Interpreting the Presence of an Additional Oxide Layer in Analysis of Metal Oxides–Metal Interfaces in Atom Probe Tomography

Mukesh Bachhav,* Gorakh Pawar, François Vurpillot, Rémi Raphaëlle Danoix, Frédéric Danoix, Beatrice Hannoyer, Yan Dong, and Emmanuelle Marquis

†Idaho National Laboratory, Idaho Falls, Idaho 83415, United States
‡Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States
§Normandie Univ, UNIROUEN, INSA Rouen, CNRS, GPM, 76000 Rouen, France

ABSTRACT: Atom Probe Tomography (APT) analysis of specimens embedded with metal oxide/metal leads to nonintuitive observations of a very thin layer of oxide at the interface due to oxygen migration under the influence of electric field in metal oxides. Detailed analyses of the FeO/Fe and ZrO2/ZrO interfaces are presented, explaining observation of the interfacial oxide layer with APT. These findings are relevant to the observation made for APT analysis of devices such as resistive switching, solar cells, oxides grown on metal/ alloy during oxidation and corrosion wherein metal oxide is in interface with metallic layers. Because the APT technique is based on the application of an electric field on the oxide/metal interface, oxygen ions are driven toward the metal electrode and leads to a reaction with the metal and the formation of the additional interfacial oxide layer. Atomistic simulation performed on the FeO/Fe layer subjected to electric field confirms finding of oxygen migration from the oxide layer toward the oxide/metal interface.

1. INTRODUCTION

In the field of material characterization, the Atom Probe Tomography (APT) technique is routinely employed for elucidating chemistry and the three dimensional distribution of elements at nanometer length scale from small volumes of materials.1–4 This is achieved by controllably removing atoms from the surface of a needle-shaped specimen using electrical fields of the order of 10’s V/nm. Depending on the material, evaporation may be triggered by the voltage or laser pulses from the specimen. Time-of-flight measurements provide the chemical identity of the evaporated atoms while a position sensitive detector is used to calculate the coordinates of the atom information that is then used to reconstruct the data into 3D volumes.

The magnitude of the electric field established on the apex of the APT specimens is comparable to that used in other techniques or devices that include field emitters,5 atomic force microscopy,6 and resistive switching.7–9 It is important to remember that APT data provide a direct or indirect access to physical phenomena taking place on the very small surface of the specimen that is subjected to pulsed electric field or to laser pulses. Thus, beyond the nanoscale spatial and chemical information provided in 3D by APT data, the technique also provides a mean to understand the underlying physics of small volumes of materials subjected to high electric fields and laser pulses.10–15

Numerous examples of APT analyses of oxide/metal interfaces can be found in the literature, examples of devices with Fe/MgO/Fe multilayers16–18 or Co-doped ZnO,19 oxidation studies with RhO2 formation from a Pt–Rh alloy,20,21 or oxide dispersion-strengthened (ODS) steels,22,23 oxides grown in a Ni-supper alloy,24 or switching behavior in a TiO2/NbO2/Ta structure.25 The challenges in reconstruction of interfacial regions in APT due to trajectory aberrations due to local magnification are well documented.15,26–30 However, one might wonder about the chemistry of the oxide/metal interfaces in these selected examples and how the measurements might modify the structures.

A significant hint can be taken from dielectric metal oxides used for resistive switching applications that are subjected to electric fields, analogous to those used to trigger field evaporation during APT analyses. In resistive switching devices (usually composed of a dielectric layer sandwiched between two metal contacts), the resistance of the dielectric layer suddenly changes under the application of a strong electric field.7–9 Although the mechanism responsible for the switching behavior is still debated, the interfacial chemistry of the dielectric layer and metal contact is the key to understand the...
underlying mechanisms controlling the behavior of the devices. Recent experimental observations on resistive switching devices with Pt in contact with HfO2 found PtO formed at the interface of Pt−HfO2 under the influence of the applied field.31,32 Despite Pt being highly resistant to oxidation under normal conditions for processing these devices, it underwent a reaction with oxygen ions because of the presence of an electric field inside the dielectric layer.

In APT, the field-induced interfacial reactions might take place during analyses of the oxide/metal interface and in this article, two different metal/oxide interfaces (Fe/FeO and ZrO/ZrO2) were analyzed to elucidate interfacial reactions.

