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Energetics and kinetics of the $c(2 \times 2)$ to $(2\sqrt{2} \times \sqrt{2})R45^\circ$ transition during the early stages of Cu(100) oxidation

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The energetics and kinetics of the $c(2 \times 2)$ to $(2\sqrt{2} \times \sqrt{2})R45^\circ$ missing-row reconstruction transition on the Cu(100) surface are investigated using density functional theory calculations. First, oxygen-molecule-induced surface restructuring on the unreconstructed Cu(100) surface is compared to that on the missing-row reconstructed surface. We find that the surface-oxide energy decrease on the missing-row reconstruction (-0.149 eV/ \AA^2) is larger than that on the unreconstructed surface (-0.080 eV/ \AA^2). Cu_2O -like structures, which are found on the reconstructed surface, are not found on the unreconstructed surface. These results indicate that the missing row reconstruction is necessary for the formation of Cu_2O on the Cu(100) surface. Then, we investigate copper ejection from the $c(2 \times 2)$ phase using the nudged elastic band method. A series of ejections onto the nearest-neighbor copper atom are found to be the most probable mechanism for the formation of the missing row. The barriers for the subsequent copper diffusion events are comparable to those on the perfect $c(2 \times 2)$ phase and the clean copper surface, suggesting that the $c(2 \times 2)$ phase acts as a copper diffusion channel during surface oxidation.

I. INTRODUCTION

During the early stages of Cu(100) oxidation, the $c(2\times 2)$ phase is experimentally observed to transition into the $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phase by a missing-row reconstruction at an oxygen coverage of around 0.5 monolayers (ML).^{1–11} Based on their scanning tunneling microscopy (STM) observations, Jensen et al. proposed that the missing row forms by the ejection of every fourth row of the top copper layer.² This mechanism has been supported by experimental and computational investigations.^{4,5,8,9,11–19} The stabilities of the $c(2\times 2)$ and $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phases at an oxygen coverage of 0.5 ML at zero temperature and zero pressure have been compared using density functional theory (DFT)-predicted chemisorption energies, average oxygen atom binding energies, and surface-oxide energies.^{13,17–19} The $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phase is consistently found to be more stable than the $c(2\times 2)$ phase, but the energy differences are small (e.g., 0.002 eV/Å² for the surface-oxide energy¹⁹). Iddir et al. used *in situ* surface x-ray scattering to investigate the stability of oxygen-covered Cu(100) surface phases for temperatures between 300 and 1000 K and oxygen partial pressures between 10^{−10} and 10^{−4} Torr.¹⁴ They found that the reconstructed phases [$(2\sqrt{2}\times\sqrt{2})R45^\circ$ and a related phase that has disordered copper surface vacancies] are more stable than unreconstructed phases at oxygen partial pressure higher than 10^{−8} Torr. They also found that the transition between the unreconstructed phases and the reconstructed phases is hysteretic.¹⁴ Duan et al., using first principles atomistic thermodynamics, also found that the reconstructed phases are more stable than the unreconstructed phases (clean and 0.25 ML oxygen covered surfaces) in the same range of oxygen partial pressure.¹⁸

Two driving forces for the missing-row reconstruction have been suggested: (i) surface stress^{4,12} and (ii) long-range Coulombic interactions.¹¹ Harrison et al. found that the compressive stress on the $c(2\times 2)$ phase is larger than that on the $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phase from both experiments (crystal curvature technique in an ultra-high vacuum chamber) and DFT calculations.¹² Using temperature-dependent surface-extended x-ray-absorption fine structure measurements, Lederrer et al. also studied the $c(2\times 2)$ and $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phases.⁴ They found that adsorbate-induced forces between top-layer copper atoms in the $c(2\times 2)$ phase induce surface strains and lead to the missing-row reconstruction. They also found that the copper-oxygen bond is ionic on the unreconstructed surface but covalent on the missing-row reconstructed surface. Calculating surface Madelung potentials within the muffin-tin approximation, Stolbov et al. showed that long-range Coulombic interactions among oxygen atoms of the $c(2\times 2)$ phase make copper atoms eject, leading to the $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phase, which has stronger pO - dCu covalent coupling.¹¹ Integrating these findings, we hypothesize that long-range Coulombic interactions induce the compressive surface stress, leading to the copper atom ejection.

While the driving forces behind the missing-row reconstruction have been investigated, three fundamental questions remain. First, is the missing-row reconstruction necessary for Cu(100) oxidation? Previous investigations showed that the $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phase is more stable than the $c(2\times 2)$ phase, but did not show whether copper I oxide (Cu₂O) can form on unreconstructed Cu(100) surfaces.^{13,18,19} Second, how do the copper atoms eject and diffuse away during the missing-row reconstruction? The transition kinetics from the $c(2\times 2)$ phase to the $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phase are not well understood. Third, where do the ejected copper atoms go? Based on STM measurements, it was suggested that the ejected copper atoms diffuse away from the missing row and attach on top of adjacent missing-row reconstructions²⁰ and/or on step edges at phase boundaries.¹⁶ The diffusion paths, however, are unknown.

