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In-situ Atomic-scale Observations of Disconnection Dynamics at the Metal/Oxide Interfaces

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The terrace-ledge-kink model by Burton, Cabrera and Frank [1] is widely used to interpret crystal growth at surfaces. Over the last few decades, this concept has also been applied to solid-solid transformations, where the interfacial steps are synonymous with ledges in the fields of surface sciences and crystal growth and are called the disconnection, a line defect with both dislocation and step character [2, 3]. Obtaining fundamental information on disconnections is essential for understanding the transformation mechanisms and kinetics because the interfacial transformation relies on the lateral motion of disconnections to progressively convert atoms from the parent phase to the product phase. However, directly probing disconnection dynamics has proven extremely difficult, mainly because of the experimental inaccessibility of the buried interface. Generally, transmission electron microscopy (TEM) offers the opportunity to study static interfaces, but fundamental understanding of the disconnection dynamics not only requires resolving the local structure at the atomic scale, but also the ability to capture the fast dynamics of the structural evolution in real time during the phase transformation. Environmental TEM offers a unique window to understand the interfacial phenomena by introducing a reactive gas to the samples to drive the interfacial transformation while simultaneously monitoring the structure evolution at the atomic scale [4, 5].

In this work, we employ environmental TEM to observe the disconnection dynamics during the oxidation of copper. Cu(100) single-crystal thin films with a nominal thickness of ~ 50 nm were used for the in-situ TEM experiments. The Cu films were first annealed at ~ 450°C in H_2 gas flow to remove native oxide and generate faceted holes. These Cu facets are oxide free and ideal for in-situ TEM observations of the oxidation. Fig. 1 depicts in-situ HRTEM images of a Cu(100) surface, seen edge-on under the oxidation conditions of $pO_2=10^{-5}$ Torr and T=450°C. As seen in Fig. 1(a), a two-atomic-layer-thick oxide layer develops on the surface from the oxidation before the in-situ TEM movie was capture, where the lattice spacing matches the interplanar spacing of $Cu_2O(200)$. Cu steps are present at the Cu_2O/Cu interface, as indicated by red "T_1"in Fig. 1(a). Due to their different lattice spacings, the $Cu_2O(200)$ plane is slightly higher than the interfacial height of the monoatomic step of Cu(200), thereby resulting in a disconnection at the Cu step and giving rise to the slight lattice distortion across the stepped region. Fig.1(b) shows the formation of another disconnection (marked as red "T_2") as a two-atomic-layer thick oxide layer develops on the surface terrace in the left region. As shown in Fig. 1(c and d), the lateral distance between T_1 and T_2 increases from ~ 2.6 nm to ~3.4 nm and then to ~4.1 nm, mainly via the retraction motion of T_1 toward the bottom-right corner direction. By contrast, the position for T_2 remains relatively unchanged over the period of the observation. This difference can be attributed to the dynamic evolution of the oxide layer above the two disconnections. That is, the oxide overlayer in the T_2 region is relatively stable and maintains the two atomic layer thickness whereas the double-atomic thick oxide overlayer in the T_1 region transforms into the single atomic layer thickness via the decomposition of its topmost atomic layer. The in situ TEM visualization demonstrates the dependence of the lateral motion of the disconnections at the oxide/metal interface on the thickness of the oxide overlayer. Atomic modelling will be performed to correlate the in-situ HRTEM imaging and elucidate the disconnection activity, mainly focusing on the effects of the oxide thickness on the stability and mass transport mechanism of the interfacial disconnections [6].

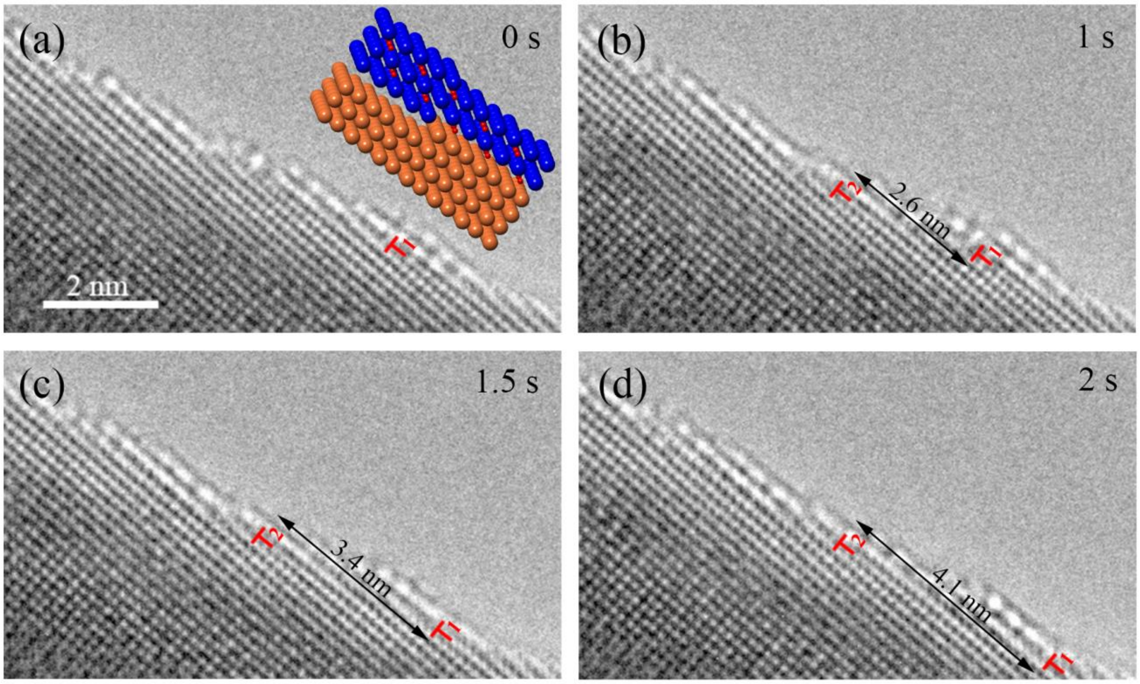

Figure 1. In-situ HRTEM imaging of the surface oxidation of Cu(100) at 450 °C and $pO_2 = 10^{-5}$ Torr. T_1 and T_2 correspond to disconnections at the buried Cu_2O/Cu interface due to the presence of monoatomic steps of Cu. Insets show schematically the atomic configuration of the disconnections and their dependence on the thickness of the oxide overlayer.

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