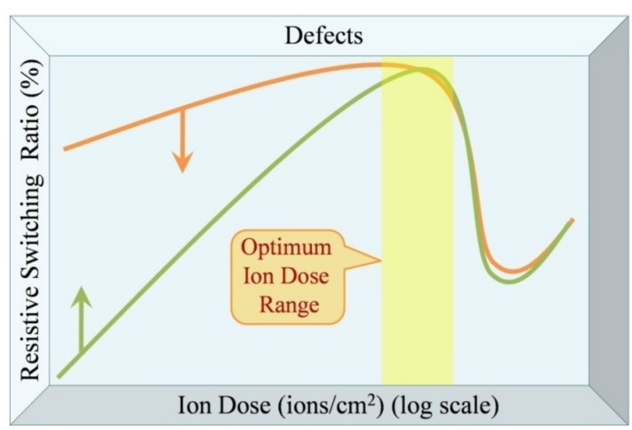

Figure 3: Model representing effect of ion dose and defects on resistive switching ratio at 300 K.

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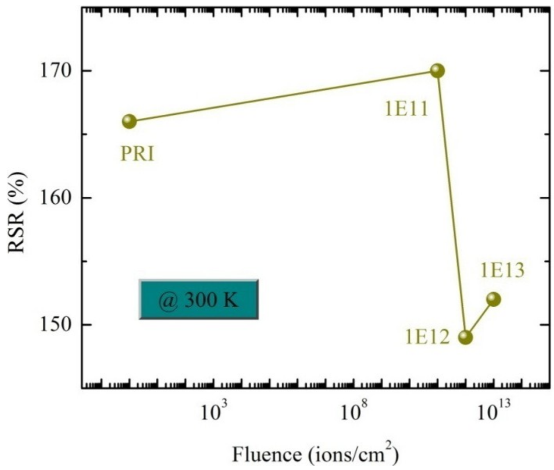

Figure 4: RSR as a function of ion fluence performed at room temperature.

SUMMARY

In summary, we have irradiated PLD grown YCMO films with 100 MeV O^{7+} ion source. RSR is found to get modified by ion irradiation in all the YCMO films. At room temperature, best RSR is observed for 1E11 film. This result is attributed to the presence of large number of oxygen vacancies in 1E11 film. Higher fluence of ion irradiation signifies reduced oxygen vacancies lead to decreased RSR. This findings spur that presently studied YCMO films can be potential candidate for future RRAM applications.

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