Correlating structural and resistive changes in Ti:NiO resistive memory elements

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Structural and resistive changes in Ti-doped NiO resistive random access memory structures that occur upon electroforming have been investigated using hard x-ray microscopy. Electroforming leads to structural changes in regions of size up to about one micrometer, much larger than the grain size of the structure. Such changes are consistent with a migration of ionic species or defects during electroforming over regions containing many crystalline grains. © 2010 American Institute of Physics. [doi:10.1063/1.3355546]

Thick films of transition metal oxides sandwiched between metal electrodes can show resistance changes of several orders of magnitude following application of small electric fields (of the order of 1 MV/cm) across the film.1–3 There is considerable interest in these materials because of their potential use in nonvolatile resistive random access memory (RRAM). One such material is Ti-doped nickel oxide (Ti:NiO) in which the addition of Ti has been shown to enhance switching properties.2–7 Switching of RRAM structures consisting of Pt/Ti:NiO/Pt, with a NiO thickness of 20–50 nm, between a high-resistance non-metallic state and a low-resistance, metallic state has been demonstrated6–8 by applying unipolar voltage pulses in the range of a few volts. As deposited, a device is usually in a high-resistance state and has to be electroformed by setting it into an initial low-resistance state by applying a moderately high voltage pulse of about 5 V. Various mechanisms have been proposed to explain the electroforming and switching behaviors, for example Schottky barriers with trapped charges at interface states,9,10 space-charge limited currents,11 electronic transitions between a Mott insulator and a metallic state,12,13 and formation and rupture of metallic (presumably metallic Ni) filaments.7,14,15

The observed electronic response of these structures may be coupled to microstructural changes of the constituent lattice and may therefore in principle be observable with a local probe of structural order. The present work reports on observed changes in the NiO (111) diffraction intensity between the as-deposited and electroformed states over a 10 μm × 10 μm Pt/Ti:NiO/Pt patterned structure, using the hard x-ray nanoprobe beamline (HXN) facility. The HXN is part of the Center for Nanoscale Materials at the Advanced Photon Source at Argonne National Laboratory. The change in resistance during electroforming was correlated with structural changes.

Samples were prepared using ultrahigh vacuum sputter deposition on a Si substrate of a Ta30 nm/Ti5 nm seed followed by a 10 nm thick Pt bottom electrode, a 50 nm thick Ti:NiO (0.5 wt % Ti), a 10 nm thick Pt top electrode, and a Ta capping layer. X-ray diffraction data from similar Ti:NiO films have shown that oxide is polycrystalline with a dominant (111) texture. An array of 10 μm × 10 μm structures was patterned using standard lithographic techniques. A sample approximately 5 mm × 5 mm was cut from the patterned wafer and mounted on the scanning probe diffraction microscopy module of the Nanoprobe. The incident synchrotron x-ray beam energy was selected from the undulator beam by a double crystal Si (111) monochromator calibrated to 10 keV and focused to an estimated absolute lateral resolution of approximately 50 nm. The sample and detector angles were adjusted to optimize the diffraction intensity of the NiO (111) diffraction peak (θ = 13.22°, 2θ = 26.44°). By moving the sample perpendicular to the incident beam a two-dimensional (2D) scan of the NiO(111) diffraction intensity across a specific selected structure could then be recorded with a resolution of about 100 nm. The sample was then removed from the beamline and placed in an electrical probing station. The same structure that had been scanned in the Nanoprobe was identified and electroformed, and then returned to the Nanoprobe beamline where the 2D diffraction scan at the NiO(111) peak was repeated on the electroformed structure. Changes in Bragg diffraction intensity between these two scans indicate changes in structural alignment (or integrity) due to the electroforming process having altered the diffraction condition beyond the illuminated angular divergence given by the focused beam. Transmission electron microscopy (TEM) analysis of a cross-section sample was performed using a JEOL 2010 FEGTEM operated at 200 kV with a resolution of approximately 0.2 nm.

In Fig. 1 are shown I-V curves obtained in the electrical probing station on the structure analyzed in the Nanoprobe. We did not attempt to reset and set this structure as the present work was focused on the electroforming process. Similar structures from the same wafer, and structures with
FIG. 1. Current-voltage loops for the structure examined in the Nanoprobe during electroforming (solid line), and in electroformed (dashed line) state. The arrows indicate sweep direction of applied voltage during forming: the I-V curve is reversible in the electroformed state. Current compliance limit was set at 2.1 mA.

35 nm thick Ti:NiO were successfully electroformed, set and reset in separate electrical probing. More than 90% of the electroformed 35 nm Ti:NiO could be reset and set. All of the 50 nm Ti:NiO structures could be electroformed at a higher compliance current (50–60 mA). About 20% of those could subsequently be reset, a percentage limited only maximum current compliance of our current supply (100 mA). These electrical data, and the fact that the electroforming process used for the present structure was more gentle in order to avoid irreversible damage, make us confident that the electroformed state of the present structure is representative of the electroformed state of structures that could subsequently be reset and set. Figure 2 shows a cross-section TEM image of a patterned structure from the same wafer. The top surface of the Ti:NiO is rather rough on a length scale of a few nanometer. From this image, we determined the Ti:NiO grain size to be about 15 nm.

