Spectromicroscopy of tantalum oxide memristors

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We report experiments to measure material changes in tantalum oxide-based memristive devices. The high endurance and low power demonstrated in this material system suggests a unique mechanism for the switching, which we investigated using x-ray based spectromicroscopy and nanospectroscopy. Our study nondestructively identified a localized (<150 nm diameter) Ta-rich phase surrounded by nano- or polycrystalline Ta2O5. © 2011 American Institute of Physics.

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Thin film metal oxides exhibit a dynamical resistance switching, or memristive, behavior with the application of an electrical bias across a metal/oxide/metal (MOM) device structure. This phenomenon is pervasive across many material systems and has been studied1–6 particularly for developing a high density nonvolatile memory. These motivations and the desire to perform analyses nondestructively have driven significant recent advances in device development and materials research.7–12 One promising material system is tantalum oxide,1,3,14 which has demonstrated over 109 cycles of write/erase endurance, relatively low power operation, and no required electroforming step. As yet, there is little understanding of the microscopic switching mechanism, including, for example, the presence and material composition of any conductive channels.

Generally speaking, the chemical and structural characterization of resistive switching devices is challenging, because of the extremely small volume of material involved and the desire to perform analyses nondestructively. Many resistance switching systems15–19 are now known to operate based on the formation of localized anion-deficient (e.g., oxygen vacancy rich) channels. However, many of the techniques applied require special device preparation, are destructive, or operate on structures substantially different from the usual MOM devices. Additionally, none of the heretofore studied systems has exhibited the high endurance of tantalum oxide, thus making a material understanding of this system particularly important to guide future device improvements.

With this goal, we performed a synchrotron-based microcopy and spectroscopy study after the electrical cycling of a tantalum oxide resistance switching device without using any destructive sample preparation. We discovered a localized (<150 nm diameter) Ta-rich channel within a 7.5 × 7.5 μm2 device. The Ta-rich channel was surrounded by a modified phase of the oxide, which had a spectral signature distinct from the as-grown layer. We discuss the most likely interpretation for the observed spectroscopy and microscopy.

Our memristive device had a bottom electrode of Pt (15 nm)/ Ti (5 nm), a top electrode of Pt (30 nm) and a switching layer of tantalum oxide (22 nm) fabricated on a SiO2/Si substrate. The tantalum oxide film was unpatterned, extending across the substrate and was sputter-deposited from a tantal target with an Ar pressure of about 1.5mTorr at 270 °C substrate temperature. Transmission electron microscopy measurements of an identically grown film revealed a uniform amorphous structure, while core-level x-ray photoelectron spectroscopy analysis indicated that the tantalum was present in multiple oxidation states: 92% Ta5+, 4% Ta4+, and 4% Ta0. Thus, the film is essentially amorphous tantalum pentoxide (a-Ta2O5) with a high concentration of oxygen vacancies. A top electrode of Pt, rather than Ta,13 was used here to ensure that the only Ta present in the device was from the switching oxide layer, thus eliminating a potential source of ambiguity in the following materials characterization.

The devices with Pt top electrodes were highly resistive in the virgin state and required an initial electroforming step to enable bipolar resistive switching. This was performed with a −10 V bias applied to the top electrode with the bottom electrode grounded [Fig. 1(a), inset] While this electroforming step can be eliminated by using a Ta top electrode and a thinner tantalum oxide switching layer,13 the bipolar switching operation following the electroforming step [Fig. 1(a)] is qualitatively very similar in both types of devices.

Following electroforming and switching, the memristive device was studied at the Advanced Photon Source ID-26 Hard X-ray Nanoprobe beamline.20 A Fresnel zone plate focused the x-rays to a ~70 nm full width at half maximum spot size at the sample. X-rays were incident nearly perpendicular to the plane of the sample while being scanned laterally using an optomechanical nanopositioning system based on laser doppler interferometry.21 The element-specific fluorescence was detected at each point in the scan allowing simultaneous mapping of the different material components in the device as well as more detailed material information by sweeping the incident x-ray energy. In this case, the photon energy was scanned around the Ta L3 absorption edge (~10 keV) with a fine structure that is sensitive to microscopic structural, valence state, and chemical bonding information. The probing depth of the fluorescence measurements was longer than the thickness of the entire device material stack. No pre- or postpreparation of the sample was required, making this technique well-suited for characterizing and imaging all material layers within a standard resistance switch-
Electroforming and switching of a tantalum oxide-based crossbar memristor. (a) Device was cycled ON and OFF, after a forming step (inset), exhibiting bipolar operation. X-ray fluorescence microscopy following electrical operation showing the Pt (b) and Ta (c) elemental signal. Within junction, a <400 nm region with enhanced signal was observed and is indicated by an arrow.

