

## Communication: Calculations of the $(2 \times 1)$ -O reconstruction kinetics on Cu(110)

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Density functional theory calculations are used to study the elementary processes of the formation of the  $(2 \times 1)$ -O reconstruction on the Cu(110) surface. The  $(2 \times 1)$ -O reconstruction requires additional Cu atoms to form Cu–O rows on top of the surface. Both terrace and step sites are considered as the source of Cu adatoms. On terraces, adsorbed oxygen induces the ejection of Cu atoms to form –O–Cu–O– units, leaving Cu vacancies behind. The barrier for subsequent unit growth, however, is prohibitively high. Cu(110) step sites are also considered as a source of Cu atoms. Dissociated oxygen triggers the formation of stable Cu–O chains along the [001] step edges. This process, however, blocks the diffusion of Cu atoms so that it is not a viable mechanism for the  $(2 \times 1)$ -O reconstruction. Oxygen adsorption on the  $[1\bar{1}0]$  edges also allows the nucleation of [001] oriented Cu–O rows. The short Cu–O rows act as diffusion channels for Cu atoms that detach from the step, which append to the end of the Cu–O chains. Our calculations of the formation of the  $(2 \times 1)$ -O phase on Cu(110) provide a mechanistic description of the experimentally observed reconstruction. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4978578>]

The chemisorption of oxygen and the reconstruction of the Cu(110) surface have attracted interest from theoretical and experimental groups.<sup>1–6</sup> It is clear that oxygen adsorbs dissociatively on the Cu(110) surface at room temperature.<sup>7–9</sup> Atomic oxygen forms two stable reconstructions<sup>10–19</sup> by combining with Cu adatoms: an “added-row”  $(2 \times 1)$ -O structure with a  $\theta = 0.5$  oxygen coverage and a  $c(6 \times 2)$  structure with a  $\theta = 2/3$  oxygen coverage. Steps are assumed to be the source of Cu adatoms for the oxygen-chemisorption induced  $(2 \times 1)$  phase formation.<sup>20–22</sup> Cu–O chain formation was the mechanism by which atomic oxygen was able to combine with Cu adatoms detaching from step edges and diffusing on the surface. Other experiments found that the ejection of Cu atoms from terraces was also a route for Cu adatom formation.<sup>9,23</sup> This process occurs at temperatures below 250 K and leads to the formation of short Cu–O strings, leaving monolayer deep vacancies on the terraces. These vacancy islands heal at elevated temperatures and form a well-ordered  $(2 \times 1)$  phase.

Despite numerous studies regarding the mechanism of oxygen chemisorption induced Cu(110)- $(2 \times 1)$  reconstruction, the kinetic mechanism(s) controlling the crossover from an un-reconstructed Cu(110) surface to the added-row structure has largely been ignored. Additionally, the mechanisms of surface ejection or step-edge detachment of Cu atoms that are activated by oxygen have not been established. In this work, we employ density functional theory (DFT) calculations to study the nucleation and growth of the  $(2 \times 1)$  phase from the un-reconstructed Cu(110) surface. The nucleation mechanisms of

the  $(2 \times 1)$  phase on the terraces and step edges are identified, as well as the Cu–O growth into the early stage of the  $(2 \times 1)$  phase.

We performed DFT calculations with the Vienna *ab initio* simulation package,<sup>24–27</sup> using the Perdew–Burke–Ernzerhof (PBE) functional.<sup>28</sup> The projector augmented wave framework described the core electrons, and a plane wave basis with a cutoff energy of 350 eV described the valence electrons.<sup>29,30</sup> Slab structures included four layers where the bottom layer was fixed and the top layers were free to relax until all force components dropped below 0.01 eV/Å. Periodic images in the direction perpendicular to the surface were separated by 15 Å of vacuum. Brillouin-zone integration was performed using a  $(2 \times 3 \times 1)$  Monkhorst–Pack grid for the  $(4 \times 4)$  surface unit cell.<sup>31</sup> All calculations were spin-averaged except for those involving free molecular O<sub>2</sub>, which included spin-polarized. The climbing image nudged elastic band method<sup>32</sup> was used to calculate reaction barriers.

Adsorption energies per oxygen atom,  $E_{ads}$ , were calculated as

$$E_{ads} = E_{Cu/O_2}^{slab} - E_{ref} - \frac{1}{2}E_{O_2}, \quad (1)$$

where  $E_{Cu/O_2}^{slab}$  is the total energy of the Cu–O system,  $E_{O_2}$  is the energy of an isolated oxygen molecule, and  $E_{ref}$  is the energy of the substrate without oxygen adsorption.

