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TEM investigation of interfaces during Cu_2O island growth

Guangwen Zhou
Department of Mechanical Engineering & Multidisciplinary Program in Materials Science and Engineering, State University of New York, Binghamton, NY 13902

The oxidation of metals results in formation of various interfaces including grain boundaries in the oxide scale and the metal-oxide interface. These interfaces play a critical role in the oxide growth and can have a dramatic effect on the properties of the oxide film. For example, the passivation behavior of metals is strongly influenced by the microstructures of the oxides that form. A large number of interfaces formed in the oxide film often leads to poor oxidation-resistance because the diffusion of cations/anions along these interfaces is likely much faster than through a perfectly coalesced oxide film. On the other hand, point defects supporting diffusion during oxide growth are generated or annihilated at the metal-oxide interfaces and the processes governing ionization and incorporation of metal atoms into the oxide phase are closely dependent on the interface structure. There have been a few experimental studies concerning the effect of the structure of metal-oxide interfaces on the oxide scale growth [1, 2]. However, the study on the microstructure and shape evolution of interfaces during early stages of oxidation of metals is still very limited.

Copper is an important metal with wide industrial applications. The oxidation of copper has been proving to be a rich source of information to understand the corrosion of metals [3-7]. In this work, we report a detailed transmission electron microscopy (TEM) study of the interface geometry, configuration and epitaxial relationships for the growth of oxide nanoislands during the early-stage oxidation of Cu(100) thin films. Two types of interfaces, i.e., metal-oxide interfaces associated with the growth of individual Cu_2O islands and grain boundaries formed from coalescence of oxide islands, are examined. Our experimental system is single crystal, 70-nm-thickness Cu(001) films grown epitaxially on freshly cleaved NaCl(001) substrates by sputter deposition at ~ 250°C. The Cu films were removed from the substrate by flotation in deionized water, washed, and mounted on a TEM Cu grid. The Cu films were first annealed at 700°C in Ar-2%H_2 for 2 hours to remove the native oxide. The Cu films were oxidized at 700°C in oxygen partial pressure of 5×10^{-5} Torr for 5 min. TEM observations using a JEOL 2100F electron microscope was made immediately after removal from the oxidation chamber. TEM techniques including electron diffraction, high-resolution TEM, and electron moiré fringe imaging were utilized to determine the orientation relationships between oxide islands and the Cu substrate and between coalesced Cu_2O islands. TEM thickness fringe contrast was employed to analyze the geometry of interfaces associated with the growth of individual oxide islands. The predominant orientation relationship between Cu_2O islands and the Cu substrate is found to be cube-on-cube growth ($[001]_{Cu_2O} \| [001]_{Cu}$), whereby equivalent planes and directions of oxide islands and the metal substrate are matched across the interface, while other epitaxies including $[\bar{1}12]_{Cu_2O} \| [001]_{Cu}$ and $[\bar{1}\,\bar{1}2]_{Cu_2O} \| [001]_{Cu}$ are occasionally observed. A 6 × 7 coincidence site lattice configuration is observed at the Cu-Cu_2O interface for the cube-on-cube epitaxy and misfit dislocations are formed at the interface to release the coincidence misfit strain. The geometry of Cu_2O-Cu interfaces is found to depend on the specific epitaxial orientations of Cu_2O islands with the Cu substrate: wedge-shaped interfaces are developed for cube-on-cube epitaxial growth and edge-on interfaces are formed for non cube-on-cube epitaxy. Coherent boundaries are formed from the coalescence of Cu_2O islands having different epitaxial orientations

with the Cu substrate. Since oxide islanding during oxidation has been observed for many metals, including Fe, Pd, Ni, Co, Ti, Pb, and Sn, as well as Cu, we expect that our results obtained from the oxidation of Cu may have broader impact for manipulating metal oxidation to affect the reaction product morphology and perhaps the oxidation kinetics.

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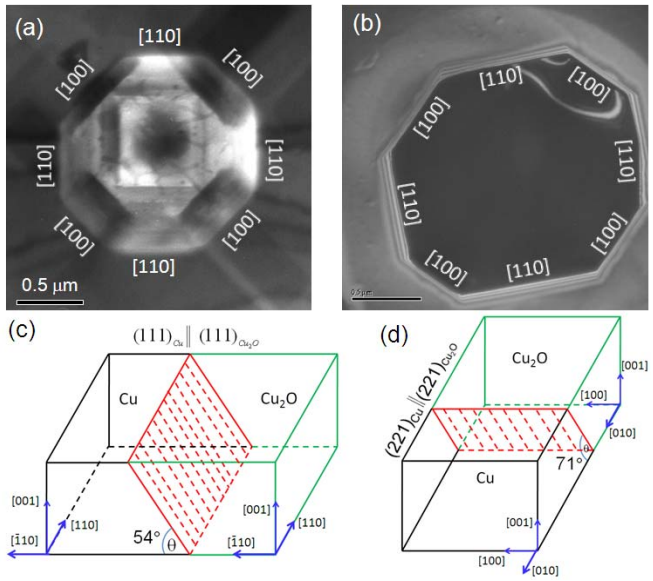

Fig. 1: BF-TEM image of a Cu_2O island on Cu(100), the island has a truncated pyramid shape; (b) DF-TEM image of a truncated pyramid using Cu(220) reflection; (c) 3D schematic representations of the determined wedge-shaped interfaces along [110] edge: $(111)_{Cu_2O} \| (111)_{Cu}$ and along [100] edge: $(221)_{Cu_2O} \| (221)_{Cu}$.

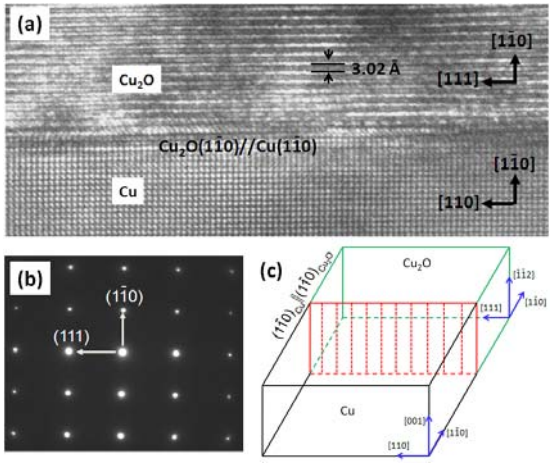

Fig. 2: (a) HRTEM image showing an edge-on Cu_2O-Cu interface. The shared planes at the Cu_2O-Cu interface are $(1\bar{1}0)_{Cu_2O} \| (1\bar{1}0)_{Cu}$. (b) SAD pattern from the Cu_2O region in (a), the epitaxial orientation of the Cu_2O with respect to the Cu substrate is $[\bar{1}\,\bar{1}\,2]_{Cu_2O} \| [001]_{Cu}$; (c) A schematic 3D representation of the shape of this edge-on interface.

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