2. MATERIALS AND EXPERIMENTS

A 99.5% pure Fe specimen was prepared by electrochemical polishing using a solution of perchloric acid and 2-butoxyethanol electrolyte. The specimen with its native oxide (as shown in Figure 1a) was analyzed using a laser-assisted wide angle tomographic atom probe (LAWATAP).33 Then, the needle-shaped specimen was oxidized in 10⁻⁴ to 10⁻⁵ Torr of O₂ at 500 °C for 1 h and analyzed using a laser-assisted tomographic atom probe (LATAP).34 For both samples, field evaporation was conducted using a laser with a wavelength of λ = 515 nm, a laser pulse energy of 20 nJ/pulse while the specimen was held at a temperature of 80 K. The applied dc voltage was adjusted to maintain a constant detection rate of 0.005 atoms/pulse. Data processing was done with the data treatment software developed in the GPM laboratory, University of Rouen.

The analysis of the Zr-oxide/Zr interface was obtained from the Zr alloy that had been corroded in water for 60 days at 360 °C. APT specimens were prepared using a standard focused ion beam lift-out procedure.35 Samples were analyzed with CAMECA LEAP 4000XHR operated in a laser pulsing mode with 200 kHz pulse repetition rate and 70 pJ laser energy. The temperature of the specimens was maintained at 50 K while the standing voltage was varied automatically to maintain a detection rate of 0.005 ion/pulse. The collected data was reconstructed and analyzed using the reconstruction software, IVAS 3.6.8.

The native oxide formed at the apex of the Fe needle consisted of a 5−6 nm thick iron oxide layer as observed by Transmission Electron Microscopy (TEM) (Figure 1a) and was identified as the wüstite phase from the composition measured by APT. The scanning TEM and fast Fourier transform (FFT) results of the tip are shown in Figure S1. The Fe signal came from Fe⁷⁺, FeO⁷⁺, and FeO²⁺ while the contribution to the O concentration came from the evaporated...
O$_2^{−}$, O$, FeO^{1+}$, and FeO$_2^{2+}$ ions. Surprisingly, FeO$_2^{2+}$ ions that were not present in the oxide scale appeared at the interface between the metal substrate and the metal oxide scale as illustrated from a slice of the projected desorption map in Figure 1b,c and from the 1D profile taken across the interface shown in Figure 1d. The thermally grown oxide was thicker (Figure 2a) than the native oxide but in both cases, the contribution to the Fe and O concentration came from same molecular species as mentioned before. A concentration profile for Fe, O, and FeO$_3^{+}$ taken across the bottom interface of the thermally grown oxide is shown in Figure 2b and confirms the uniform O concentration inside the oxide region, as well as a very small O concentration in Fe (0.5 at. %). However, the interfacial region exhibits a different Fe/O ratio and appears to be correlated with the evaporation of FeO$_{2+}$ ions.

An interfacial layer was also observed when field evaporating ZrO$_2$ in contact with sub stoichiometric ZrO (denoted as ZrO$_{1−x}$). In the ZrO$_2$ oxide phase, oxygen was primarily evaporated as O$_2^{−}$, ZrO$_{2+}$, and ZrO$_{2,3+}$. O$_2^{−}$ was only observed in the ZrO$_2$ phase, so it is considered as a marker for that phase. In the ZrO$_{1−x}$ phase, the O signal mainly came from ZrO$_{2,3+}$ and ZrO$_{2,5+}$. For APT needles with ZrO$_2$ above ZrO$_{1−x}$ a super stoichiometric layer (ZrO$_{1−x}$) was observed at the ZrO$_2$/ZrO$_{1−x}$ interface region. The ZrO$_{1−x}$ layer was associated with the evaporation of ZrO$_{1,2+}$ ions and a higher level of ZrO$_{2,5+}$ ions (shown in Figure 3a–c). In the upside down scenario where ZrO$_{1−x}$ evaporates first, the ZrO$_{1−x}$ layer was not observed (Figure 3d–f).

This behavior, whereby an oxide-like interfacial layer is observed when the field evaporating an oxide phase in contact with a metallic phase, is not an isolated case and is certainly not limited to native or thermally grown oxides. These layers are systematically observed in APT data when the oxide is evaporated first. Yet, they are not always reported and whether they should be interpreted as the true structure of a material or an analysis artefact remains an open question. Such APT observations include the presence of Fe$_2$O$_{2+}$ ions at the interface of Fe–Y$_2$O$_3$ in an ODS alloy,$_{19}$ Co$_2$O$_{2+}$ ions at the ZnO–Co interface in Co-doped ZnO,$_{19}$ FeO$^+$, and Fe$_2$O$_{2+}$ ions at the MgO/Fe–Co interface,$_{16,17}$ or a PtO$^+$ layer at the interface between RhO$_2$ and Pt.$_{20,21}$ The latter directly supports the abovementioned observations of migration of oxygen at the metal electrode–metal oxide interface in several resistive switching devices.$^{31,38−45}$