We begin with the nucleation of –O–Cu–O– units on the Cu(110) terrace. Since O<sub>2</sub> dissociation is rapid on Cu(110), the unconstructed Cu surface is rapidly covered by O atoms. These O atoms preferentially bind to the shifted hollow (shH) sites with an adsorption energy of –1.70 eV per O atom. Our initial configuration, therefore, is chosen to have two O atoms adsorbed at nearby shH sites. The minimum energy

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path (MEP) of Cu ejection from the surface is shown in Figure 1. The mechanism has two steps: first, a surface Cu atom (labeled as “a”) is pulled up from the surface to bridge between two O adatoms (IM2); second the vacancy diffuses away to stabilize the formation of the  $-\text{O}-\text{Cu}-\text{O}-$  unit (IM3). The entire process is exoergic by 0.50 eV and has a barrier of 0.39 eV.

Ejection of a Cu atom from the subsurface layer was also considered, but the barrier for this process is significantly higher, at 0.60 eV. A calculation based upon the harmonic transition state theory<sup>33</sup> indicates that the rate for surface Cu ejection is three orders of magnitude faster than for subsurface Cu at 250 K.

Once the  $-\text{O}-\text{Cu}-\text{O}-$  units form, one can ask how they grow to form longer Cu–O chains. The mechanism of the second Cu atom ejection from the substrate is similar to that of the first Cu atom as shown in Figure 2(a). However, the overall barrier of 0.77 eV for the second Cu atom to form a stable  $-\text{O}-\text{Cu}-\text{O}-\text{Cu}-\text{O}-$  unit is higher than for the initial  $-\text{O}-\text{Cu}-\text{O}-$  unit formation. We ascribe the higher barrier to the reduced attraction between the Cu and O atoms. A second possible mechanism for forming longer Cu–O chains is by linking units through an additional Cu atom. Figure 2(b) shows this unit association process. When two neighboring units are aligned, the two adjacent terminal O atoms can pull a Cu atom out from the substrate by first Cu ejection (0.60 eV barrier) and then vacancy diffusion (0.73 eV barrier).

These results indicate that extracting Cu atoms from the substrate to nucleate short Cu–O units is a fast process, but growing longer  $-\text{O}-\text{Cu}-\text{O}-$  chains is slower. This result is consistent with the experimental observation<sup>9</sup> that O adsorption on the surface results in short Cu–O units formed by the ejection of Cu atoms at a low temperature. Previous STM studies<sup>9,23</sup> showed that Cu–O row formation is accompanied by the generation of Cu vacancies on the terrace. We find that the

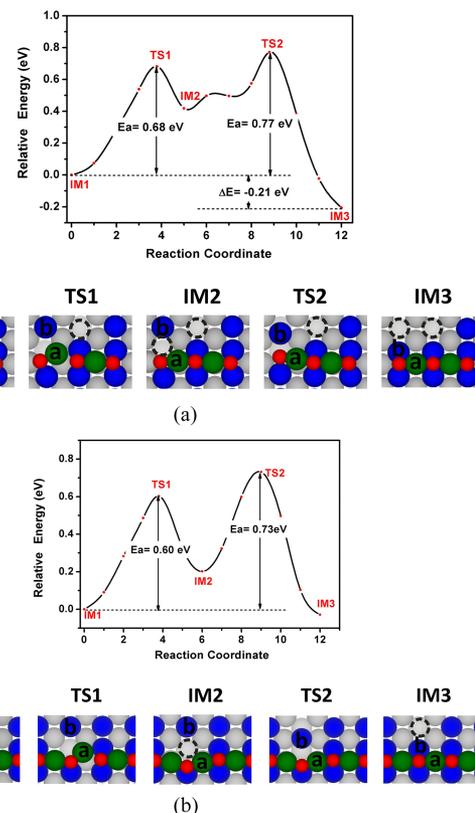
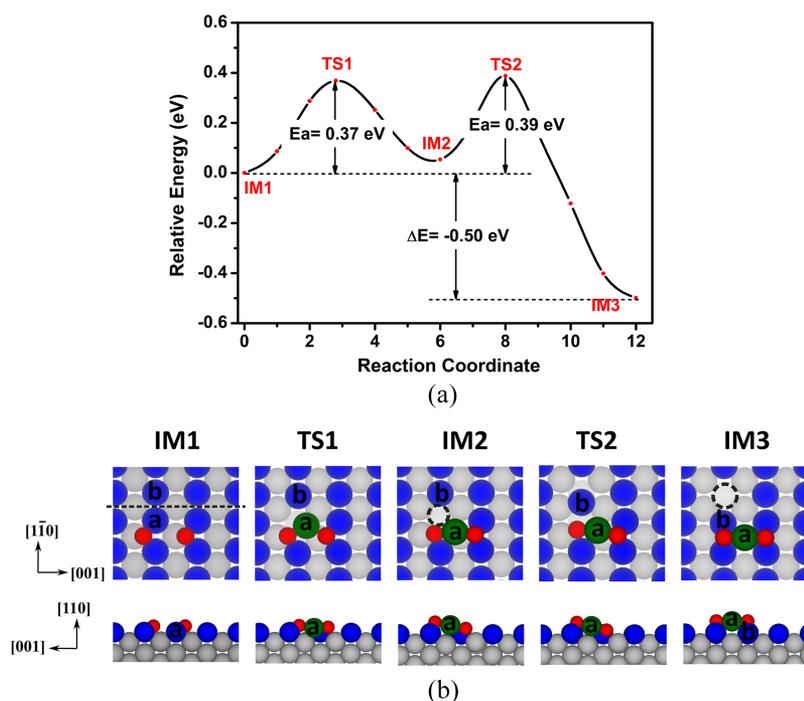