Figure 3 displays the normalized diffracted intensity at the NiO(111) peak across the same Pt/Ti:NiO/Pt structure in the as-deposited and in the electroformed states. The vertical axes have been rescaled by a factor of 1/\sin \theta to account for the foreshortening effect arising from the diffraction angle.

In order to match the dimensions along the vertical axis between the two scans, the scan shown in the right panel was scaled by a factor of 1.3, which is within the expected range as a result of thermal drift. The solid-lines in Fig. 3 demarcate some of the (changed) regions that are larger than the step size or the projected spot size, indicating regions in which structural changes have occurred that are at least 400 nm in size and consist of many crystalline grains, with several regions being considerably larger. Areas in which the initial (as-deposited) normalized intensity map had an intensity >0.83 and <0.73 were mapped out (the average intensity across the map was 0.74). Similarly, areas were mapped out in the post-forming intensity map with an intensity >0.75 and <0.68 (the average was 0.68). A cross-correlation between the intensity maps before and after electroforming was then performed, which allowed the area fractions that had changed upon electroforming to be determined. Note that the choice of cutoff values gives a more conservative estimate of the areas that have changed than had the average intensities been chosen as cut-offs. With these cutoffs, the area fraction with unchanged intensity was 0.20; the area fraction where the intensity changed was 0.17. There are many areas larger than 1 \mu m^2 in which the intensity changed, which is much greater than the pixel size of the scans (0.056 \mu m^2). If the intensities were uncorrelated between pixels, the probability of having a contiguous area of 1 \mu m^2 in which the intensity changed is <3 \times 10^{-11}. Therefore, the areas in which the intensity changed (or did not change) are statistically significant. A change in diffraction intensity is consistent with structural changes that could arise from a number of mechanisms. Migration of defects or ionic species can change local diffraction conditions due to lattice expansions or contractions. Local reorientation of the (111) axes in the crystalline grains would also lead to a change in diffraction conditions, as would a change in the diffracting volume, or changes in local dislocations that strain the lattice. However, we believe the first mechanism is the most likely one. We do not believe that strain fields due to migration of defects or ionic species can extend beyond single grains, as grain boundaries would be expected to absorb such strain. Therefore, the changes in diffraction condition must occur simultaneously in many neighboring crystalline grains.
The changes in diffraction conditions occur very inhomogeneously across the structure, since the as-deposited Ti:NiO film itself is structurally inhomogeneous, and the interface with the Pt top electrode is very rough (see Fig. 2). Therefore, electric fields and the resulting current densities will also be very inhomogeneous during the electroforming process. Threshold electric fields for the onset of structural changes reached inhomogeneously across the sample but were prevented from being initiated across the entire structure by the current compliance. The structural changes that follow electroforming are rather subtle in that we observed changes in the NiO (111) diffraction amplitude, but no complete loss of diffraction amplitude.

One mechanism frequently attributed to electroforming and switching is the formation and rupture of metallic filaments.12,14-21 For patterned structures of the size studied here, the resistance of the metallic state scales poorly with area, implying that there are a small number of dominant current paths in the metallic state. The formation of only a few filamentary metallic paths within one region is not consistent with the observation of structural changes in regions of the size of a micrometer. More recently, there have been observations of some scaling of the resistance in the metallic state with device area,6 consistent with the formation of multiple filaments.15,22,23 There are two possible mechanisms consistent with the observations presented here. The first one is the migration of ionic species or defects (e.g., oxygen ions and Ni vacancies), creating metallic Ni filaments. There would have to be many filaments distributed over the crystalline grains in each of the regions in which the diffraction intensity was observed to change upon electroforming.24 The origin of the inhomogeneous nature of the structural change is then associated with the inhomogeneous nature of the electroforming field across the structure together with the initial inhomogeneous microstructure. Alternatively, the filaments could consist of many subtle structural changes over a larger region with a concomitant change in electronic structure, leading to metallic conductivity. A second possible mechanism that is also consistent with our observations is the migration of vacancies or ions to interfaces, coupled with a change in electronic structure leading to metallic conductivity in these regions.12,13 A change in Schottky barrier height9,10 is inconsistent with the observation that the conduction in the electroformed state is metallic, and does not have the I-V characteristics of a Schottky barrier.

In summary, correlations between structural and resistive changes in Pt/Ti:NiO/Pt structures upon electroforming from an initial insulating state to a metallic state have been investigated. X-ray diffraction microscopy of the NiO (111) peak clearly shows that electroforming gives rise to structural changes in regions of size up to about 1 μm. The observed structural changes are consistent with an electroforming process that involves migration of ionic species or defects over regions containing many crystalline grains.

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