3. DISCUSSION

The presence of an additional oxide layer at an oxide/metal interface may be explained by two mechanisms. The simplest case is an intermediate oxide layer that is formed by solid-state reaction before analysis. The second possibility is an oxide layer that originates from the application of a high electric field on a thin oxide layer and its interactions with the underlying metal during APT analysis. Application of electric field to an oxide layer can drive oxygen either through a bulk diffusion mechanism or through a surface mechanism wherein O could possibly diffuse along the shank of the needle-shaped specimen. However, in the case of resistive switching behavior observed in the HfO$_2$ film, it was shown that the O ions migrated because of the electric field inside the dielectric HfO$_2$ layer and reacted with the bottom Pt electrode to form PtO$_{2,5+}$. Similar migration of O ions under the influence of electric field has been reported for a wide range of metal-oxide systems.$^{9,31,32,38,43,44}$ In the case of APT, possibility of surface diffusion of O ions toward the apex of the tip during analysis could not be ruled out.$^{46}$ Indeed, it has been reported that certain ions move along the apex of the tip because of inhomogeneous distribution of electric field. Blavette and Duguay reported migration of boron in the doped Si sample at the apex of the tip using both Field Ion Microscopy (FIM) and APT.$^{37}$ Other such examples on migration of ions during APT analysis include H,$^{48}$ N, and C.$^{49}$ To the best of our knowledge, such migration along the apex of the tip has not been reported for O ions using APT or FIM in the open literature. In this report, we focus on migration of O ions originating from the metal oxide film toward the metal interface under the influence of electric field.

In the case of a sandwich structure of MgO between two Fe–Co magnetic layers, it was shown that the additional layer is a
result of an evaporation artefact.\textsuperscript{17} TEM did not show presence of any kind of metal oxide phase at the interface and the apparent oxide layer disappeared when the analysis was performed so that the metal alloy would evaporate before the oxide phase. Thus, it was shown that the additional oxide appeared when analysis was performed from metal oxide to metal and not when analysis if performed from metal to metal oxide. This is a similar case to the ZrO\textsubscript{2}/ZrO\textsubscript{1+x} case (Figure 3) where the artificial ZrO\textsubscript{1+x} layer was observed when the analysis was performed so that ZrO\textsubscript{2} would evaporate before the metallic region of ZrO\textsubscript{1+x}. However, it is not always possible to determine whether this layer exists or is the result of an artefact.

The molecular dynamics (MD) simulation technique was used to investigate the possible oxygen-ion migration process from the FeO phase toward the FeO/Fe interphase under the influence of electric field. A general bond order-dependent reactive force field (ReaxFF)\textsuperscript{50} was used to simulate atomic interactions where the ReaxFF allowed the breaking of the existing and the formation of new chemical bonds during the simulation. Different energies contributed to the total energy including bond order-dependent (e.g., bond energy and valence energy) and bond order independent (electrostatic interactions and Van der Waals interactions) energy terms. A detailed description of the individual energy contributions to the total energy can be found elsewhere.\textsuperscript{50} The FeO/Fe ReaxFF parameters used in the present investigation were taken from the literature.\textsuperscript{51}

The initial Fe systems comprised of 3000 Fe atoms and the FeO system containing 4000 atoms. A systematic simulated annealing method was used to construct the optimized atomistic FeO and Fe phases that were consequently used to construct the FeO/Fe interphase as shown in Figure 4a on the left. The simulated annealing method included the following stages: initial energy minimization with steepest descent algorithm with a force tolerance of 10\textsuperscript{-6} kcal/mol Å → heating in canonical (NVT) ensemble at 2000 K for 0.2 ns → quenching from 2000 to 50 K with a quenching rate of 5 K/ps. The simulated annealing method ensured that the atoms in the system are fully relaxed and the system is not trapped at any local energy minima. Newton’s equations of motion were used to evaluate the temporal evolution of atomic positions and atomic velocities, which were subsequently used to understand the oxygen-ion migration process in FeO. The LAMMPS\textsuperscript{52} MD simulation package was used to perform all simulations, whereas the OVITO package\textsuperscript{53} was used to visualize the time-dependent atomic trajectory information. The periodic boundary conditions were used in x and y directions, whereas nonperiodic boundary conditions were used in the z-direction to mimic the realistic APT experimental conditions. The Nose–Hoover thermostat was used to maintain the system temperature during all stages with a damping constant of 100 fs. Further, a time step of 0.5 fs was used throughout the simulations.