FIG. 2. Growth of a  $-\text{O}-\text{Cu}-\text{O}-$  chain by (a) incorporating one more Cu–O unit from an adsorbed O atom, (b) linking to another  $-\text{O}-\text{Cu}-\text{O}-$  unit.

barriers for vacancy diffusion on a non-reconstructed Cu(110) surface along the  $[\bar{1}\bar{1}0]$  and  $[001]$  directions are 0.65 and 0.86 eV, respectively. The barrier for vacancy diffusion through Cu–O chains is about 1.0 eV (shown in Figure S1 of the [supplementary material](#)). Because of high diffusion barriers, the vacancies are immobile on the surface at a low temperature.

FIG. 1. (a)  $-\text{O}-\text{Cu}-\text{O}-$  unit formation from two adsorbed O atoms on the Cu(110) terrace. (b) The upper panels are top views and the lower panels are side views of the intermediate (IM) and transition (TS) states. The top-layer and the substrate Cu atoms are blue and grey; adsorbed O and prominent Cu atoms are red and green, respectively. The Cu vacancy is indicated by the black dotted circle.

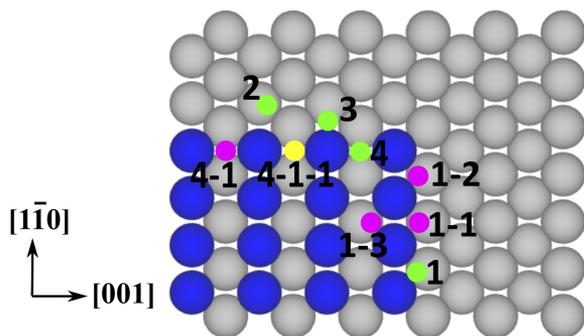


FIG. 3. O adsorption sites at step edges. Step Cu atoms are blue; substrate atoms are grey; the initial adsorbed O atom sites are green; the second magenta; and the third yellow.

As a result, one would expect randomly distributed Cu–O units located in the vicinity of vacancies—as is observed in experiment.

Steps are another possible source of Cu adatoms for oxygen-chemisorption induced surface reconstruction. The barriers (shown in Fig. S2 and Table S1 of the [supplementary material](#)) for Cu atoms re-attaching to the step edge are lower than for Cu atoms detaching. In the presence of O atoms, however, the energy landscape for Cu detachment from the step edge is not as simple.

Figure 3 shows the possible binding sites for O adsorption around a step edge. The binding energies are listed in Table S2 of the [supplementary material](#). Compared to the most stable oxygen adsorption site on the terrace (the sh-H site)<sup>6</sup> where

the binding is  $-1.70$  eV, the step edges have an affinity to oxygen atoms:  $-2.02$  eV on the  $[\bar{1}10]$  orientated step (site 1) and  $-1.84$  eV on the  $[001]$  orientated step (site 4). The effect on the adsorption energy from neighboring oxygen atoms is also considered. If site 1 is occupied, a second O atom prefers to bind on sites 1-2 and 1-3 rather than site 1-1 because of the repulsion between O atoms. The adsorption energy increases with more oxygen atoms accumulating on the  $[001]$  edges (sites 4, 4-1, 4-1-1), which is attributed to the formation of a Cu–O chain along the  $[001]$  direction.