Here, we will focus on the first two questions by investigating the $c(2\times 2)$ to $(2\sqrt{2}\times\sqrt{2})R45^\circ$ transition using DFT calculations. In Section II, the computational unit cells, set-up, and procedures are presented. In Section III, we demonstrate that the $c(2\times 2)$ to $(2\sqrt{2}\times\sqrt{2})R45^\circ$ transition is necessary for subsequent Cu₂O formation using both energetic and structural arguments. In Section IV, we predict the energy barriers for copper atom ejection and diffusion during the $c(2\times 2)$ to $(2\sqrt{2}\times\sqrt{2})R45^\circ$ transition. The results are used to propose a mechanism by which the missing row reconstruction occurs.

II. CALCULATION METHODOLOGY

We perform the DFT calculations using the Vienna Ab-initio Simulation Package (VASP),^{21–25} which uses a plane-wave basis set.^{23,25} We use ultra-soft pseudo potentials, the PW91 generalized gradient approximation,²⁶ and a 350 eV plane-wave energy cutoff. The $p(2\times 2)$, $p(2\sqrt{2}\times\sqrt{2})$, $p(2\sqrt{2}\times 2\sqrt{2})$, and $p(4\times 4)$ unit cells were initially considered. We found that the $p(4\times 4)$ unit cell is required to eliminate size effects brought about by the periodic images. All $p(4\times 4)$ slab structures include 5 copper layers (the bottom layer is fixed) and the vacuum gap size is 11 Å. There are 81 copper and 8 oxygen atoms in the unreconstructed $p(4\times 4)$ unit cell, the biggest that we consider. The k -point mesh is $6\times 6\times 1$ and is generated by the Monkhorst-Pack scheme.²⁷ The k -point mesh, the energy cutoff, and the number of copper layers are chosen based on convergence tests performed for the $p(2\sqrt{2}\times 2\sqrt{2})$ missing-row reconstructed surface, which we reported previously.¹⁹

On-surface coverage [ML]	Sub-surface coverage [ML]	E_S [eV/Å ²]			
		No O ₂	TB	FCC	UFC
0	0	0.184	-	-	-
0.25	0	0.109	0.109	0.118	0.104
0.50	0	0.047	0.053	0.056	0.052
0.75	0	0.047	0.025	0.040	0.037
0.6875	0.0625	0.032	0.024	0.024	0.022
0.75	0.25	-0.027	-0.033	-0.031	-0.029
0.75	0.50	-0.016	-0.029	-0.031	-0.027

TABLE I. Surface-oxide energy, E_S , of unreconstructed $p(4\times 4)$ Cu(100) surfaces relaxed without and with an additional oxygen molecule. For each oxygen coverage, the configuration of surface oxygen atoms is chosen so as to minimize the energy [i.e. $c(2\times 2)$ phase for 0.5 ML oxygen coverage]. The initial positions of the additional oxygen molecule are the top-bridge (TB), fcc hollow (FCC), and unoccupied fcc hollow (UFC) sites [see Fig. 1(a)]. “-” indicates no data. The unit cell area is 106.58 Å².

The stabilities of the relaxed structures described in Section III and IV are compared using the surface-oxide energy, E_S ^{17,19,28}:

$$E_S = \frac{1}{A_{surf}} \left[E_{O/Cu} - N_{Cu} E_{Cu,bulk} - N_O \frac{E_{O_2}}{2} \right]. \quad (1)$$

Here, $E_{O/Cu}$ is the total system energy, $E_{Cu,bulk}$ is the energy of one atom in bulk fcc copper, and E_{O_2} is the energy of an isolated oxygen molecule. N_O and N_{Cu} are the total number of oxygen and copper atoms in the system and A_{surf} is the unit cell surface area. Because the surface-oxide energy is normalized by the unit cell area, it can be used to compare surfaces with different unit cell sizes. A spin-polarized DFT calculation is used to obtain E_{O_2} . Spin-averaged calculations are used for all other calculations.

To investigate the ejection of copper atoms and their subsequent diffusion during the $c(2\times 2)$ to $(2\sqrt{2} \times \sqrt{2})R45^\circ$ transition, the climbing image nudged elastic band (NEB) method is applied.^{29–32} The NEB method is a computational approach for finding the minimum energy path between specified initial and final equilibrium states. To specify the initial and final states, separate single-point DFT calculations are performed to ensure relaxed structures. We use five images between the initial and final states.

