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DFT study of reconstructed Cu(100) surface with high oxygen coverages

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ABSTRACT

Adsorption energies and structures of a Cu(100) surface with an oxygen coverage from 0.5 ML to 1.5 ML have been studied using DFT methods. The calculations include both on-surface and mixed on- and sub-surface sites for oxygen. Also several energy barriers for oxygen transfer below the surface have been calculated. Calculations show that mixed structures are energetically more favourable than pure on-surface adsorption at coverages higher than 0.75 ML and barriers for oxygen atoms are low, around 0.5 eV. Experimental results show that during the oxidation process, disordered metal penetrating islands were not seen until after several structural changes, where the oxygen is expected to be on the surface. This is an opposite trend to what we observed in our calculations. An explanation for this discrepancy is that the dissociation of oxygen molecules is very slow on a reconstructed Cu(100) surface. However, after dissociation, oxygen atoms will diffuse easily below the reconstructed surface and our calculations are in agreement with the experimentally observed disordered islands.

1. Introduction

Copper has been used thousands of years in various applications. During the past years, copper has received more attention due to new application areas. Increasing needs for new compounds in microelectronics has created a demand for new, improved and inexpensive materials [1]. Copper has proven to be a usable interconnecting material in microprocessors [2]. At present, Cu_2O is also utilized in superconducting strands and in photovoltaic solar cells [3–7].

The oxidation of metals is inevitable, since metal oxides are energetically more favourable than pure metals. In practical applications, this inflicts large economical costs. However, oxidation can also be a desirable phenomenon. Several metals, like aluminium, are protected from further oxidation by a thin oxide layer. There are also studies which show that the oxides formed can have better catalytic properties than the corresponding metals [8].

In this paper, we have studied the oxidation process of the Cu(100) surface. There are several studies concerning approaching and dissociation of oxygen on this surface [9–12]. Also oxidized surfaces are quite well examined [13–14]. However, the oxidation process is still quite poorly studied at the atomic level.

Cu(100) surface does not oxidize uniformly. First it goes through reconstruction, where every fourth copper row comes out from the surface [15]. This is completed when oxygen coverage increases to 0.5 ML. Several experimental studies have also displayed the growth of oxide structures and islands during the oxidation of copper surface [16–22]. Therefore, the oxidation of Cu(100) surface seems to be a very complex process.

It is known that the adsorption of oxygen happens quite easily at low coverages [10,23–25]. Also, the diffusion of oxygen and copper is rather easy until the surface goes through reconstruction and diffusion becomes substantially more difficult [26]. After reconstruction, the dissociation of a coming oxygen molecule seems to be almost impossible. The dissociation barriers are around 4 eV on ideal reconstructed surface.

However, the oxidation proceeds, and in the work of Lampimäki et al. STM pictures showed three different oxide structures [27]. First, most of the surface is reconstructed with an oxygen coverage of 0.5 ML. The copper released during the reconstruction is attached either to the step edges or it forms elongated islands. These elongated islands have a rather constant width of ca. 2 nm, and the length varies from 2 to 30 nm. The islands heights are ca. 2 Å. Later in the oxidation process, disordered islands, which do not have specific structure, are also formed. In the disordered islands the oxygen is expected to penetrate below the surface. Thus the surface goes through a lot of structural changes before oxygen atoms finally get into the sub-surface sites and real oxidation starts.

In our earlier study [28], we have reported energetics of sub-surface oxygen on the ideal and reconstructed Cu(100) surface and found that at high coverages, the mixed on-surface and sub-surface oxygen site combinations are more favourable than pure on-surface sites, indicating a starting of oxide formation. In the present investigation, we expand this study by calculating more site combinations and concentrating on structures at the higher coverage. We also examine the barriers for oxygen atoms to diffuse from on-surface to sub-surface sites.

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To model the high coverages, we added more and more oxygen to the upper part of the copper slab, but not to the lower part, thus an interface of metal and oxide is formed. The details of this interface are not known. Also, problems arise from the different lattice parameters of copper and copper oxide. The copper oxide lattice parameter is 12% larger the metal one. This causes problems when we have to choose a lattice parameter for the simulation. We discussed in detail some aspects of this strained lattice in Section 3.2.

2. Method

All calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [29] with the projector augmented wave (PAW) [30–33] method. The generalized gradient approximation (GGA) [34] for the exchange and correlation functional and a cut off energy of 430 eV for the plane waves were used. We used the reconstructed surface with a $(2\sqrt{2} \times \sqrt{2})R45^\circ$ cell since it is known that a Cu(1 0 0) surface has undergone full reconstruction when the oxygen coverage reaches 0.5 ML [15]. The surface and the cell have been presented in Fig. 1. In this structure, one copper row is missing and the oxygen atoms are on the hollow sites right beside the missing copper row. For this cell we used Monkhorst–Pack mesh of $8 \times 4 \times 1$. We used a computed lattice parameter (3.64 Å) for Cu, the experimental value is 3.61 Å [35].