Our calculations show that dissociated O atoms prefer to adsorb along the  $[\bar{1}10]$  step edge in a “zig-zag” pattern to form linear Cu–O chains along the  $[001]$  edge. The  $[001]$  edge is then passivated because any Cu atom detaching from this edge has a barrier of 0.95 eV (shown in Figure S3 of the [supplementary material](#)). Therefore, Cu–O rows only grow from the  $[\bar{1}10]$  edge.

Considering that the coverage of O adatoms at sh-H sites is high, we place two adsorbed O adatoms at sh-H sites near the step edge as the reactant state, as shown in Figures 4(a) and 4(b). The Cu atom (labeled by a) in the immediate vicinity of the step on the lower terrace is ejected by two O atoms (labeled as 1 and 3); this process is facile with a barrier of 0.06 eV and has an energy decrease of 0.34 eV. Another Cu atom (b) follows the first to form IM3. Next, the Cu atom (c) fills the vacancy, which is produced by the ejected Cu atom (a) on the terrace with a barrier of 0.1 eV. The Cu atom (e) then moves in the same way as the Cu atom (c) to fill another vacancy to form IM5 with a barrier of 0.25 eV. Finally two

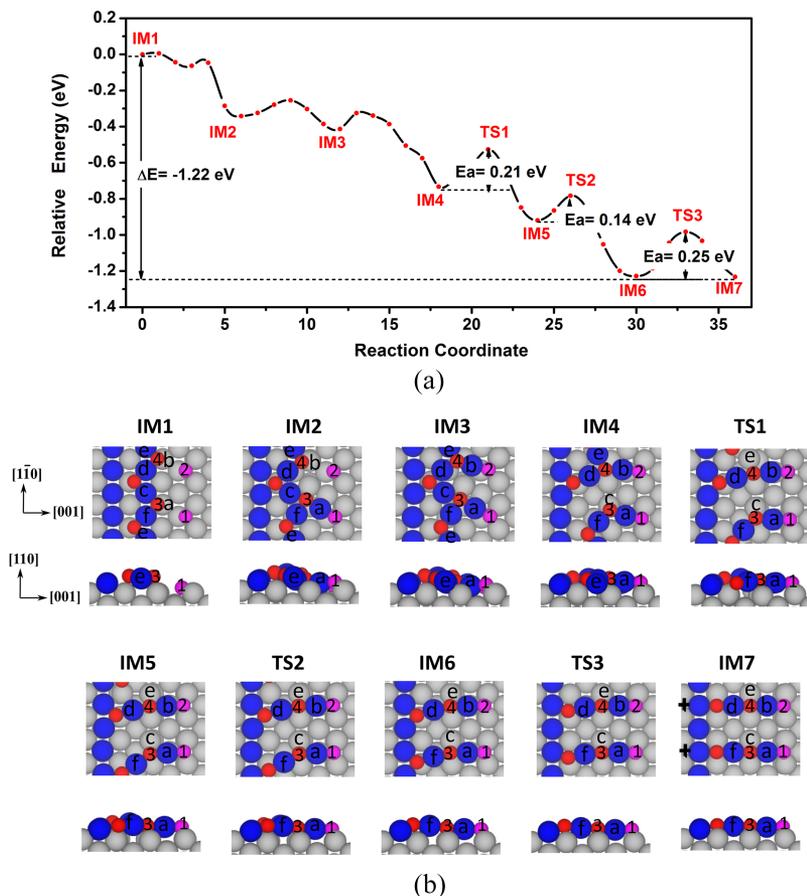


FIG. 4. (a) Formation of Cu–O chains along the  $[\bar{1}10]$  step, (b) top and side views of intermediate and transition states.