III. OXYGEN-INDUCED SURFACE RESTRUCTURING ON UNRECONSTRUCTED Cu(100) SURFACES

To determine if the missing-row reconstruction is a necessary state in the early stages of Cu(100) oxidation, we will investigate the stabilities and structural changes of unreconstructed Cu(100) surfaces exposed to additional oxygen molecules. We previously performed a similar study on reconstructed surfaces.¹⁹ To examine the changes of surface stability and structure as the oxygen coverage increases, it is not sufficient to only consider an initial oxygen coverage of 0.5 ML, as done previously.^{13,18} We therefore relaxed unreconstructed Cu(100) surfaces at 0.25, 0.5, and 0.75 ML oxygen coverages with an oxygen molecule located at the initial positions shown in Fig. 1(a). Although an oxygen coverage of 0.75 ML is not observed by experiments, we believe that it can exist locally.

We previously used DFT calculations to predict the energy barriers for oxygen embedment into unreconstructed surfaces. For oxygen coverages of 0.25 ML, 0.5 ML, and 0.75 ML, the energy barriers are 2.65, 2.37, and 0.49 eV.¹⁷ Based on these results, we will only consider subsurface oxygen for 0.75 ML oxygen coverage. For the sub-surface site, we use the octahedral site on the second copper layer, as shown in Fig. 1(b).

As presented in Table I, at 0.25 and 0.5 ML oxygen coverages, an extra oxygen molecule causes the surface-oxide energy [Eq. (1)] to increase except for one case (0.25 ML, UFC), where there is a slight decrease. For an oxygen coverage of 0.75 ML, however, the surface-oxide energy of surfaces with an oxygen molecule (TB, FCC, and UFC) is smaller than that of the surface without an oxygen molecule (No O₂). The surface-oxide energy decreases (i.e., the stability increases) because of the surface restructuring induced by the oxygen molecule. For on-surface coverage of 0.6875 ML, one of the surface-adsorbed oxygen atoms at 0.75 ML oxygen coverage was placed into the sub-surface region. The surface-oxide energy of this structure is smaller than that of 0.75 ML, indicating that sub-surface oxygen contributes to the structural stability. The smallest surface oxide energy is found for an on-surface coverage of 0.75 ML and a sub-surface coverage of 0.25 ML and the oxygen molecule initially at the TB site. We note, however, that all cases with 0.25 ML subsurface oxygen have a much smaller surface oxide energy than those without.

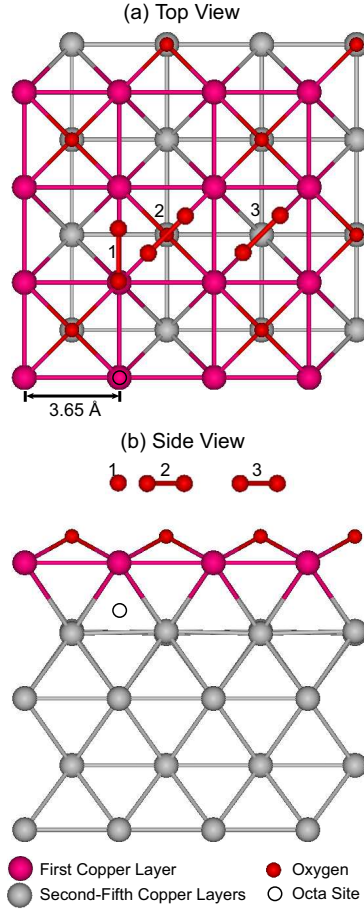


FIG. 1. Initial positions of the oxygen molecule on the unreconstructed Cu(100) surface before structural relaxation. (a) Top and (b) side view of the unreconstructed $p(4\times 4)$ unit cell at 0.5 ML oxygen coverage. The initial positions are labeled: 1. Top-bridge (TB), 2. Fcc hollow (FCC), and 3. Unoccupied fcc hollow (UFC). There are 16 octahedral (octa) sites in sub-surface region, one of which is shown.

After the surface restructuring on the unreconstructed Cu(100) surfaces at 0.75 ML oxygen coverage with or without sub-surface oxygen, the top copper layer is elevated and tetrahedral copper-oxygen structures exist. The Cu-O-Cu and O-Cu-O angles range from 93.18° to 132.15° and the Cu-O bond lengths range from 1.883 Å to 2.388 Å. These tetrahedral structures do not have the characteristics of Cu₂O [our DFT-predicted (PW91) Cu-O-Cu and O-Cu-O bond angles are 109.471° and 180° , and the Cu-O bond length is 1.849 Å]. We also added two oxygen molecules to the unreconstructed surface at 0.75 ML oxygen coverage, but no Cu₂O-like structures were produced. In contrast, we previously showed that surface restructuring induced by an additional oxygen molecule on the missing-row reconstructed Cu(100) surface can produce Cu₂O-like structures with comparable bond angles and lengths to that of Cu₂O when there is sub-surface oxygen.¹⁹

