



# Oxygen chemisorption-induced surface phase transitions on Cu(110)



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## ABSTRACT

From an interplay between variable temperature scanning tunneling microscopy and density-functional theory calculations, the evolution of oxygen chemisorption-induced surface reconstructions of the Cu(110) surface is determined. The surface reconstructions proceed via a sequential pathway with increasing oxygen surface coverage. The  $(2 \times 1)$  reconstruction occurs first and then transits to the  $c(6 \times 2)$  phase with a higher oxygen coverage through a mechanism that consumes the existing  $(2 \times 1)$  phase with the supply of Cu adatoms from step edges and terraces. The temperature dependence of the  $(2 \times 1) \rightarrow c(6 \times 2)$  transition demonstrates that the surface phase transition is an activated process for breaking up added Cu–O–Cu rows in the  $(2 \times 1)$  structure. Comparison between the experimental observations and the theoretical surface phase diagram obtained from first-principles thermodynamic calculations reveals that the  $(2 \times 1) \rightarrow c(6 \times 2)$  transition takes place at the oxygen chemical potentials that are far above the chemical potential for  $\text{Cu}_2\text{O}$  bulk oxide formation, reflecting the existence of kinetic limitations to the surface phase transition and the bulk oxide formation.

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## 1. Introduction

Effects resulting from the interaction between oxygen and a metal surface are of great interest in many areas such as oxidation, corrosion, and heterogeneous catalysis. Acquiring a fundamental understanding of the nature of the interactions is critical to elucidate the role of oxygen for these important technological processes. For instance, many current industrial processes are centered on catalytic oxidation reactions. Upon exposure to an oxygen-containing atmosphere, the metal surface undergoes a series of structural changes varying from the formation of initial oxygen chemisorbed adlayers to oxygen sub-surface diffusion and then to bulk oxide formation, depending on the oxidation conditions including the oxygen gas partial pressure, temperature, and orientation of the metal surface. It has been increasingly apparent that the active phase of some catalytic oxidation catalysts under operating conditions is in fact their oxides rather than the pure metal [1,2]. During catalytic reactions different compositions and structures of the metal surface may be present depending on the operation conditions. However, not all oxide phases are equally active to fulfill multiple catalytic functions. Thus, a detailed study of the formation of each surface reconstruction and the mechanism governing their transitions to other phases will provide insight for finely tuning the operating conditions to favor one phase over the other for better activities and selectivities.

Copper-based catalysts are well known to be active for various catalytic reactions including the water–gas shift reaction [3,4], methanol

synthesis and methanol oxidation [5], the reduction and decomposition of nitrogen oxides [6], and fuel cell electrodes [7]. Dissociative adsorption of oxygen, for instance, represents the first step in the synthesis of formaldehyde by methanol oxidation over copper [5]. Surface oxidation and the formation of oxide overlayers are believed to play a critical role in copper catalysis [8,9]. Consequently, Cu has been studied as a prototype system dealing with the oxygen surface chemisorption. Particularly, the oxygen chemisorption on Cu(110), the most open of the low-index surfaces, is among the most studied systems, involving oxygen adsorption, interdiffusion of Cu and O, and various restructuring phases [10–23]. A consensus has been established on some aspects of the behavior of oxygen adsorption on Cu(110) under ultrahigh vacuum (UHV) conditions. Two superstructures occur upon UHV oxygen exposures: an added-row  $(2 \times 1)$ -O structure with  $\theta = 0.5$  oxygen coverage, and a  $c(6 \times 2)$  structure with  $\theta = 2/3$  oxygen coverage for increased oxygen exposure [17,19–21].

However, even though the formation of these reconstructed structures has been known for over 20 years, the detailed kinetic and thermodynamic mechanisms controlling the crossover from the added-row  $(2 \times 1)$  to the  $c(6 \times 2)$  reconstruction are still open for debate. The added-row  $(2 \times 1)$  was found to nucleate homogeneously on well-ordered terraces and the process can be described as a two-dimensional precipitation of a solid phase from a dilute, mixed fluid of Cu and O [10–23]. Compared to the detailed understanding of the  $(2 \times 1)$  reconstruction, very little is known about the formation process of the  $c(6 \times 2)$ . For instance, it is unclear if the  $c(6 \times 2)$  reconstruction can occur directly on an un-reconstructed Cu(110) surface or has to follow a sequential pathway via the  $(2 \times 1) \rightarrow c(6 \times 2)$  conversion process when a clean Cu(110) surface is directly exposed to the oxygen

