Direct Observation of Localized Radial Oxygen Migration in Functioning Tantalum Oxide Memristors

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Oxygen migration in tantalum oxide, a promising next-generation storage material, is studied using in-operando x-ray absorption spectromicroscopy and is used to microphysically describe accelerated evolution of conduction channel and device failure. The resulting ring-like patterns of oxygen concentration are modeled using thermophoretic forces and Fick diffusion, establishing the critical role of temperature-activated oxygen migration that has been under question lately.

Tantalum oxide memristors are frontrunners for next generation memory technology due to their promise of long endurance, long retention and low power.1–4 Recent efforts to uncover the nanophysics behind resistance switching in tantalum oxide and several related materials suggest local conductive channel formation by oxygen-ion migration as the mechanism of operation.5–9 A more complete understanding of the migration microphysics is required to construct improved compact models that are necessary for circuit design and simulation. In particular, while it is generally acknowledged that elevated local temperatures10,11 are reached during switching, there is uncertainty on the role of thermally-driven oxygen migration in memristors12,13 and its influence on eventual device failure.14,15 Here we present x-ray spectromicroscopy images at the O K-edge and Ta L3-edge of in-operando electrically-cycled TaOx memristor devices which reveal radial lateral oxygen migration. Following electrical cycling using high-voltage (±5 V) pulses, we observed irreversible sub-micrometer sized insulating oxygen-rich ring-like features with an oxygen-deficient, highly conductive core. We show that these features are well described by a microphysical model containing thermally-driven diffusion, in the form of thermophoresis and Fick diffusion, during accelerated evolution of the conduction channel. As TaOx devices were further cycled with over 1 million voltage pulses, we observed the oxygen-rich rings breaking into oxygen-rich and oxygen-poor clusters which eventually shorted the electrodes and caused actual device failure. The O K-edge spectra of the oxygen-rich and oxygen-deficient regions in the rings and clusters are consistent with clusters of oxygen interstitials and vacancies, respectively, indicating strong clustering forces. These results directly observe the nanoscale motion of oxygen in a functional memristor especially during the course of accelerated device evolution and failure, and also demonstrate the importance and sign of the thermophoretic forces on oxygen during evolution of conduction channels.
The migration of oxygen was investigated using O K-edge x-ray absorption spectromicroscopy\(^{[16]}\) on 2 μm x 2 μm crosspoint TaOx memristor devices during in-situ electrical cycling (Figures 1a-b). Memristor devices (Pt/TaO\(_x\)/Ta/Pt) were specifically fabricated to enable x-ray transmission measurements and exhibited >10 million switching cycles with a \(R_{\text{off}}/R_{\text{on}}\) ratio of 10-100 at low voltage amplitudes (see Supporting Information). To amplify the material changes and accelerate device failure, we used larger amplitude cycling pulses of ±5 V (following device forming and DC switching), and tracked the associated material changes by acquiring x-ray absorption images over the course of several million cycles (Figure 1b). After 100 cycles, x-ray images at the lowest conduction band revealed barely discernible rings with a perimeter darker than the surrounding film area, indicating an increased absorption of the resonantly-tuned x rays in the ring perimeter. As the device reached \(10^6\) cycles, dark and bright regions, indicating areas of even greater and reduced x-ray absorption, appeared and grew in number and contrast as the rings faded. We confirmed the ring formation with additional x-ray images on fresh devices after \(10^5\) cycles (Figures 1c-1d), before the dark and bright regions appeared, where we again observed a dark ring (increased x-ray absorption) with a bright center (reduced x-ray absorption) relative to the rest of the device. We also further examined the spatial and contrast evolution of the rings and bright and dark regions with increasing electrical cycling (Figures 2a-2b). A prominent dark ring perimeter had appeared by \(10^6\) cycles, and the subsequently diminished in intensity by \(6\times10^7\) cycles (Figure 2b), coinciding with a significant contrast increase of previously existing dark and bright regions and the appearance of a new bright region (at ~0.3 μm). Therefore, the rings appear to fragment to form smaller and more concentrated clustered bright and dark regions. Upon formation of the rings, the device required higher voltages to undergo resistive switching (>5 V) than under normal operation (<2 V). After about \(7 \times 10^6\) cycles, when a significant number of bright spots were prominently observed, the device became irreversibly stuck in its high conductance state and could not be switched back to a lower conductance state, while the rings themselves were stable over several months. This is an indication that conducting channels observable as bright spots essentially shorted the top and bottom electrodes of the device and caused device failure.
The bonding and electrical nature of the bright and dark regions of the ring and clusters was investigated with O K-edge absorption spectroscopy (Figure 2c). The spectra were aligned at 528 eV (before the absorption edge) to enable a comparison of changes associated purely with oxygen bonding and oxygen concentration and subtract any electrode effects. The lowest conduction band of the bright region ($\pi^*$, $t_{2g}$), was significantly downshifted (by ~0.3 eV) indicating a higher electrical conductivity than the dark region.[17,18] Also, the bright region spectra revealed lower absorption in the post-edge, indicating a lower oxygen concentration relative to the dark regions. Relative to the rest of the grey crosspoint area, the bright center and dark perimeter of the rings had a -17±2% deficiency and a +14±2% excess of oxygen atoms, and are therefore ascribed to O vacancies and interstitials respectively (see Supporting Information for calculation details). Similarly, the bright and dark regions had a -14±2% deficiency and a +12±2% excess of oxygen atoms (after $6\times10^7$ cycles). In a surprising observation, the dark regions displayed a spectral feature in the 535 eV region of the spectrum. This sub-band was significantly smaller, and nearly absent, in the bright region (see the dashed blue sub-band indicated by green arrow in Figure 2c). A similar feature has been previously associated with a superoxide species ($O_2^-$) that binds with an electropositive element such as tantalum,[17,19-24] supporting the existence of oxygen interstitials within the dark regions. Further evidence of this physical picture is indicated by observing where the current flows in the device.

