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## Theoretical study on the structure of Cu(110)- $p2 \times 1$ -O reconstruction

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**Abstract.** The empirical tight-binding molecular dynamic simulations on the Cu(110) surface with an oxygen coverage of 0.5 ML (monolayers) are performed at room temperature. The calculated structures are in good agreement with the results obtained by various experiments. It is shown that the atomic and electronic structure can be calculated reasonably with the present kind of tight-binding model and repulsive potentials. The dynamic studies on the formation of added rows and buckled rows are also included.

### 1. Introduction

The Cu(110) surface covered with oxygen has been intensively studied. This is not only because this system has been a well known model system in surface science [1], but also because studies on the O/Cu system can provide helpful insights into two-dimensional peculiarities of the Cu–O bonding which is relevant to the high- $T_C$  copper oxide superconductors.

Originally, Ertl [17] initiated the studies on the oxygen covered Cu(110) surface and showed that oxygen atoms were absorbed on the Cu(110) surface. The structure of Cu(110) covered with oxygen has been studied extensively using various experimental techniques, such as impact collision ion scattering spectroscopy (ICISS) [2, 23], near-edge extended x-ray absorption fine structure (NEXAFS) [3], surface x-ray diffraction (XRD) [4], LEED [5, 15], tensor LEED (TLEED) [24], scanning tunnelling microscopy (STM) [6, 26], high resolution electron microscopy (HREM) [7], He diffraction [19], angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) [8] and angle-resolved inverse photoemission spectroscopy (ARIPS) [9]. There are also some theoretical methods adopted in this system, including the *ab initio* molecular orbital approach [10], the effective-medium theory [11], the full potential linearized augmented plane wave method (LAPW) [12], first principles total energy calculation within the local density approximation (LDA) [18, 22] and the tight-binding method [13, 14]. It is now well established that oxygen chemisorption on Cu(110) surfaces leads to Cu(110)- $p2 \times 1$ -O reconstruction with an oxygen coverage of 0.5 ML.

However, this is still in controversy though a large number of studies have been carried out. Firstly, the understanding of the underlying physical mechanisms of these effects is still far from complete. A historical review of the O/Cu(110) system from the experimental and

theoretical results shows that the equilibrium ( $2 \times 1$ ) phase can be thought of mainly as two kinds of structure. One is the buckled-row (BR) model with every second [001] row shifted outward, and the other is the missing-row (MR) model with every second [001] row absent. The later study also shows an added-row (AR) model. Although AR and MR models are identical at 0.5 ML, the actual mechanism of formation of this structure has been found to be not removing (MR), but adding copper atom rows (AR). AR is more appropriate than MR according to the STM study [20].

Secondly, there also exists divergence on its electronic structure which is closely related to corresponding atomic arrangements. The electronic structure of Cu(110)- $p2 \times 1$ -O has been investigated mainly by APUPS, which has been reported by Didio *et al* [29], Ozawa *et al* [14], Courths *et al* [30] etc. The energy bands reported by the two groups have quantitative agreement except symmetry of states. The order of O 2p states at  $\Gamma$  is given as  $2p_x$ ,  $2p_y$ ,  $2p_z$  with increasing binding energy in [14, 29]. While Courths *et al* [30] identified  $2p_x$ ,  $2p_z$ ,  $2p_y$ , which has reversed the  $2p_y$  and  $2p_z$  states ( $x$ ,  $y$  and  $z$  refer to  $[1\bar{1}0]$ ,  $[001]$  and  $[110]$  axes, respectively). At Y, both of them report an order of  $2p_x$ ,  $2p_z$ ,  $2p_y$  with increasing binding energy. It can be easily seen that Didio *et al* show a cross and hybridization between  $2p_y$  and  $2p_z$  states. Two theoretical approaches, the LAPW calculation by Weimert *et al* [12] and TB calculation by Tjeng *et al* [13] are also used in determining the electronic structure of the Cu(110)- $p2 \times 1$ -O reconstruction. However, the band of MR calculated by Tjeng *et al* has poor agreement with experiments as a whole, although they obtain the two bands crossing between  $\Gamma$  and Y. In addition, their calculation on BR cannot reproduce correctly at  $\Gamma$  the band observed by Didio *et al* [29].