Figures 1(b) and 1(c) show imaging of the tantalum oxide device, detecting fluorescence from Pt and Ta, respectively, in response to incident x-rays at an energy of 9885 eV. The x-ray energy was chosen to be within the steep absorption edge of the Ta L₃ resonance, allowing spatially localized material changes in the tantalum oxide layer to be more easily detected. The vertical and horizontal bright regions in Fig. 1(b) show the bottom and top Pt electrodes, respectively, with the bottom electrode less bright due to a reduced thickness as well as partial absorption of the fluorescence by the oxide layer. The measured Ta fluorescence in Fig. 1(c) might be expected to be spatially uniform since the oxide layer was unpatterned but attenuation by the top electrode caused the appearance of a darker horizontal stripe. A bright spot near the bottom of the junction area was observed in Fig. 1(c), indicated with an arrow. This spatially nonuniform Ta fluorescence signal was less than 400 nm in diameter, consistent with previously observed conductive channels in titanium oxide memristors with similar device size and power applied during operation. The brighter contrast of this spot is consistent with (1) an increased Ta concentration, (2) a chemically or structurally altered local region of the oxide, or (3) an enhanced fluorescence signal due to reduced top electrode thickness or another enhancement mechanism. Possibility (3) is unlikely as there was no indication of less Pt in this region, as evident from Fig. 1(b) and additional higher resolution scans.

Figure 2 shows spectromicroscopy measurements of the device region of interest, starting with a reference Ta L₃ spectrum of the as-grown, primarily a-Ta₂O₅ layer in Fig. 2(a). Changes in the fine structure of this absorption spectrum can reveal regions in the layer having an altered chemistry or structure. Thus, this spectrum served as a guide and Figs. 2(b)–2(e) show high resolution scans taken at different x-ray energies near and within this absorption line. The image at 9985 eV, Fig. 2(e), is in the postedge energy region, therefore, revealing elemental Ta concentration levels, and shows a spatial region (brighter, near center of image) with a higher Ta concentration by up to 8.9% (±0.7%). It is observed in Figs. 2(b)–2(d) that surrounding this Ta-rich spot is a region showing another material change. This is evident by the different absorption contrast in this surrounding region, evolving from brighter than neighboring regions at 9885 eV to darker (a 6.1% reduced intensity) at 9889 and 9893 eV. This semicircular region in the device had an absorption spectrum that differed from the as-grown film in Fig. 2(a), yet has an unchanged Ta concentration, thus, showing a more subtle and localized material change. Figure 2(f) is a composite image formed by an overlay of the regions for this new phase (red), the Ta-rich region (blue), and the a-Ta₂O₅ (black) obtained from Figs. 2(b)–2(d).

The stability of the NanoProbe beamline allowed the performance of nanospectroscopy: sweeping the incident x-ray energy while holding the position of the x-ray focus fixed within a 70 nm spot of the sample to measure the localized absorption spectrum. The nanospectroscopy results
are shown in Fig. 3 in which two spots in the device, one within the modified phase and another roughly two micrometers away, as indicated in the Fig. 3 inset, were analyzed. The observed spectrum was consistent with the microscopy of Fig. 2; the absorption intensity matched the as-grown region in the pre-edge and postedge energies while showing reduced absorption within the Ta L3 white line, resulting in the darker contrast observed within this region in Figs. 2(c) and 2(d). Moreover, there was an overall reduced intensity through the white line from 9880–9900 eV. The peak intensity was reduced by 6.8% while the integrated area (proportional to the unoccupied valence states) was reduced by 3.1%. There was also an observable shift in the peak to lower energy by approximately 0.2 eV. Prior studies24 comparing the Ta L3 x-ray absorption spectra in Ta2O5 amorphous and crystalline films have shown similar spectral features, specifically a decreased white line absorption in the crystalline film which was attributed to reduced covalent (increasingly ionic) Ta–O bonding. Thus, a likely interpretation is that this nanoscale region has undergone a change from an initially a-Ta2O5 to a nano- or polycrystalline Ta2O5. Our nanospectroscopy work thus suggests that a crystallization of the Ta2O5 has occurred in this region of the device.

The exact location of the nano- or polycrystalline Ta2O5 phase surrounding the more metallic, Ta-rich channel [Fig. 2(e)] suggests that the crystallization was driven by Joule heating during electrical operation. Prior studies of initially amorphous films of Ta2O5 having a comparable thickness showed that crystallization occurred at temperatures greater than 600 °C.25,26 Such structural changes surrounding a conductive channel have also been observed in TiO2-based memristors19,22 with similar temperature levels27 attained from the Joule heating in a nanoscale channel. Since oxygen was not probed in this study, we were unable to determine the precise composition of the Ta-rich phase, which will require different techniques.

Our work highlights that resistance switching, especially the electroforming step, in tantalum oxide memristors involves a bulk material change in the oxide layer itself, eliminating several mechanisms, for example, the migration of electrode (Pt) atoms, or purely interface effects. Instead, we directly observe (1) a Ta-rich channel surrounded by (2) an altered material phase which was identified as Ta2O5 with additional short-range order, both of which evolved from the initially amorphous film, which was multivalent, but mostly Ta2O5. This provided evidence for local heating to a temperature greater than 600 °C. The only thermodynamically stable phases in the Ta–O system are a metallic TaO (solid solution and an insulating Ta2O5. Thus, it is likely that any metastable phases evolve and segregate in favor of these two phases, particularly, during electrical operation and the associated Joule heating. Growth of a metallic Ta-rich channel within the insulating Ta2O5 matrix will increase the conductivity (ON switching), while reoxidation (OFF switching) will decrease it. While more work is needed to understand the kinetics and electric field dependence of the observed material changes during ON and OFF switching, such a study is possible with the nondestructive technique employed here, and the present analysis should provide a framework for understanding this operation.

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