

# Thermodynamic modeling of the initial microstructural evolution of oxide films grown on bare copper



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Available online 1 August 2007

## Abstract

A thermodynamic model is presented that predicts the initial growth of either a (semi-) coherent crystalline oxide phase or an amorphous oxide phase (with a subsequent amorphous-to-crystalline transition) on a bare metal as function of the substrate orientation, growth temperature and film thickness. The model accounts for possible relaxation of growth stresses by plastic deformation. The direct formation and growth of semi-coherent, crystalline Cu<sub>2</sub>O is predicted by application of the model to oxide overgrowth on bare Cu{111}, Cu{100} and Cu{110}. For oxide overgrowths on Cu{111} and Cu{110}, a *square grid* of misfit dislocations with a dislocation distance of about six Cu<sub>2</sub>O unit cells would occur on the basis of the model calculations, which agrees with experimental observations reported for Cu{111} in the literature. On Cu{100} an *array* of misfit dislocations is formed along the single direction of high lattice mismatch.

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**Keywords:** Copper; Interfaces; Solid phase epitaxy; Cu<sub>2</sub>O; Oxide film growth; Microstructural evolution; Misfit dislocations; Thermodynamics

## 1. Introduction

The ability to control the properties of ultra-thin (<10 nm) oxide films grown on bare metal surfaces by tailoring their microstructure is of great interest in numerous application areas such as microelectronics and catalysis [1]. On the basis of thermodynamic model calculations accounting for the relaxation of growth strain by plastic deformation [2,3], the microstructural evolution of the initial Cu<sub>2</sub>O overgrowth on different crystallographic faces of the Cu substrate has been evaluated in this work as function of the growth conditions.

## 2. Summary of theoretical background

A homogeneous oxide film, MO<sub>x</sub>, on a single-crystalline metal substrate, ⟨M⟩, is considered. The oxide film can either be amorphous, {MO<sub>x</sub>}, with thickness  $h_{\{MO_x\}}$ , or crystalline, ⟨MO<sub>x</sub>⟩, with corresponding thickness  $h_{\langle MO_x \rangle}$ . The braces { } and the brackets ⟨ ⟩

refer to the amorphous state and the crystalline state, respectively. The composition of the amorphous and crystalline oxides is the same and both films contain the same molar quantity of oxygen in cells of volume  $h_{\{MO_x\}} \times l_{\{MO_x\}}^2$  and  $h_{\langle MO_x \rangle} \times l_{\langle MO_x \rangle}^2$ , respectively. The difference in total Gibbs energy between the amorphous and crystalline oxide overgrowths,  $\Delta G = G_{\{MO_x\}} - G_{\langle MO_x \rangle}$ , can be given as (per unit area of the ⟨M⟩–{MO<sub>x</sub>} interface; [2]):

$$\Delta G = h_{\{MO_x\}} \left( \frac{\Delta G_{\{MO_x\}}^f - \Delta G_{\langle MO_x \rangle}^f}{V_{\{MO_x\}}} \right) + \gamma_{\{MO_x\}-vac} + \gamma_{\langle M \rangle - \{MO_x\}} - \chi(\gamma_{\langle MO_x \rangle - vac} + \gamma_{\langle M \rangle - \langle MO_x \rangle}), \quad (1)$$

where  $\Delta G_{\{MO_x\}}^f$  and  $\Delta G_{\langle MO_x \rangle}^f$  are the Gibbs energies of formation per mole of the amorphous and the crystalline oxide;  $V_{\{MO_x\}}$  is the molar volume of the amorphous oxide;  $\gamma_{\{MO_x\}-vac}$  and  $\gamma_{\langle MO_x \rangle - vac}$  are the surface energies (per unit area) of the amorphous oxide and the crystalline oxide;  $\gamma_{\langle M \rangle - \{MO_x\}}$  and  $\gamma_{\langle M \rangle - \langle MO_x \rangle}$  are the interfacial energies (per unit area) of the interface between the metal substrate and the amorphous oxide and the metal substrate and the crystalline oxide, respectively. The ratio  $\chi$  corresponds to the surface area ratio of the unstrained amorphous cell and the (strained) crystalline cell (see Ref. [2]). If  $\Delta G < 0$ , the amorphous oxide is thermodynamically preferred (with respect to the corresponding crystalline oxide), and vice versa for  $\Delta G > 0$ .