Furthermore, as we know, there are few molecular dynamic (MD) simulation studies on the O/Cu(110) system among various methods, although a careful first principles calculation based on density-functional theory (DFT) [21] has been carried out with surface relaxation only to three Cu layers and a short MD simulation. It is well known that, dynamic study is very important to study the mechanism of reconstruction and can obtain the stable structure by system relaxation.

In many methods for describing the structures and forces, first principles methods such as LDA give a very accurate and reliable results. However, they require a great computational workload for larger systems. Thus, they have been applied only to limited small-structure units. Moreover, it is also quite difficult to trace the dynamical process of the system for longer periods of time with these methods.

We therefore adopt the empirical tight-binding molecular dynamics (ETBMD) scheme to study the structure of the O/Cu(110) system in this work. In the TB scheme, the procedure of generating a Hamiltonian can be simplified by parametrization [16]. Furthermore, the Cu d-d interactions are included in this paper which have been ignored in most of the TB models for Cu-O systems [13, 14]. This made the method more reliable, accurate and applicable to larger systems.

Recently, we have studied extensively the structural parameters of the Cu(110)- $p2 \times 1$ -O reconstruction [26] and the dynamic course of the formation of the Cu(110) surface reconstruction [27]. Our aim in the present work is first to study the formation conditions and course of the AR and BR models using the molecular dynamics method. Then, a TB calculation on the band structure of the AR reconstruction obtained by the above MD relaxation is performed, especially on whether the oxygen-derived bands cross or not. In MD simulations, generally speaking, in contrast to experiments, the features of the system can be investigated under well defined conditions. As a result, stable structures can be found easily.

## 2. Empirical TBMD simulation method

TBMD simulation is a method that incorporates quantum mechanical effects into the MD simulation through explicit evaluation of the electronic structure of the system at each MD step [5]. The tight-binding Hamiltonian involving ionic motion can be written as

$$H = \sum_I \frac{\Phi_I^2}{2m} + \sum_n^{\text{occupied}} \langle \psi_n | H_{TB} | \psi_n \rangle + \sum_{I>J} \phi(r_{IJ}). \quad (1)$$

Here the first term is the kinetic energy of ions and the second term represents the electronic energy of the parametrized TB Hamiltonian. The third term is a pairwise potential of ion–ion repulsive interactions. The calculation is based on a two-centre orthogonal Slater–Koster TB method [25], taking into account offsite matrix elements up to the second nearest neighbours. The present calculation uses 3d, 4s and 4p orbitals of copper and the 2s, 2p orbitals of oxygen as basis functions which are orthogonal. The TB parameters for the Cu–Cu and Cu–O interactions are adopted respectively from the report [13] and [14] which have been adjusted to the ARUPS results carefully. The popular exponential scaling [31] is adopted.

The next step is to calculate the forces on each atom. The force is calculated by taking the derivative of the total potential energy with respect to each ionic position.

$$F_I = - \sum_{J,n} \left\langle \varphi_{J,n} \left| \frac{\partial H_{TB}}{\partial r_{IJ}} \right| \varphi_{J,n} \right\rangle - \sum_{I>J} \frac{\partial \phi(r_{IJ})}{\partial r_I} \quad (2)$$

where the first term is called the Hellmann–Feynmann force, which is calculated from the orthogonality of the TB wavefunction, and the second term expresses the pairwise repulsive interaction. Here, it is chosen to be of the form

$$\phi_{IJ}(r) = 2B_{IJ} \exp \left[ -\frac{\beta_{IJ}}{2}(r - r_{IJ}^*) \right] - C_{IJ} [1 + \alpha_{IJ}(r - r_{IJ}^*) \exp[-\alpha_{IJ}(r - r_{IJ}^*)]]. \quad (3)$$

$\phi_{IJ}$  are defined uniquely for unique combination of atom types. The repulsive potential used in the present study is empirical and its parameters come from [32], as listed in table 1.