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gas under which the  $c(6 \times 2)$  reconstruction is thermodynamically more favored over the  $(2 \times 1)$  reconstruction. Alternatively, if the  $c(6 \times 2)$  reconstruction occurs by consuming the existing  $(2 \times 1)$  structure, it will involve massive surface restructuring, the break-up of Cu–O–Cu rows in the  $(2 \times 1)$  (i.e., a solid–solid transition may be more appropriate), and thus, the effects of kinetic limitations may be equally important in addition to the thermodynamic driving force for the phase transition. Particularly, the requirements of temperature and oxygen pressure delineating the transitions of these surface phases have not been established. Due to the lack of systematic experimental data on the temperature and pressure effects on the surface phase transition, comparisons with theoretical thermodynamic calculations have not been made in the past studies. Our goal in this work is to bridge this information gap by performing a set of experiments with well-controlled temperature and pressure conditions for elucidating the temperature/pressure requirements leading to the crossover from the  $(2 \times 1)$  to  $c(6 \times 2)$  reconstructions. Addressing these thermodynamic and kinetic processes governing the surface phase selection is expected to have significant technological implications for controlling the surface structure and reactivity.

In this work we present a systematic study of the effect of oxygen gas exposure and oxidation temperature on the formation of the  $(2 \times 1)$  and  $c(6 \times 2)$  phases during the oxidation of Cu(110). Variable temperature scanning tunneling microscopy (STM) is employed to monitor the structure evolution of the surface reconstructions induced by oxygen chemisorption at different temperatures. By examining the oxygen exposure at the oxygen pressure up to  $1 \times 10^{-5}$  Torr at three different temperatures (27 °C, 100 °C, and 350 °C), we demonstrate that the  $c(6 \times 2)$  formation is temperature dependent, where a critical oxygen coverage is required for the phase transition, thereby supporting the sequential pathway of the surface reconstructions (i.e., the  $c(6 \times 2)$  reconstruction occurs via the  $(2 \times 1) \rightarrow c(6 \times 2)$  conversion process). From an interplay between the experiments and the first-principles thermodynamic calculations, we find that a significant kinetic barrier exists for the  $(2 \times 1) \rightarrow c(6 \times 2)$  phase transition, and toward the bulk oxide formation.

## 2. Experimental and computational methods

The experiments were performed by an ultrahigh vacuum (UHV) variable-temperature scanning tunneling microscope (Omicron VT-STM XA) with a base pressure of  $\sim 1 \times 10^{-11}$  Torr. An electrochemically etched polycrystalline tungsten wire was used for the STM tip. The STM tips were flashed (1 kV and 2 mA) for several times to evaporate adsorbates and native oxide. Meanwhile, the oxygen dosing was performed in a separate chamber than the STM chamber to ensure the pristine nature of the tip. The Cu(110) single crystal is a ‘top-hat’ disk (1 mm thick and 8 mm in diameter), purchased from Princeton Scientific Corp., cut to within  $0.1^\circ$  to the (110) crystallographic orientation and polished to a mirror finish. The crystal was cleaned by repeated cycles of Ar<sup>+</sup> sputtering at room temperature ( $5 \times 10^{-5}$  Torr of Ar<sup>+</sup>,  $1 \mu\text{A cm}^{-2}$ , 1.0 keV) followed by annealing at 600 °C for 10 min. Cleanliness of the Cu(110) surface was checked by STM imaging prior to oxidation by oxygen gas dosing at different temperatures ( $T = 27^\circ\text{C}$ ,  $100^\circ\text{C}$ , and  $350^\circ\text{C}$ ). All the oxidation experiments were carried out on freshly cleaned Cu(110) surfaces. Oxygen gas (purity = 99.9999%) was introduced to the system through a variable-pressure leak valve and the sample was oxidized under a controlled oxygen pressure ( $p\text{O}_2$ ) ranging from  $1 \times 10^{-10}$  Torr to  $1 \times 10^{-5}$  Torr. All the STM images were acquired at room temperature in constant-current mode with bias on the sample.

Density-functional theory (DFT) calculations are performed using the generalized gradient approximation (GGA) of Perdew–Wang (PW91) [24] for the exchange and correlation functional, as implemented in the Vienna Ab-initio Simulation Package (VASP) [25–29]. We used projector augmented wave (PAW) potentials in conjunction with a