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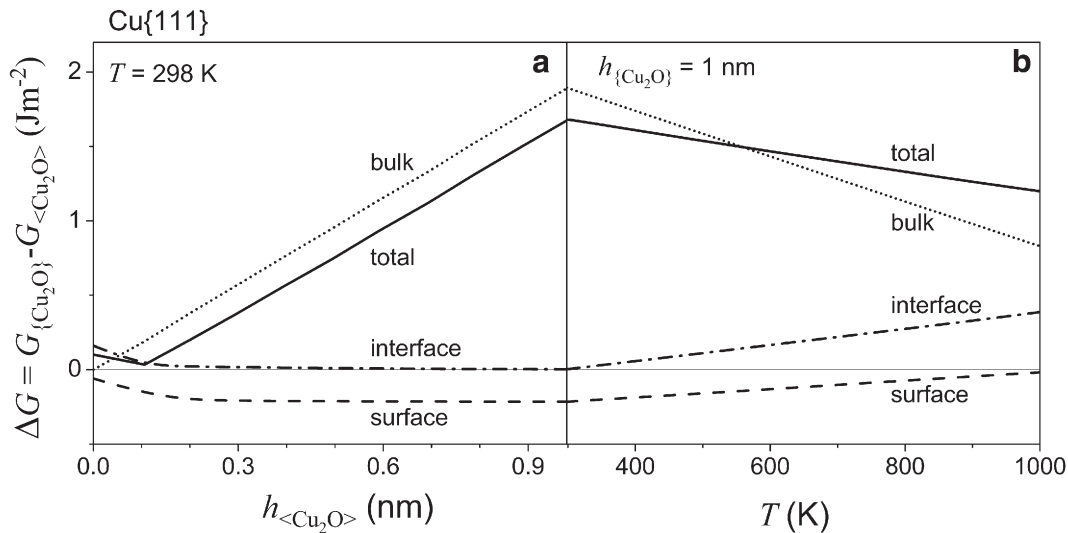


Fig. 1. Calculated difference in total Gibbs energy,  $\Delta G = G_{\{Cu_2O\}} - G_{\langle Cu_2O \rangle}$  (“total”), as well as the separate bulk, surface and interface energy contribution differences (Section 2), between the amorphous  $\{Cu_2O\}$  and crystalline  $\langle Cu_2O \rangle$  overgrowths on a Cu $\{111\}$  substrate as function of (a) the oxide-film thickness ( $h_{\langle Cu_2O \rangle}$ ) at  $T = 298$  K and (b) the growth temperature ( $T$ ) for  $h_{\{Cu_2O\}} = 1$  nm.

Approximate expressions for the solid–solid interfacial energies in Eq. (1) have been derived on the basis of the macroscopic atom approach [2–4]. To this end, the energy,  $\gamma_{\langle M \rangle - \{MO_x\}}$ , of the crystalline–amorphous interface,  $\langle M \rangle - \{MO_x\}$ , is expressed as the resultant of three additive energy contributions (for details, see Ref. [2]): (i) the negative interaction contribution ( $\gamma_{\langle M \rangle - \{MO_x\}}^{\text{interaction}}$ ) resulting from the chemical bonding between the amorphous oxide and the metal substrate across the interface, (ii) the positive entropy contribution ( $\gamma_{\langle M \rangle - \{MO_x\}}^{\text{entropy}}$ ) due to the ordering (i.e. the decrease of configurational entropy) of the amorphous oxide near the interface with the crystalline metal substrate, and (iii) the positive enthalpy contribution ( $\gamma_{\langle M \rangle - \{MO_x\}}^{\text{enthalpy}}$ ) arising from the relative increase in enthalpy of the metal substrate atoms at the interface (as compared to the bulk) due to the liquid-type of bonding with the amorphous oxide at the interface.