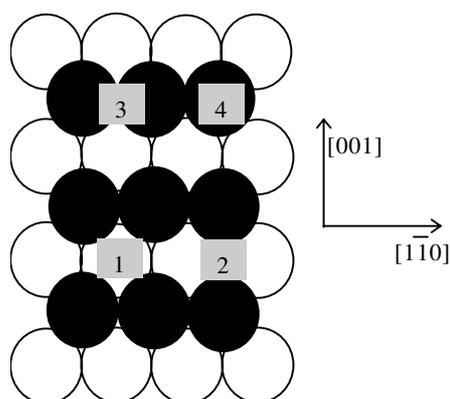
**Table 1.** Parameters in repulsive potential.

	$r^*$ (Å)	$\alpha$ (Å <sup>-1</sup> )	$\beta$ (Å <sup>-1</sup> )	$B$ (eV)	$C$ (eV)
Cu–Cu	3.365 875	1.767 488	2.017 519	0.075 016	0.159 472
O–O	2.005 092	8.389 842	6.871 329	1.693 145	1.865 072
Cu–O	2.358 570	4.233 670	4.507 976	0.154 548	0.094 594

## 3. MD study on the formation of the Cu(110)-p2×1-O reconstruction

### 3.1. AR reconstruction of Cu(110) surface

Using the method described in section 2, MD simulation is performed on the O/Cu(110) system at room temperature. We assume a repeated slab model which is composed of seven Cu layers including one topmost Cu layer and O layer on each side. The dimensions of one layer are 15.30 Å × 14.44 Å in the  $x$  ([1 $\bar{1}$ 0]) and  $y$  ([001]) directions, respectively. Periodic boundary conditions are applied to  $x$  and  $y$  directions with oxygen atoms terminated on the top and bottom layer. Each supercell contains 144 Cu atoms with 12 Cu atoms on each topmost layer and 24 O atoms. MD simulations are carried out at the temperature of 300 K. MD calculations are performed with unit time step of  $2.0 \times 10^{-14}$  s. The band structure energy is evaluated at each MD step by direct diagonalization only at the  $\Gamma$  point.

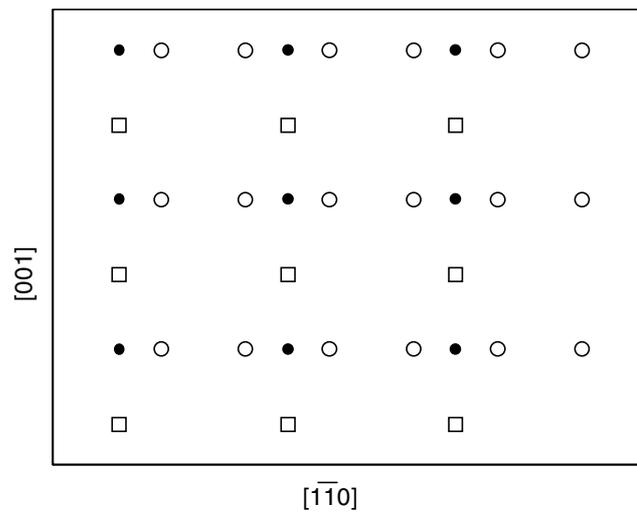


**Figure 1.** Diagram of atomic arrangements on the Cu(110) surface. The solid circles represent the surface copper layer; the empty circles represent copper atoms beneath the surface layer. The numbers 1–4 represent different adsorption sites: 1—hollow (HL); 2—long bridge (LB); 3—short bridge (SB); 4—top (TP).