The equilibrated Fe and FeO phases were used to construct the Fe/FeO system (shown in Figure 4a on the right) that comprised a total of 7000 atoms. The energy minimization of the newly constructed Fe/FeO system was performed with steepest descent algorithm with a force tolerance of 10\textsuperscript{-6} kcal/mol Å followed by the final equilibration simulation at 50 K for 1 ns. Forty oxygen atoms were manually removed from the FeO phase to create ∼1\% vacancies or the point defects in the FeO phase. The modified Fe/FeO system subsequently subjected to a uniform electric field of $5 \times 10^9$ V/m and time-dependent atomic trajectory information was obtained. The values for diffusion barrier for O migration subjected to high electric field in the FeO layer were derived from recent work of Sankaranarayanan et al. for the ZrO system.\textsuperscript{54} Figure 4b shows the temporal evolution of the Fe/FeO system under the influence of the applied electric field. It can be observed that the oxygen atoms in FeO show diffusion from the FeO phase toward the Fe/FeO interphase that validates the observations from APT-based experimental investigation. The atomistic simulation model further enhances understanding of electromigration of oxygen ions in the metal-oxide layer as observed in APT findings and resistive switching devices. It must be noted that the current MD simulation model does not take into account other kind of electronic conduction that would inhibit the interface field developed inside the dielectric layer because of direct tunneling and surface conduction.\textsuperscript{55} Such effects are most likely playing a crucial role in field evaporation behavior of metal oxides in APT; however, the mechanism of field evaporation for oxides is outside the scope of current work.

Going back to the APT technique, an analog can be applied wherein the electric field inside the dielectric layer (metal oxide) drives the oxygen ions toward the metal enabling the interfacial reaction with the bottom metal electrode. Typical values for the electric field applied on a needle-shaped specimen are of the order of few tens of $10^9$ V/m. However,
determination of the electric field inside the metal oxide layer in APT can be complex due to geometry of the specimen and band bending in the oxide layer. With a dielectric constant of iron oxide of 5–14 for film thicknesses between 5 and 10 nm, the electric field inside the layer is estimated to be of the order of $10^9$ V/m ($E_{\text{inside}} = E_{\text{external}}/k$). The setup of APT does not provide direct access to measure the internal temperature. Hence for simplicity, the temperature rise during laser pulsing which is typically around 250 K for the metal oxides. Note that there is no data value is derived from ref 54 for the Zr-oxide system. Using abovementioned values, the diffusion distance for oxygen ions ($x$) for $t_p = 0.2$ s is calculated (using $x = \sqrt{D_{O^2} t_p}$) to be approximately 50 nm while the oxide thicknesses analyzed are 5–10 nm. Thus, it is conceivable that oxygen migrates through the oxide during the APT analysis to react with the bottom interface. This hypothesis of electromigration of oxygen ions in the metal-oxide layer agrees with the mechanism suggested for resistive switching devices showing migration of oxygen ions during analysis in APT. To support the experimental findings, an atomistic simulation was performed on the FeO/Fe interface with oxygen vacancies added to the FeO layer subjected to high electric field. The presence of oxide layer in APT results is attributed to the movement of oxygen ions because of application of an electric field inside the dielectric layer (FeO in this case). This has important consequences for the proper interpretation of APT data, that is, whether the additional layer is originally present or induced by the analysis process or technological applications as in the case of resistive switching devices, protective layers in oxidation/corrosion, solar cells, and complementary metal-oxide semiconductors.

4. CONCLUSIONS

In summary, we have shown and discussed the formation of an additional oxide layer at the metal/oxide interface during analysis in APT. To support the experimental findings, an atomistic simulation was performed on the FeO/Fe interface with oxygen vacancies added to the FeO layer subjected to high electric field. The presence of oxide layer in APT results is attributed to the movement of oxygen ions because of application of an electric field inside the dielectric layer (FeO in this case). This has important consequences for the proper interpretation of APT data, that is, whether the additional layer is originally present or induced by the analysis process or technological applications as in the case of resistive switching devices, protective layers in oxidation/corrosion, solar cells, and complementary metal-oxide semiconductors.

Figure 5. Schematic of the tip in the Atom Probe setup analogous to resistive switching devices showing migration of oxygen ions during analysis of metal oxide sandwiched between metal layers.
(16) Larson, D. J.; Marquis, E. A.; Rice, P. M.; Prosa, T. J.; Geiser, B. P.; Yang, S.-H.; Parkin, S. S. P. Manganese diffusion in annealed magnetic tunnel junctions with MgO tunnel barriers. Scr. Mater. 2011, 64, 673–676.


(52) Plimpton, S.; Crozier, P.; Thompson, A. LAMMPS-Large-Scale Atomic/Molecular Massively Parallel Simulator; Sandia National Laboratories, 2007; Vol. 18, p 43.