Based on these results and those presented in our previous report,¹⁹ there are two potential oxidation paths starting from the $c(2\times 2)$ phase (see Fig. 2). The first path is through the unreconstructed surfaces at an on-surface coverage of 0.75 ML with subsurface oxygen followed by further oxygen exposure. The second path is through missing-row reconstruction at an on-surface oxygen coverage of 0.5 ML with subsurface oxygen followed by further oxygen exposure. The surface-oxide energy eventually decreases along both paths, but the magnitude of the drop is bigger through the missing-row reconstruction path (-0.149 eV/Å²) than through the unreconstructed path (-0.080 eV/Å²). This result indicates that the missing-row reconstructed path enhances the structural stability more than the unreconstructed path. Previous investigations did not capture this result because they fixed the oxygen coverage at 0.5 ML.^{13,18} Based on these energetics and structural arguments, we believe that the missing-row reconstruction is a highly probable step for Cu₂O nucleation during Cu(100) oxidation.

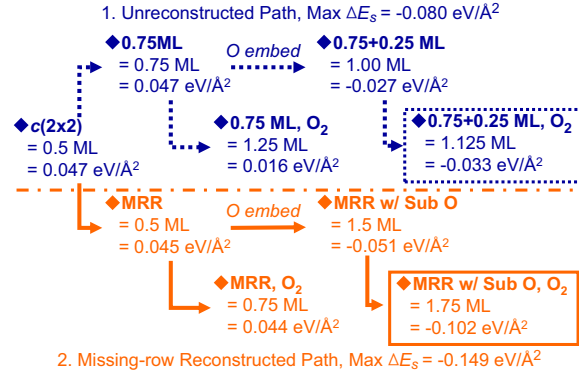


FIG. 2. Potential oxidation paths on the unreconstructed and missing-row reconstructed Cu(100) surfaces. The surface-oxide energies (E_S) are calculated from the $p(4 \times 4)$ unit cell for the unreconstructed path and from the $p(2\sqrt{2} \times 2\sqrt{2})$ unit cell for the missing-row reconstructed path.¹⁹ The surface-oxide energies are presented in Table I for the unreconstructed path. “0.75+0.25 ML” indicates an on-surface coverage 0.75 ML and a sub-surface coverage 0.25 ML. For the missing-row reconstructed path, “MRR” denotes the missing-row reconstructed Cu(100) surface and “MRR w/ Sub O” denotes the missing-row reconstructed Cu(100) surface with sub-surface oxygen. The structures with an oxygen molecule are denoted with O_2 .

IV. $c(2 \times 2)$ TO $(2\sqrt{2} \times \sqrt{2})R45^\circ$ TRANSITION

A. Copper atom ejection

To investigate the energetics and kinetics of the copper ejection, we will propose a set of potential paths and then compare their energy barriers. The initial (A) and final positions (B, C, and D) of the copper atom in the three possible initial ejection paths from the $c(2 \times 2)$ phase are shown in Figs. 3(a) and 3(b). Relaxed configurations of these structures are used in the NEB calculations. The energetics are shown in Fig. 3(c) and reported in Table II. The energy barriers are comparable, ranging from 1.92 eV (A \rightarrow B) to 2.12 eV (A \rightarrow D). We note that the B site lies on what would be the missing row. The only relevant next event is therefore a diffusion to a C or D site, which is discussed in Section IV B. The magnitudes of these barriers are comparable to the activation energy of Cu_2O formation on the Cu(100) surface (1.4 ± 0.2 eV)³³ and to the activation energy for Ag on the Ag 1ML/Mo(100) surface (2.5 eV).³⁴

Once one copper atom has been ejected, the question arises as to what happens next. Does a second copper atom eject while the first is still nearby? Or, does the first atom diffuse away before the second atom ejects? Or, can two copper atoms eject at the same time? We investigated these possibilities using the ejection paths shown in Figs. 4(a)[ejection with vacancy and adatom (w/ V&Ad)], 4(b)[ejection with vacancy (w/ V)], and 4(c)[coordinated ejection ($\times 2$)]. The energy barriers are provided in Table II. The energy barriers of all the A \rightarrow D paths are similar. We believe that the A \rightarrow D paths are not affected by the adatom or vacancy because they all go over an oxygen atom. Large structural changes result, which supersede any effect of the adatom or vacancy. When the first ejected copper atom stays at the C site (on top of the nearest-neighbor copper atom) and the second copper atom ejects (A \rightarrow C w/ V&Ad), the energy barrier decreases from 1.95 eV to 1.41 eV. The initial state to final state energy difference (E_{diff}) of the A \rightarrow C w/ V&Ad ejection is much smaller than those of the other ejection paths (see Table II). In the final state of the A \rightarrow C w/ V&Ad ejection, an O-Cu-O-Cu-O chain is found along the missing-row direction, which is not found in the other cases. If the first ejected copper atom diffuses away (A \rightarrow C w/ V), the energy barrier for the second copper ejection near the vacancy decreases to 1.66 eV. These results suggest that once one copper atom is ejected through any of the three initial paths, many copper atoms will soon follow on A \rightarrow C paths. The continuous ejection of an entire row is consistent with experimental observations.^{1,2,6}