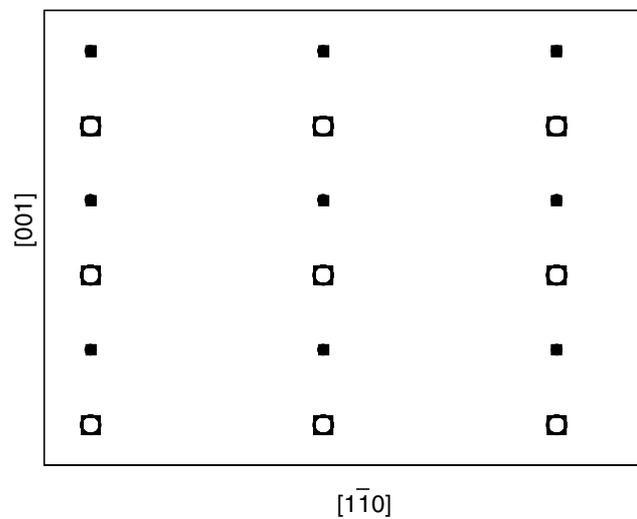
For MD simulations, the original positions of atoms, especially the oxygen atoms and the added copper atoms in the present work, may affect directly the equilibrium structure. For the added copper atoms on the topmost layer, we set up their original structure according to the recent STM observations [28] which have clearly shown that copper atoms migrate from the edges of the Cu(110) terraces before reacting with the exposed oxygen atoms present on the edge of terraces. Therefore, we first put artificially half the number of copper atoms above the surface as the added copper atoms in order to simplify the calculation. Then the surface relaxation is carried out on this system at room temperature. The results show that the added copper atoms occupy the fourfold hollow (HL) sites as shown in figure 1 corresponding to the subsurface below the topmost copper layer which have been proved to be the most possible sites for copper absorptions [21], and the structure we obtain is similar to that reported in [12]. For oxygen atoms, we adopt two more possible absorption sites, the fourfold hollow (HL) and the short bridge along the direction of  $[1\bar{1}0]$  (SLB) site which are determined according to the topmost copper layer, as the original position of oxygen, respectively. We call the two kinds of original structure the ‘HL system’ and ‘LB system’ in this paper, respectively.

**3.1.1. LB system.** The original projected atomic arrangements for the LB system along the  $[110]$  direction are shown in figure 2. The relaxation added copper atoms (empty squares in figure 2) occupy the HL sites of the subsurface, with oxygen atoms (solid circles in figure 2) lying on the SB sites of the topmost copper layer along the  $[001]$  direction. Then the MD simulations are carried out at 300 K. The energy of this system has stabilized only for very short time steps. The results obtained by MD simulation are shown in figure 3, which displays the changes of atomic positions of added copper atoms and oxygen atoms before and after MD relaxation.

From figure 3, we can identify that there are small displacements for both added copper atoms and the oxygen atoms by MD relaxation at 300 K. In fact, the original atomic arrangements of the LB system are the same as the classical AR model as shown in figure 2. This indicates that the AR model of Cu(110)- $p2 \times 1-O$  is very stable at room temperature because all of the atoms in this system shift little from their original positions by MD relaxation. Therefore, it is very difficult to destroy the AR model without strong external forces at room temperature.