To investigate this, we plot the difference between spectrum with no current flow and spectrum with current flow for the bright and dark regions separately, leveraging an in-operando synchronous time-multiplexed technique developed for this study (Figure 2c). The difference spectra of the bright regions shows more recognizable and sharper features at peak O K-edge energies as compared to that in the dark region, indicating that current preferentially flowed through the bright region, causing a measurable change during joule heating, which is again consistent with reduced oxygen concentration within the bright regions.
The Ta atomic distribution and chemical changes within the rings was investigated utilizing Ta L₃-edge spectroscopy (Figures 3a) on a fresh device, whose corresponding O K-edge image is shown in Figure 3b. X-ray images were taken at energy points across the Ta L₃ absorption edge, revealing an increased x-ray absorption within the oxygen-rich interstitial ring. To separate the increased absorption effects due to increased Ta concentration and oxidation state, we compare the images of on-edge (more sensitive to the Ta oxidation state) and post-edge (more sensitive to Ta elemental concentration), normalized to a corresponding pre-Ta-absorption edge image. The clear dark ring in the on-edge image is consistent with chemical changes to the Ta bonding and oxidation states to accommodate the change in oxygen concentration. Additionally, the lack of a ring feature in the post-edge image, indicates that migration of tantalum was less significant relative to migration of oxygen, possibly because of the relatively larger size of Ta (see Supporting Information for more data). As shown in recent investigations, it is possible there was Ta migration below the spatial, spectral, and signal resolution of our technique.