The coordinated ($\times 2$) and non-coordinated with vacancy and adatom ejections (A \rightarrow C followed by A \rightarrow C w/ V&Ad) ejections lead to the same final structure. As shown in Fig. 5(a), there are two energy barriers for the non-coordinated ejection and one energy barrier for the coordinated ejection. To determine which event is more probable, we use transition state theory (TST), a theoretical method for calculating the transition rate between two equilibrium states using thermodynamics, kinetic theory, and statistical mechanics.^{35,36} The transition rate can be calculated under the harmonic approximation as

$$k_{path}^{TST,H} = \nu_o \cdot \exp \left[-\frac{E_{barrier}}{k_B T} \right], \quad (2)$$

where ν_o , k_B , and T are the atomic vibrational frequency, the Boltzmann constant, and temperature.³⁷ We take ν_o

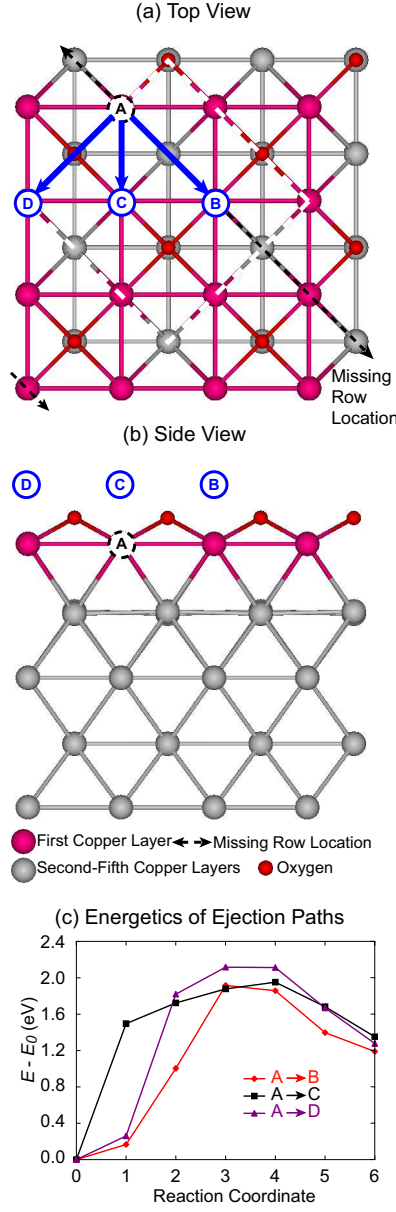


FIG. 3. (a) Top view and (b) Side view of the $p(4 \times 4)$ unit cell showing the initial (A) and final positions (B, C, and D) for copper ejection (the structures shown here are unrelaxed). For reference, the $p(2\sqrt{2} \times 2\sqrt{2})$ unit cell is contained by the white dashed line in (a). (c) Energetics of copper ejection (E = image energy, E_0 = energy of image 0), see Table II.

to be $1.0\text{E}+13$ [Hz], the typical period of an atomic vibration.³⁸ The transition rates of the non-coordinated ($A \rightarrow C$ followed by $A \rightarrow C$ w/ V&Ad) and coordinated [$(A \rightarrow C) \times 2$] ejections are $k_{A \rightarrow C}^{TST,H} \cdot k_{A \rightarrow C \text{ w/V\&Ad}}^{TST,H}$ and $k_{(A \rightarrow C) \times 2}^{TST,H}$, and are plotted versus temperature in Fig. 5(b). The most probable ejection mechanism changes from the coordinated ejection to the non-coordinated ejection at 344 K for the $A \rightarrow C$ paths and at 356 K for the $A \rightarrow D$ paths (not shown). Experimental observations of Cu(100) oxidation have all been done at temperatures higher than 450 K.^{2,6,14,39} Our results suggest that the missing-row reconstruction observed in these experiments is produced by non-coordinated ejections.

Based on the results presented in this section, we believe that the missing row forms through $A \rightarrow C$ ejections once the initial copper atom has ejected. In the next section, we will investigate the subsequent diffusion processes.

