

A multi-scale Monte Carlo study of oxide structures on the Cu(100) surface

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Abstract

We present a multi-scale Monte Carlo study of the oxidation of the Cu(100) surface based on the Bortz–Kalos–Lebowitz model with the equilibrium energetics obtained from *ab initio* calculations. The radial and island size distribution functions are examined and Cu–O structures are analyzed at different temperatures and coverages. We concentrate on the coverages of 0.3 monolayer O or less, with variable sub-monolayer coverages of Cu. The results show that even though the *ab initio* calculations yield a higher barrier for O than for Cu adatom diffusion on Cu(100), the stability of Cu structures causes the O adatoms to be more mobile on the Cu(100) surface than the Cu adatoms. We are able to reproduce the $c(2 \times 2)$ -O domains seen in the experiments. However, we give an alternative explanation based on the repulsive interactions of O that, on one hand, cause the local ordering and, on the other hand, prohibits large well-ordered domains. We also give interpretation on the formation of the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ -O reconstruction of Cu(100) above the O coverages of 0.3 monolayer based on the *ab initio* energetics.

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1. Introduction

The oxidation of metal surfaces is, in general, of great practical importance since it may dramatically change the properties of metals and metal surfaces. The oxidation can be utilized for example in applications including gate oxides and catalytic metal oxides [1], and especially in growing nanometer scale devices. The oxidation of copper is a commercially important problem because Cu is a widely used material having applications ranging from the large scale usage of water pipes and building construction to the usage of electric conductors in electronics. The oxidation problem is common on all of the length scales and in all of these applications. The oxidation of Cu surfaces has also scientific relevance because of its interesting features, involving domain formation and surface reconstruction. It

is not completely understood how the oxidation proceeds on the atomic scale and how the reconstruction begins and evolves. To gain deeper knowledge on these processes and to be able to control them, it is crucial to know the oxidation mechanisms at the nanometer scale.

There are several experimental [2–9] and computational studies [10–18] on the behavior of oxygen on the Cu(100) surface. For example, the formation of different kinds of oxygen covered domains on Cu(100) have been seen in the STM experiments [3]. When the oxygen coverage is less than roughly 0.3 monolayer (ML) Cu resides in large and quite stable islands having only very little or no O atoms adsorbed into them. O adatoms occupy the space between the Cu islands forming separate $c(2 \times 2)$ -O domains. At higher O coverages the Cu(100) surface undergoes an oxygen induced surface reconstruction. This $(2\sqrt{2} \times \sqrt{2})R45^\circ$ -O missing row reconstruction is observed to occur when the oxygen coverage on the Cu(100) surface exceeds 0.34 ML and is complete with 0.5 ML O [6]. On Cu(111)

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surfaces the long range interactions are so strong that they should not be neglected [19]. On the other hand, on Cu(100) surfaces the self-diffusion barriers are quite high showing strong local interactions and thus the relative effect of the long range interactions becomes smaller and less relevant [20].

In this paper, we perform multi-scale modeling of hetero epitaxial growth of oxide structures on Cu(100) by combining *ab initio* energetics and statistical Monte Carlo (MC) simulations. We have previously made an extensive set of *ab initio* simulations for O and Cu diffusion processes and the break-up energies of small islands up to three adatoms [13]. From these calculations we can deduce a bond counting energetics model which we use to conduct statistical MC simulations. The MC method gives us an opportunity to see the emerging of larger scale structures than we are able to simulate with the *ab initio* methods. It also allows us to study the temperature dependence of stable and meta-stable structures, growth of the Cu islands and self-assembling of the oxide structures. This paper is arranged as follows: in Section 2 we introduce the details of the computational methods, in Section 3 we present our results and discussion, and finally in Section 4 we give some conclusions.

2. Model

2.1. *Ab initio* energies

The previous *ab initio* energies [13] and the present ones for different Cu–O structures on the Cu(100) surface have been obtained by using the Vienna *Ab initio* Simulation Package (VASP) [21–23]. In these calculations we use the projector augmented wave (PAW) method [24] for potentials with the generalized gradient approximation (GGA) functionals (PW91) [25] and a cutoff of at least 450 eV for the plane-wave expansion. A computational lattice constant of 3.64 Å which is used throughout the calculations is slightly larger than the experimental value of 3.61 Å [26]. A $7 \times 7 \times 1$ Monkhorst–Pack mesh [27] is used for the Brillouin zone sampling. For the atomic oxygen in the vicinity of the surface the magnetic moment is quenched out and therefore spin-averaged calculations can be used. We use a 4×4 surface unit cell and a slab of four layers with a vacuum of 8 Å and with the bottommost layer fixed. The nudged elastic band (NEB) method [28] is applied to find the minimum energy path and transition state for each migration process.

2.2. Monte Carlo simulations

Our Monte Carlo algorithm is based on the model developed by Bortz, Kalos and Lebowitz (BKL) [29], where the system is evolved on every simulation step. Our MC simulations are based on the bond counting energetics in a lattice gas model with a regular square lattice, i.e. the geometry of the Cu(100) surface. In previous works it

has been shown that the local bond counting energetics on Cu surfaces can successfully be applied both to equilibrium island diffusion and non-equilibrium surface growth [30,31]. In this work, the implementation of the model is an extended and refined version of the previous ones, which were specifically designed for pure Cu surfaces [30]. The lattice size used is 40×40 sites. We tested the system with an 80×80 lattice which yielded essentially the same results. The particle number is conserved and the system is relaxed with respect to the total energy. Once the equilibrium is reached, the island size and particle radial distribution functions are measured. The simulations have been made with different O and Cu coverages and at a few different temperatures. The temperatures are between 300 and 600 K, since the experimental studies have usually been done within this temperature range.

The energetics model of the MC simulations is based on the *ab initio* energetics of the equilibrium configurations of Cu and O adatoms on Cu(100) excluding the barriers for different jump processes. Thus, this MC model can be applied to study the equilibrium conditions and distribution functions only. For kinetic modeling the barriers should also be included in the model. However, we keep the present model simple enough to be sure that we reproduce the correct ground-state properties before one could study the dynamics of the system. The kinetic modeling is left out of the scope of the present paper.

The processes for evolving the MC system are monatomic jumps. On Cu(100) monatomic jumps are the most common processes and the collective jumps of small Cu clusters on Cu(100) are unlikely to occur [32]. The energetics model is a bond counting model including the nearest (N) and next-nearest (NN) neighbors in the square lattice. The bond energy values have been derived from the *ab initio* energies of static configurations [13]. For a site i the energy is

$$E_i = \sum E_N + \sum E_{NN}, \quad (1)$$

where E_N (E_{NN}) is the bond energy when one nearest (next-nearest) neighbor is added, and the sum goes over all of the nearest and next-nearest sites and over both species O and Cu. We have fitted the *ab initio* energies in Ref. [13] to Eq. (1) using the method of least squares. In Table 1, we list the bond energies for different neighbor combinations. Note

Table 1
Energy values for different types of bonds, N referring to the nearest neighbor and NN to the next-nearest neighbor

| Bond type | Bond energy (eV) |
|-----------|------------------|
| O–O N | 0.370 |
| O–O NN | 0.123 |
| Cu–O N | 0.295 |
| Cu–O NN | 0.037 |
| Cu–Cu N | –0.340 |
| Cu–Cu NN | –0.087 |

The negative (positive) sign tells that the interaction is attractive (repulsive).

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