planewave cutoff energy of 380 eV. The Brillouin-zone integration for the  $(2 \times 1)$  and  $c(6 \times 2)$  unit cells is performed using  $(5 \times 7 \times 1)$  and  $(2 \times 4 \times 1)$  Monkhorst–Pack grids [30], and with broadening of the Fermi surface according to Methfessel–Paxton smearing technique [31] with a smearing parameter of 0.2 eV. All of our calculations are spin-averaged except those for the oxygen atom and molecule which are spin polarized. In our modeling of the chemisorbed species on the surface, we used a slab model with five layers where the bottom layer is fixed. Periodic images along the direction perpendicular to the surface are separated by a vacuum region of 12 Å. Adsorption is done on one side of the slab only. Atomic and molecular oxygen are studied using a large cubic cell. The positions of all of the atoms, except those of the bottom layer, are relaxed until the forces are less than 0.015 eV/Å. Various tests have been performed to verify our computational framework such as  $\mathbf{k}$ -grid convergence, vacuum size, and planewave cutoff. As a validity check, our calculated lattice constant for Cu is 3.64 Å which is in good agreement with the experimental value 3.61 Å [32] and with previous calculations [33–35].

We employed a first-principles atomistic thermodynamic framework to assess the relative stability of the considered surface structures as a function of  $p(\text{O}_2)$  and  $T$  [8,13]. The average adsorption energy for single oxygen atom can be defined as,

$$E_{\text{O}}^{\text{ads}} = \frac{1}{N_{\text{O}}} \left( E_{\text{O/Cu}}^{\text{tot}} - E_{\text{Cu}}^{\text{slab}} - \Delta N_{\text{Cu}} E_{\text{Cu}} - \frac{N_{\text{O}}}{2} E_{\text{O}_2} \right), \quad (1)$$

where  $E_{\text{O/Cu}}^{\text{tot}}$  is the total energy of the Cu–O system, and  $E_{\text{Cu}}^{\text{slab}}$  is the energy of a clean, non-reconstructed Cu surface.  $\Delta N_{\text{Cu}}$  accounts for differences in the number of Cu atoms between the reference clean Cu surface and the Cu–O system, and  $E_{\text{Cu}}$  is the energy of a single Cu atom in bulk state.  $E_{\text{O}_2}$  is the energy of an isolated oxygen molecule and  $N_{\text{O}}$  is the number of oxygen atoms adsorbed on the Cu substrate. The Gibbs free energy  $\Delta\gamma$  of the Cu–O system relative to the clean non-reconstructed Cu surface is calculated as,

$$\Delta\gamma = \frac{1}{A} \left[ E_{\text{O/Cu}}^{\text{tot}} - E_{\text{Cu}}^{\text{slab}} - \Delta N_{\text{Cu}} \mu_{\text{Cu}} - N_{\text{O}} \mu_{\text{O}}(T, p) \right]. \quad (2)$$

Here  $A$  is the surface unit area and  $\mu_{\text{Cu}}$  and  $\mu_{\text{O}}$  denote the Cu and O chemical potentials, respectively. The chemical potential of Cu is taken to be that of a Cu atom in bulk phase, thus assuming that the slab is in equilibrium with the bulk phase that acts as the Cu reservoir. The oxygen chemical potential depends on temperature and pressure according to

$$\mu_{\text{O}}(T, p) = \frac{1}{2} \left[ E_{\text{O}_2}^{\text{total}} + \tilde{\mu}_{\text{O}_2}(T, p^0) + k_{\text{B}} T \ln \left( \frac{p\text{O}_2}{p^0} \right) \right], \quad (3)$$

where  $p^0$  represents the standard atmospheric pressure and  $\tilde{\mu}_{\text{O}_2}(T, p^0)$  denotes the chemical potential of oxygen gas at 1 atm, which is tabulated in ref. [36]. In Eqs. (2) and (3), we neglected the vibrational and configurational terms in the Gibbs free energy as these contributions are small [37,38]. Additionally, the  $-pV$  contribution is also small for pressures less than 100 atm [38]. By redefining the chemical potential as  $\Delta\mu_{\text{O}} = \mu_{\text{O}} - \frac{1}{2} E_{\text{O}_2}$  and combining Eqs. (1) and (3), we can express the Gibbs free energies in Eq. (2) as,

$$\Delta\gamma = \frac{1}{A} \left( N_{\text{O}} E_{\text{O}}^{\text{ads}} - N_{\text{O}} \Delta\mu_{\text{O}} \right). \quad (4)$$

Before concluding this section, we point out that the GGA/PW91 error for the binding energy for  $\text{O}_2$  (the energy that is needed to dissociate an  $\text{O}_2$  molecule) is large [35,39,40]. Our calculated value is 6.3 eV while the experimental value is 5.1 eV [41]. Our GGA/PW91 value agrees with previous results [35,39,40]. This error in the binding energy of  $\text{O}_2$  affects the thermodynamic analysis. To remedy this, previous studies have used the calculated  $\text{O}_2$  binding energy for computing the

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