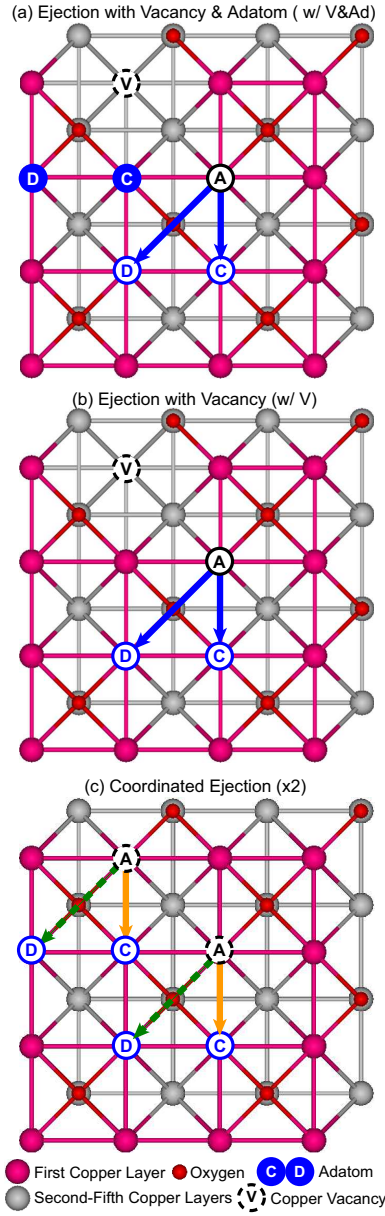


FIG. 4. Three possibilities for the second copper ejection: (a) with vacancy and adatom (w/ V&Ad), (b) with vacancy (w/ V), and (c) coordinated ejection (two neighboring copper atoms eject at the same time, $\times 2$). The energy barriers are provided in Table II.

B. Copper atom diffusion

We now examine the copper diffusion events that will follow the copper ejection, again using the NEB method. All the energy differences and barriers are provided in Table III. Because the ejection barriers for the first ejection are comparable for all three paths, we also investigate diffusion from the B and D sites. As shown in Fig. 6(b), there are four distinct diffusion paths ($B \rightarrow B$, $B \rightarrow C$, $B \rightarrow D$, and $D \rightarrow C$). Note that $D \rightarrow D$ and $D \rightarrow B$ are equivalent to $B \rightarrow B$ and $B \rightarrow D$. To investigate the diffusion away from C sites [see Fig. 4 and Table II], there are four diffusion paths ($C1 \rightarrow I$, $C1 \rightarrow II$, $C2 \rightarrow II$, $C2 \rightarrow III$), as shown in Fig. 6(a). We study the $C2 \rightarrow I$ path but found that the copper adatom at the C1 site returned to V1 because of the periodicity of the computational cell. We also investigated copper diffusion on the perfect $c(2 \times 2)$ phase as shown in Fig. 6(c) (paths α , β , and γ).

To increase the probability of the second copper ejection, as discussed in Section IV A, a copper atom needs to be at a C site. Although a copper atom may initially eject to a B or D site, it can diffuse to a C site through $B \rightarrow C$ or $D \rightarrow C$. The energy barriers of the $B \rightarrow C$ and $D \rightarrow C$ diffusions are smaller than all the ejection barriers and the

Index	E_{diff}	$E_{barrier}$
	[eV]	[eV]
A→B	1.19	1.92
A→C	1.35	1.95
A→C w/ V&Ad	0.62	1.41
A→C w/ V	1.58	1.66
(A→C)×2	1.97	2.47
A→D	1.28	2.12
A→D w/ V&Ad	1.33	2.03
A→D w/ V	1.28	2.12
(A→D)×2	2.60	3.23

TABLE II. Energy difference, E_{diff} , and energy barrier, $E_{barrier}$, for the copper ejection paths shown in Figs. 3(a), 4(a), 4(b), 4(c), and 5(a).

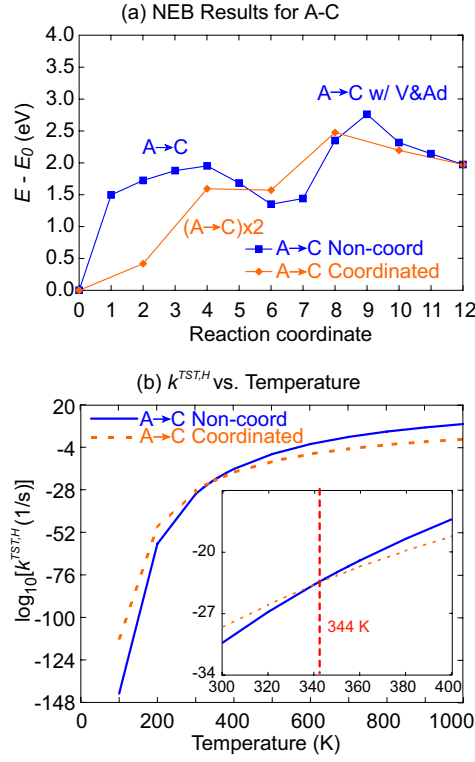


FIG. 5. Comparing the energetics of coordinated and non-coordinated copper atom ejection for the A→C path. (a) Reaction pathways. (b) Transition rates vs. temperature. The energy barriers are provided in Table II. The non-coordinated ejection is more probable than the coordinated ejection at temperatures higher than 344 K.

other diffusion barriers [see Tables II and III], such that there will be a source of atoms available to promote further ejection.