Similarly (see further Ref. [3]), the energy,  $\gamma_{\langle M \rangle - \langle MO_x \rangle}$ , of the coherent or semi-coherent crystalline–crystalline interface,  $\langle M \rangle - \langle MO_x \rangle$  is expressed as the resultant of the negative interaction contribution ( $\gamma_{\langle M \rangle - \langle MO_x \rangle}^{\text{interaction}}$ ) and two positive energy contributions originating from the initial lattice mismatch between the metal substrate and the crystalline oxide film: i.e. the strain contribution ( $\gamma_{\langle M \rangle - \langle MO_x \rangle}^{\text{strain}}$ ) due to residual homogeneous strain within the oxide overgrowth and the dislocation contribution ( $\gamma_{\langle M \rangle - \langle MO_x \rangle}^{\text{dislocation}}$ ) due to the periodic, inhomogeneous strain field associated with misfit dislocations at the oxide/metal interface. The dislocation energy contribution ( $\gamma_{\langle M \rangle - \langle MO_x \rangle}^{\text{dislocation}}$ ) equals the sum of the energies of two perpendicular, regularly spaced arrays of misfit dislocations with Burgers vectors parallel to two corresponding perpendicular directions within the oxide/metal interface plane and is calculated here using a first approximation approach of Frank and van der Merwe (for details, see Refs. [3,5]). The energy contributions due to the residual homogeneous strain and the misfit dislocations in the crystalline oxide film are attributed to the interface energy instead of to the bulk energy of the film [see Eq. (1)], and hence it follows that a minimum in the total Gibbs free energy of the crystalline cell (thermodynamic equilibrium) is attained if  $\gamma_{\langle M \rangle - \langle MO_x \rangle}$  is at its

minimum value [3] (the minimization of  $\gamma_{\langle M \rangle - \langle MO_x \rangle}$  can only be performed numerically).

### 3. Energetics of copper-oxide films on copper substrates

The thermodynamic model sketched in Section 2 has been applied to the case of a thin  $Cu_2O$  film of variable, uniform thickness (“overgrowth”) on the  $\{111\}$ ,  $\{100\}$  and  $\{110\}$  crystallographic faces of a single-crystalline (face centered cubic) Cu substrate,  $\langle Cu \rangle$ , for growth temperatures,  $T$ , in the range of 298 to 1000 K. The competing oxide overgrowths on the  $\langle Cu \rangle$  substrates are the amorphous  $\{Cu_2O\}$  and crystalline  $\langle Cu_2O \rangle$  (cuprite, primitive cubic crystal structure; e.g., Ref. [6]) modifications. The following orientation relationships between the  $\langle Cu \rangle$  overgrowth and the Cu $\{111\}$ , Cu $\{100\}$  and Cu $\{110\}$  faces have been adopted [7–9]:  $\{111\}_{Cu} \parallel \{111\}_{Cu_2O}$  with  $[1\bar{1}0]_{Cu} \parallel [1\bar{1}0]_{Cu_2O}$ ,  $\{100\}_{Cu} \parallel \{111\}_{Cu_2O}$  with  $[011]_{Cu} \parallel [11\bar{2}]_{Cu_2O}$  and  $\{110\}_{Cu} \parallel \{110\}_{Cu_2O}$  with  $[001]_{Cu} \parallel [001]_{Cu_2O}$ , respectively. It then follows that the initial lattice mismatch at  $T = 298$  K for  $\langle Cu_2O \rangle$  overgrowths on Cu $\{111\}$  and Cu $\{110\}$  equals  $-15.3\%$  in all directions parallel to the interface plane. For  $\langle Cu_2O \rangle$  overgrowths on Cu $\{100\}$ , the corresponding mismatch in one direction (here:  $[011]_{Cu} \parallel [11\bar{2}]_{Cu_2O}$ ) is only  $-2\%$ , whereas in the other perpendicular direction (here:  $[0\bar{1}1]_{Cu} \parallel [1\bar{1}0]_{Cu_2O}$ ) the mismatch equals  $-15.3\%$ . Thus, a compressive strain would reside within the oxide overgrowths, which is anisotropic only for the  $\langle Cu_2O \rangle$  overgrowth on Cu $\{100\}$ .

Evidently, if only the bulk Gibbs energies of the competing overgrowths are considered, the crystalline  $\langle Cu_2O \rangle$  overgrowth is always thermodynamically preferred (Fig. 1). That is the bulk energy difference,  $h_{\{Cu_2O\}} \cdot (\Delta G_{\{Cu_2O\}}^f - \Delta G_{\langle Cu_2O \rangle}^f) / V_{\{Cu_2O\}}$ , per unit area of the  $\langle Cu \rangle - \{Cu_2O\}$  interface [cf. Eq. (1); as calculated using data from Ref. [10] and taking  $V_{\{Cu_2O\}} = 2.51 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ] is always positive and increases (obviously) with increasing oxide-film thickness (Fig. 1a), but decreases with increasing temperature (Fig. 1b).

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