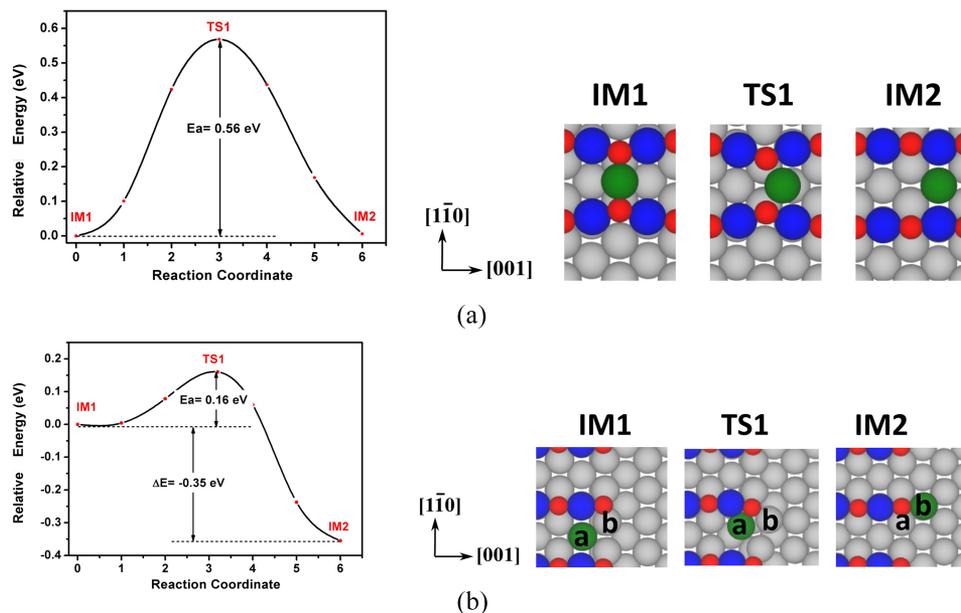


FIG. 5. (a) Cu diffusion along the channel between two Cu–O chains, and (b) Cu addition to the O terminus of a Cu–O chain via an exchange mechanism.

Cu–O chains form along the [001] direction along every-other  $[1\bar{1}0]$ - $(1 \times 1)$  row (IM7). This entire process is exoergic by 1.22 eV. Based on this mechanism, the nucleation of Cu–O chains from the  $[1\bar{1}0]$  oriented step edge is both thermodynamically favorable and kinetically viable. Previous calculations suggested that Cu–O chains grew from the [001] oriented step,<sup>22</sup> but here, considering O atoms on the upper terrace of the step Cu–O chain formation along the step edge is shown to be facile.

A final question that we ask is if the Cu–O rows can continue growing. We find that once Cu–O units form along the  $[1\bar{1}0]$  step, adsorbed O atoms prefer to bind at the long-bridge sites (black crosses in IM7) at the base of the Cu–O chain, extending them into the step by one unit. Then the Cu atoms at the step edge located between the Cu–O chains can diffuse along the channels formed by the Cu–O chains, as shown in Figure 5(a). Diffusing Cu atoms bind to two O atoms between the Cu–O rows in the initial state, IM1, and then hop to the neighboring site between two Cu atoms. This process requires an energy barrier of 0.56 eV (TS1). Subsequent diffusion to a site between two O atoms is equivalent so that the Cu atoms can freely diffuse along the Cu–O chains.

Once a Cu adatom diffuses to the end of the Cu–O chain, one possibility is that the detached Cu atom diffuses onto the terrace; another is that it connects to the O terminus to increase the length of the chain through an exchange mechanism<sup>34,35</sup> as shown in Figure 5(b). This later process has a barrier of 0.16 eV and is exoergic by 0.35 eV. The terminal Cu atom is then saturated by an O atom, and the subsequent detached Cu atom can follow the same mechanism to append onto the chain.

In summary, DFT calculations are used to investigate the mechanism of Cu–O chain formation on the Cu(110) surface. The formation of O–Cu–O units on the terrace requires overcoming a small kinetic barrier of 0.37 eV; the formation of longer Cu–O chains has a significantly higher barrier of 0.73 eV. At steps, O atoms occupy the long-bridge sites to form stable Cu–O chains along the [001] oriented step edge which prevent additional Cu atoms diffusing away from the

steps and subsequent chain growth. Along the  $[1\bar{1}0]$  step edge, oxygen atoms adsorb until the Cu edge atoms are saturated. Our calculations show a novel mechanism by which short Cu–O chains form with a barrier of 0.25 eV and then Cu atoms detach from the step with a barrier of 0.56 eV and diffuse along the channels between the Cu–O chains to the terminus to oxidize a surface Cu atom and increase the length of the chains. The overall barrier for the Cu–O chain growth from the step edge is 0.19 eV higher than the short chain forming on the terrace. The energy difference is in agreement with the observed onset temperature difference of these two processes.

See [supplementary material](#) for the additional figures of Cu diffusion mechanisms and tables of binding energies and diffusion barriers.

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