From the C sites, the C1→II path has, by far, the smallest energy barrier (0.41 eV). The C2→III path has a much higher energy barrier because the diffusion is over an oxygen atom (this barrier may also be affected by the periodic image of V1). Although these energy barriers may be influenced by our computational limitations (i.e., the periodicity of unit cell), the energy barrier of the C1→II path is clearly smaller than the others. The C1→II path also has a negative energy difference (E_{diff}), indicating that the copper diffusion along C1→II path is energetically favorable. One possible explanation for this result is that in the final state of the C1→II path, there are two copper atoms at the nearest-neighbor distance (i.e., at the II and C2 sites), leading to a low-energy Cu-Cu cluster. We can thus choose the C1→II path as the most probable diffusion path following A→C ejections.

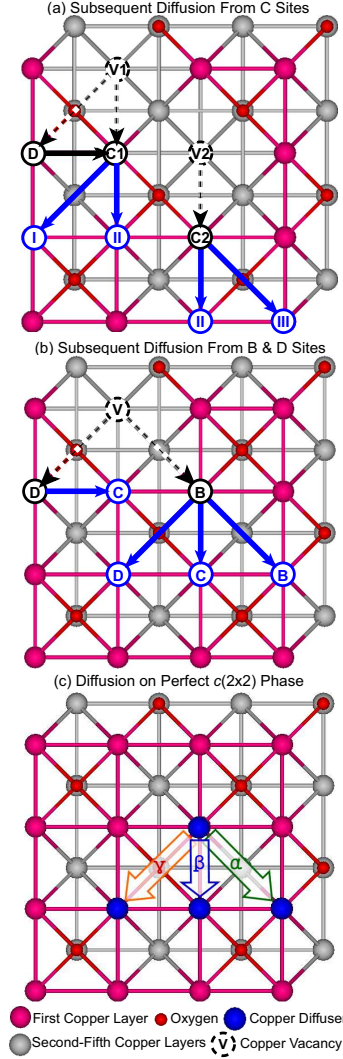


FIG. 6. (Color online) Copper diffusion paths following the copper ejection from (a) C sites and (b) B and D sites. “V” is the copper vacancy, which is the original location of the ejected copper atom. The dashed arrows are the ejection paths and the solid arrows are the diffusion paths. (c) Copper diffusion paths (α , β , γ) on the perfect $c(2\times 2)$ phase. Path γ is over an oxygen atom. There is no oxygen atom along path α .

If we ignore the copper vacancy [V in Fig. 6(b)], the $B \rightarrow B$, $B \rightarrow C$, and $B \rightarrow D$ paths are equivalent to the α , β , and γ paths on the $c(2\times 2)$ phase [see Figs. 6(b) and 6(c)]. The energy barriers for $B \rightarrow B$ and $B \rightarrow C$ are within 0.03 eV of those for the α and β paths (i.e., the vacancy does not play a role). The $B \rightarrow D$ and γ paths, however, have a 0.23 eV difference in their energy barriers. In the $B \rightarrow D$ path, the vacancy breaks the symmetry of the surface, leading to the energy barrier difference.

On the perfect $c(2\times 2)$ phase, the β path has the smallest barrier, 0.55 eV, which is comparable to copper diffusion barriers on the clean Cu(100) surface measured from experiment (0.36 ± 0.03 eV)³⁴ and predicted from a previous DFT study (0.53 eV).⁴⁰ This result indicates that the mobility of a copper adatom near the missing row is similar to that on the clean and $c(2\times 2)$ oxygen-covered Cu(100) surfaces. The $c(2\times 2)$ phase can thus play an important role as a copper diffusion channel, consistent with the experimental findings of Lahtonen et al.¹⁶

C. Most Probable Paths

Although we did not consider all possible ejection and diffusion paths, we tried to follow a logical sequence of these events. In summary, likely sequences of copper ejection and diffusion are shown in Figs. 7(a) and 7(b). In the path shown in Fig. 7(a), a copper atom ejects from A to B, then diffuses to C, and finally diffuses away from the

Path	E_{diff} [eV]	$E_{barrier}$ [eV]
C1→I	0.58	0.99
C1→II	-0.59	0.41
C2→II	0.72	0.87
C2→III	0.33	1.52
D→C	0.07	0.56
B→B / D→D	0.09	0.64
B→C	-0.13	0.52
B→D / D→B	0.00	0.97
Perfect $c(2\times 2)$ Phase		
α	0	0.63
β	0	0.55
γ	0	0.74

