

## In-situ Atomic-Resolution Observations of Surface Passivation Induced Metal/Oxide Interfacial Transformation

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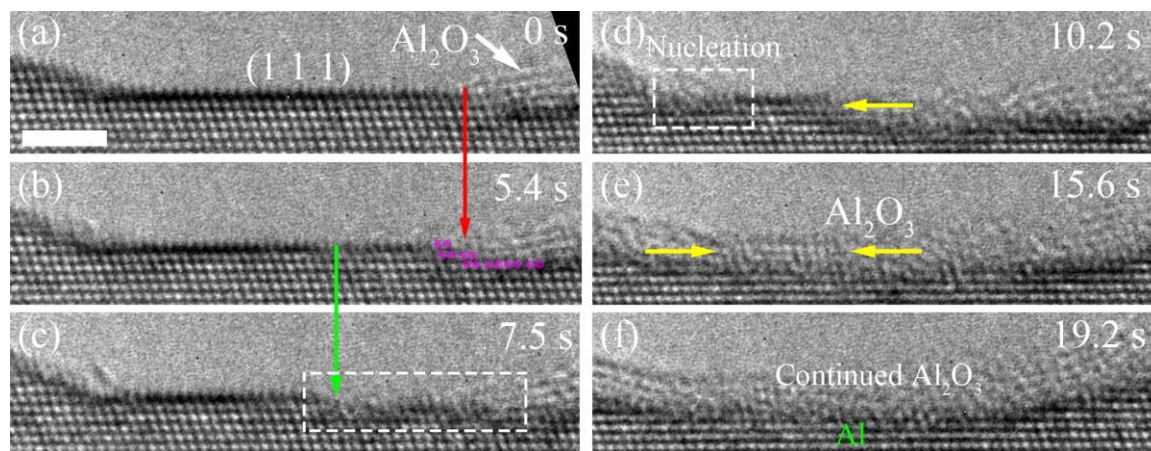
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The metal/oxide interface is a crucial zone for many technologically important processes including corrosion, catalysis and thin film growth. A better knowledge of the nature and characteristics of the metal/oxide interface is needed not only for developing fundamental understanding of these processes but also for the design of new material systems by utilizing the synergistic effect at the metal/oxide interface. Many detailed cross-sectional transmission electron microscopy (TEM) experiments have been performed across metal/oxide interfaces, demonstrating the versatility and atomic precision of the microscopic methods in elucidating interfacial structure and chemistry [1, 2]. However, these were performed predominantly on static interfaces without providing direct insight into the dynamic nature of the interfacial transformation. This is particularly challenging to study the surface passivation induced metal/oxide interfacial transformation because of the ultrathin thickness (~ a few nanometers) of the amorphous passivating oxide film, for which the TEM study requires complex sample preparation and suffers from the possibility of introducing artifacts and contamination to the interface region.

Environmental TEM offers unique opportunities to study the metal/oxide interface transformation by flowing oxygen gas in the sample region while simultaneously monitoring the dynamic evolution of the atomic structure at the metal/oxide interface and in the subsurface region. Here we choose the surface passivation reaction of aluminum (Al) as a model system to study the oxide/metal (i.e., Al<sub>2</sub>O<sub>3</sub>/Al) transformation because of the wide uses of Al for applications where surface passivation is required. Our experiments were performed in a dedicated field-emission environmental TEM (FEI Titan 80-300) equipped with an objective-lens spherical aberration corrector. Our in-situ TEM experiment involves a two-step process. First, the thin Al specimen cut from an aluminum single crystal is illuminated with condensed electron beam in the TEM column, which results in holes inside the Al film. The edges along these freshly created holes are oxide-free and ideal for in-situ TEM observations of the oxide/metal interface transformation by introducing oxygen gas into the specimen area at room temperature.

Figure 1 illustrates a time sequence of high-resolution TEM images of the Al(111) surface, in a cross-sectional view along [1-10] direction. The surface is initially atomically flat in the terrace region (Fig. 1(a)) before oxidation. Upon the flow of O<sub>2</sub> gas, oxide starts to form preferentially at the location where the pre-existing oxide intersects with the clean (111) terrace (Fig. 1(b)). This results in a small Al<sub>2</sub>O<sub>3</sub>/Al interface, as indicated by the red, green, and yellow arrows in Fig. 1(b-d)), respectively. The aluminium oxide layer is observed to propagate laterally toward the corner on the left through the flow of the atomic steps at the Al<sub>2</sub>O<sub>3</sub>/Al interface, as marked by the purple circles in Fig. 1(b). This lateral propagation of the atomic steps at the oxide film indicates that the metal/oxide interfacial steps are the preferred locations for oxygen uptake and incorporation. As indicated by the yellow arrow in Fig. 1(e), aluminium oxide also forms at the corner on the left and propagates laterally toward to right. The merging of the oxide films propagating toward each other leads to the complete coverage of the oxide over the (111) terrace. The in-situ TEM observations also show that the oxide films maintain a limiting thickness of ~ 1 nm during the

lateral growth, confirming the passivating effect of the oxide film on effectively slowing down the diffusion of Al and O atoms across the oxide layer [3].



**Figure 1.** (a-f) In situ TEM images illustrating the growth of a continuous amorphous oxide film on an Al (111) surface, via the interfacial diffusion channels, induced by metal/oxide interfacial strain, at room temperature and  $pO_2 = 7 \times 10^{-5}$  Torr. The red and green arrows show the lateral promotion sites of the oxide/metal interface, as the reaction proceeds. (d-f) Time-sequenced HRTEM images displaying the initial nucleation occurs at the bunch of atomic steps, resulting in the accelerated lateral growth of oxide on the surface from the upper-left side. Scale bar, 2 nm (a).

#### References

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[3] This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0001135. This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.