ECSTM Study of the Anodic Duplex Oxide Layers Formed on Cu(111) and Cu(001) in 0.1 M NaOH

Julia Kunze [a], Vincent Maurice[b], Lorena H. Klein[b],
Hans-Henning Strehblow[a] and Philippe Marcus[b]

[a] Institut für Physikalische Chemie und Elektrochemie,
Heinrich-Heine-Univeristät, Universitätsstr. 1,

D-40225 Düsseldorf, Germany
[b] Laboratoire de Physico-Chimie des Surfaces,
CNRS/ENSCP (UMR 7045), 11 rue Pierre et Marie
Curie, F-75231 Paris Cedex 05, France

In situ Electrochemical Scanning Tunneling Microscopy (ECSTM) measurements of the surface structure of the anodic Cu(I) / Cu(II) duplex passive layers grown on Cu(111) and Cu(001) in 0.1 M NaOH are reported.

The ECSTM results obtained in the potential range of $+0.71 \text{ V} < E \leq +0.89$ V/SHE evidence the crystalline structure of the duplex passive films, consisting of a Cu(I) inner layer and a Cu(II) outer layer[1]. On both substrates, a terrace and step topography of the passivated surfaces has been observed with terraces extending up to 20 nm in width and with a step height of ~0.25 nm corresponding to the thickness of one equivalent monolayer of CuO(001). Accordingly, the atomic lattices observed are consistent with a bulk-terminated CuO(001) surface which is characterized by a distorted hexagonal symmetry with an in-plane nearest neighbor distances of ~0.28 nm along the closed packed directions.

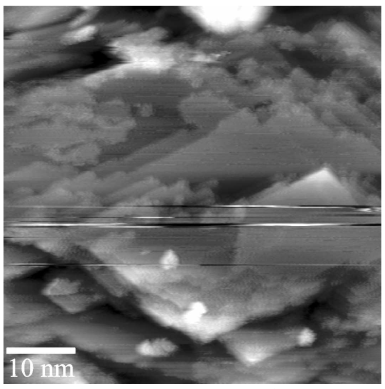
The common (001) orientation of the CuO outer layers of the duplex films on the two substrates is assigned to their surface hydroxylation at the passive film / electrolyte interface, necessary to stabilize the bulk-like termination of CuO(001) which is polar and unstable when anhydrous. This assignment is supported by the step height measurements which indicate an identical chemical termination of all terraces. It is proposed that the surface is terminated by an OH^- (or OH) layer in (1x1) registry on the topmost plane of the Cu^{2+} sub-lattice, then O^{2-} and Cu^{2+} planes alternate towards the bulk of the oxide layer.

The orientation of the CuO(001) lattices with respect to the Cu(111) and Cu(001) substrates allows to determine the epitaxial relationships between the Cu(II) outer layers and Cu(I) inner layers of the passive films based on previous measurements[2,3] of the epitaxy between the Cu(I) layers and the Cu substrates. The resulting relationships are:

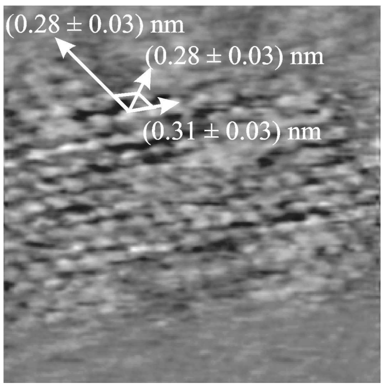
CuO(001) $[\bar{1}10]$ // Cu_2O(111) $[\bar{1}10]$ // Cu(111) $[1\bar{1}0]$
and
CuO(001) $[\bar{1}10]$ // Cu_2O(001) $[1\bar{1}0]$ // Cu(001) [100].

They correspond in both cases to the parallel alignment of the closed packed directions of CuO and Cu_2O lattices.

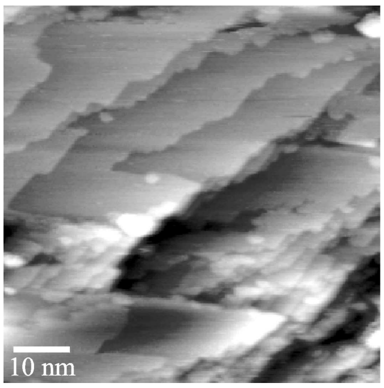
On Cu(001), a granular surface morphology has also been observed. By varying the tunneling bias and setpoint current conditions, the sample-to-tip distance could be varied to show that this morphology corresponds to a surface layer of corrosion products, presumably formed by a dissolution-precipitation mechanism and assigned to copper hydroxide species, covering the crystalline outer CuO(001) layer of the duplex passive film. This result shows the stratification of the Cu(II) oxide and hydroxide species in the outer part of the passive film which was previously described as a mixed CuO,$Cu(OH)_2$ layer. The absence of an outer granular amorphous structure of copper hydroxide species on Cu(111) is explained by the higher stability of the hexagonal densely packed Cu(111) substrate surface and the inner Cu_2O(111) oxide layer.



Crystalline surface topography of the duplex passive film grown on Cu(111) at +0.75 V/SHE; scan size = 55 nm, z range = 6 nm.



Atomic surface lattice of the duplex film on Cu(111); scan size = 4.6 nm, z range = 0.4 nm.



Crystalline duplex passive layer grown on Cu(001) at +0.77 V/SHE; scan size = 67 nm, z range = 10 nm.

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[1] H.-H. Strehblow, B. Titze, *Electrochim. Acta*, **25**, (1980), 839

[2] J. Kunze, V. Maurice, L. H. Klein, H.-H. Strehblow, P. Marcus, *J. Phys. Chem. B*, **105,** (2001), 4263.

[3] J. Kunze, V. Maurice, L. H. Klein, H.-H. Strehblow, P. Marcus, submitted to the *J. Electroanal. Chem.*.