In surface calculations, we used five atomic layers where the lowest one was kept fixed. The slabs were separated with a vacuum of around 10 Å, and adsorbates were on one side of the slab. Oxygen atoms were placed on the on-surface sites at hollow, top and bridge sites, and on the sub-surface sites at octahedral and tetrahedral sites. The sub-surface sites used have been introduced in Fig. 2. Atoms on the tetrahedral sites were located on bridge sites between the first and the second layers (Fig. 2a and b). Atoms on the octahedral sites were located on the second copper layer under the copper atoms of the first layer (Fig. 2c and d).

The calculations for the oxygen atoms on the copper surface were spin averaged, whereas the calculation for the oxygen molecule was spin polarized. For O_2, the calculated bond length was 1.235 Å and a vibrational frequency 1561 cm^{-1}, whereas the experimental values are 1.21 Å and 1580 cm^{-1}, respectively [36].

The barrier for an oxygen atom to go to sub-surface sites has been calculated using the nudged elastic band (NEB) method modified by Henkelman et al. which has been proven to be more stable than the previous implementations [37–39]. NEB searches the minimum energy path of the desired initial and final stages. Our calculations were performed using four images between initial and final stages, since in our calculation it was a sufficient accuracy.

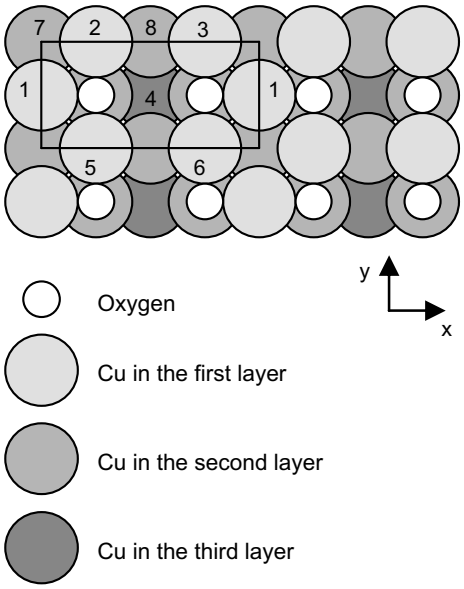

Fig. 1. Used reconstructed $(2\sqrt{2} \times \sqrt{2})R45^\circ$ surface and the simulation cell. Atoms of the simulation cell have been numbered for identifying the different oxygen sites.

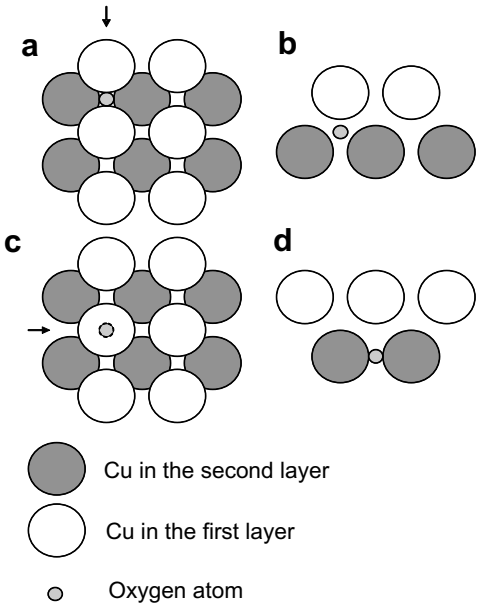

Fig. 2. Sub-surface adsorption sites. (a) Top view of the tetrahedral site. (b) Side view of the tetrahedral site. (c) Top view of the octahedral site. (d) Side view of the octahedral site. The arrows in (a and c) show the direction of views used in (b and d).

3. Results and discussion

3.1. Effects of oxygen at increasing coverage

3.1.1. Oxygen coverage of 0.5 ML

In Fig. 3, we have shown a side view of the copper slab and oxygen atoms at a coverage of 0.5 ML. The energy of this structure, E_{ref}, has been used as a reference for the calculations of adsorption energies at higher coverages. Also, we have used this structure as a reference when comparing the relaxation of other structures. The adsorption energies, E_{ads}, were calculated using formula

$$E_{ads} = \frac{E_{total} - E_{ref} - N_{add}\frac{E_{O_2}}{2}}{N_{add}}$$

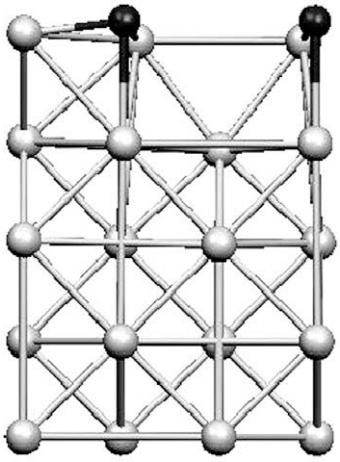

Fig. 3. The side view of the copper slab with an oxygen coverage of 0.5 ML.