TABLE III. Energy difference, E_{diff} , and energy barrier, $E_{barrier}$, for copper diffusion paths during the transition from the $c(2\times 2)$ to the missing-row reconstructed Cu(100) surface. The copper diffusion paths are shown in Figs. 6(a) and 6(b) for diffusion following the copper ejection and in Fig. 6(c) for diffusion on the perfect $c(2\times 2)$ phase.

vacancy through the β diffusion path on the perfect $c(2\times 2)$ phase. In the path shown in Fig. 7(b), there are two ejected copper atoms. The first copper atom ejects from A1 to C1 and stays there, decreasing the energy barrier for the second copper atom ejection (or, another copper atom can diffuse to C1). With the copper adatom on C1, the second copper atom ejects from A2 to C2. Finally, the first copper atom diffuses from C1 to II. The results shown in Fig. 7(c) describe the energy surface that the ejected copper atom goes through in these two paths. The energies of the final states are much bigger than that of the initial state [the $c(2\times 2)$ phase] because the NEB method must be applied to initial and final states that include the same number of atoms (i.e., the ejected copper atoms from the missing-row remain in the unit cell). To check if our results are reasonable, we removed copper atoms one-by-one from a potential missing row on the $c(2\times 2)$ phase. The surface-oxide energy decreased and converged to the value for the missing-row reconstruction, indicating that the energy differences between the initial and final states shown in Fig. 7(b) are induced by the limitation of NEB method.

V. SUMMARY

We used DFT calculations to determine if the missing-row reconstruction is necessary for Cu_2O formation on the Cu(100) surface and to investigate the kinetics and energetics of copper ejection and diffusion during the missing-row reconstruction.

In Section III, oxygen molecule-induced surface restructuring on unreconstructed Cu(100) surfaces was investigated. The results were compared to similar calculations on the missing-row reconstructed Cu(100) surface. The surface-oxide energy decrease is bigger through the missing-row reconstruction than through the unreconstructed surface. The Cu_2O -like structures that we previously observed on the reconstructed surface are not observed on the unreconstructed Cu(100) surfaces. These results led to the conclusion that the missing-row reconstruction is a necessary step in the formation of Cu_2O .

In Section IV A, we investigated copper ejection paths using the NEB method. We found that the most probable route to the missing-row reconstruction is the successive ejection of copper atoms to top sites on the nearest-neighbor copper atoms (C site). The presence of a copper adatom on the C site was found to reduce the energy barrier for the next ejection by 0.54 eV. In Section IV B, we showed that diffusion away from the C site is comparable to that on the $c(2\times 2)$ phase. This finding indicates that the $c(2\times 2)$ phase can act as a copper diffusion channel. In Section IV C, we summarized the probable ejection and diffusion paths.

After the missing-row reconstruction, Cu(100) oxidation proceeds with oxygen embedment,¹⁷ copper ad-layer formation,²⁰ and copper and copper vacancy exchange (order-disorder transition).¹⁴ Energy barriers for the oxygen embedment and the copper-vacancy exchange are available from previous investigations.^{14,17} In the future, these energy barriers and those calculated here could be used in kinetic Monte Carlo simulations^{41–45} to investigate length and time scales not accessible with DFT calculations.

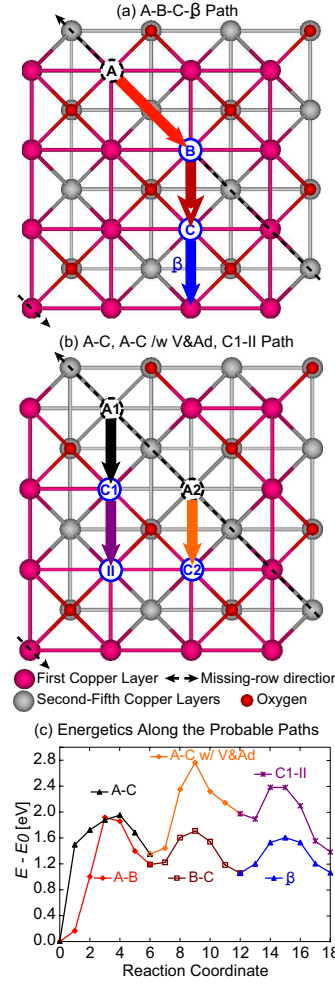


FIG. 7. (Color online) Probable copper ejection and diffusion paths during the transition from $c(2 \times 2)$ to $(2\sqrt{2} \times \sqrt{2})R45^\circ$ on the Cu(100) surface (the original position of the ejected copper atoms are indicated by dashed circles). (a) $A \rightarrow B \rightarrow C \rightarrow \beta$ path, and (b) $A1 \rightarrow C1 \rightarrow A2 \rightarrow C2$ w/ V&Ad- $C1 \rightarrow II$ path. Note that the β path can be perpendicular to the β path shown in (a). (c) NEB results for each path.

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