The observed oxygen-rich ring can be reproduced by modeling a thermally-driven diffusion of oxygen. A number of forces may act on the oxygen vacancies, for example: electric field-driven vertical drift followed by concentration-gradient-driven lateral diffusion (Fick diffusion), substitutional diffusion and/or thermophoresis. To show that a simple combination of two such lateral forces can account for the rings, we use one such example of thermophoresis in a local lateral temperature gradient, such as is expected around a conducting channel, balanced by Fick diffusion. Electric field-driven oxygen migration is usually significant in initiating and sustaining the switching mechanism, which has been addressed using fully coupled three-dimensional solutions, and is ignored here in light of highlighting a high-power-driven amplified irreversible change to the material, which is essentially a failure mechanism. Our measurements have shown that as-grown films contained numerous incipient oxygen defects, including interstitials and vacancies (Figure S2). Upon application of voltage pulses, as the first percolating current pathway is created there will be a localized temperature profile due to joule heating. In this model, the resultant lateral temperature gradients produce thermophoretic forces (Soret effect) that attract oxygen vacancies radially inward to the hot conducting channel (against the motion of oxygen interstitials), while Fick diffusion, driven by the resulting gradient of oxygen concentration, balances thermophoretic forces. We represent this process by a combined continuity equation \( \frac{\partial n_V}{\partial t} = \nabla \cdot ( J_{\text{Fick}} + J_{\text{Soret}} ) \), where \( n_V \) is the vacancy concentration, \( J_{\text{Fick}} \) and \( J_{\text{Soret}} \) are fluxes due to Fick diffusion and thermophoresis, respectively. Using this approach, we predict the resultant x-ray intensity profile and compare it to experimental data (Figures 3c-3d), which shows good agreement with each other. Details of the calculation are provided in the Supporting Information based on published analysis of thermophoresis in oxide memristors. Further experimental support for the thermally-driven nature of the oxygen interstitial rings emerges when we consider...
bands that can partially neutralize the charge on each species, as indirectly evidenced by significant band-shifts in Figure 2c. This band-bending can decrease repulsions among like-charged species and also enable them to agglomerate, as the cohesion energy for oxygen vacancies can be quite low, and is likely to stabilize the ring (7,34,39,40) (Figure 4c). We also calculated an approximate potential profile across the ring (Figure S16) that look qualitatively similar to the one proposed in this cartoon. Subsequent lateral forces followed by clustering of vacancies and interstitials follows the initial bending of bands, as shown in Figures 4b-4c. Due to continued supply of energy through cycling and the large surface-area-to-volume ratio of the rings, they break apart to form clusters of oxygen interstitials and vacancies (Figure 4d), associated with the fading of the ring observed in Figure 2b. Additionally, we observe that most of the bright regions in Figures 1b-1c are in proximity or contact with a dark region, and vice versa (pointed out in Figure S3). This suggests that there are significant vacancy-vacancy and interstitial-interstitial attractive forces or there are significant vacancy-interstitial barriers. The attractive forces likely originate from the strong clustering, as mentioned above. The barrier could originate from the oppositely charged defects in the bright and dark regions behaving as dopants, creating an electric field at the interface of these regions to prevent complete neutralization of the charged defects, much like oppositely charged dopants in a p-n junction. Direct observation of clustering of like-species is an important observation that shines light on a prominent failure mechanism of such devices. We specifically point to the fact that many real world devices are smaller than the ring features observed here and are operated at much lower power levels. Similar experiments utilizing low-power operations on identical devices have yielded strikingly different results, with the device endurance being much higher (>10^8) and no rings were observed. (17)

As our measurements show, in-operando x-ray absorption spectromicroscopy is a powerful tool for studying chemical and electronic structure in oxide materials, including device evolution and failure with electrical interstitials and positive vacancies can cause significant bending of the tantalum oxide conduction and valence bands.

![Figure 4: Schematic illustrations depicting the proposed mechanisms during the formation of rings and dark-bright spots using band diagrams. V_0 and I_0 represent oxygen vacancies and interstitials, respectively and E_F is the Fermi level. Solid lines represent the conduction (E_C) and valence (E_V) bands and, for simplicity, the energy levels of V_0 and I_0 are represented on top of E_C and E_V, respectively. (a) Existence of uniformly distributed incipient oxygen interstitials and vacancies. (b) Thermophoretic lateral separation of vacancies and interstitials due to joule heating originating from a filamentary current path. Accumulation of charges creates a change in the local potential energy, causing bending of bands. (c) As the valence and conduction bands approach the Fermi level, some of the charged species are partially or completely neutralized, hence decreasing the repulsion among identical species. (d) Formation of smaller, more stable clusters as the device is cycled.](http://dx.doi.org/10.1002/adma.201505435)
cycling and inhomogeneous localized phenomena. With in-operando, high-voltage electrical cycling of tantalum oxide devices, we observed the development of submicrometer features with a ring of oxygen interstitials and an inner core of oxygen vacancies, which could be reproduced using thermally-driven lateral forces. A key observation here is that a significant amount of displaced oxygen moved radially outward from the conduction channel and was stored as interstitials, with a unique spectral signature, in the tantalum oxide film rather than in to the adjacent tantalum metal electrode.\textsuperscript{[61,42]} These results provide experimental data that help in understanding previous models regarding oxygen ion migration.\textsuperscript{[3,5,8,17,26,32]} metastable cohesion of oxygen defects,\textsuperscript{[7,34,40]} role and sign of thermophoresis,\textsuperscript{[12-14,43]} the composition and structure of conduction channels that tend towards failure,\textsuperscript{[3,5,6,8,31]} and the localization of resistance switching.\textsuperscript{[14,37,43]} Most importantly, we directly observed a failure mechanism caused by clustering of like-species of oxygen.

Supporting Information
Supporting Information is available from the Wiley Online Library at http://onlinelibrary.wiley.com/store/10.1002/adma.201505435/asset/supinfo/adma201505435-sup-0001-S1.pdf?v=1&s=479bb0bc81fc9b8a88c310937b2736759bc6674f

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