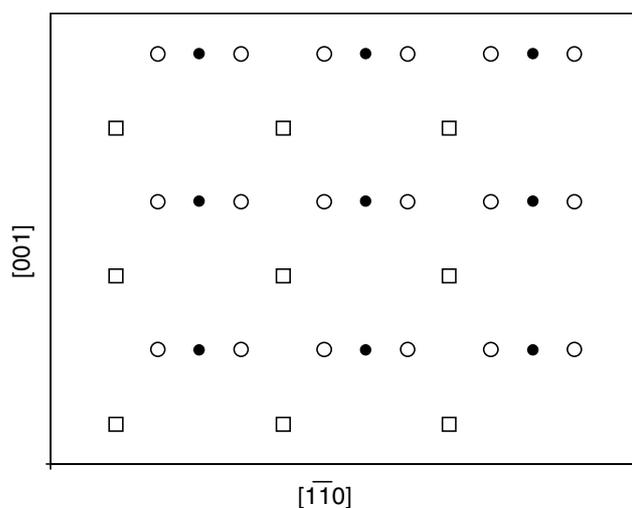


**Figure 2.** Original atomic arrangements for the LB system. Solid circles in SB sites represent oxygen atoms; empty squares in HL sites represent added copper atoms; empty circles represent copper atoms on the subsurface just below the added layer. (It should be noted that the HL and SB sites mentioned above are determined based on the subsurface.)

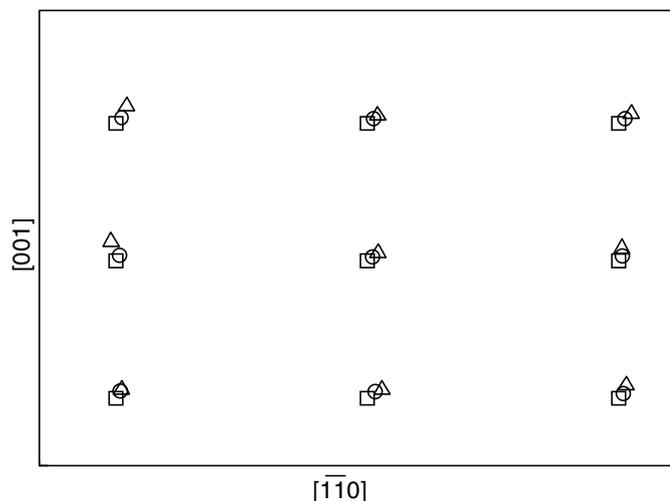


**Figure 3.** The arrangement of added copper atoms and oxygen atoms at room temperature for the LB system. Squares represent the relaxation structure. Circles stand for original LB structure. Solid and empty symbols correspond to oxygen atoms and copper atoms, respectively.

**3.1.2. HL system.** The original projected atomic arrangements for the HL system along the  $[110]$  direction are shown in figure 4. The relaxed added copper atoms (empty squares in figure 4) occupy the HL sites of the subsurface, with oxygen atoms (solid circles in figure 4) lying in the SB sites of the topmost copper layer. In fact, the setup of the LB system is more special than HL system. For the covered oxygen atoms, HL sites which are vacancies with the largest volume in the topmost copper layer and also are the most favourable place for their location. The MD simulations have been performed for 800 time steps to obtain equilibrium



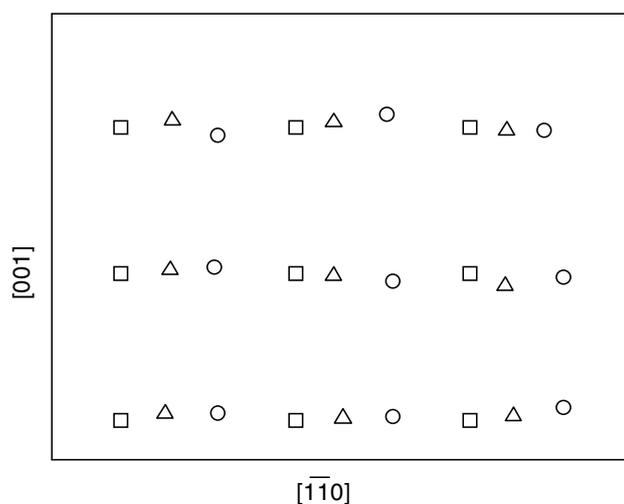
**Figure 4.** Original atomic arrangements of O/Cu(110) for the HL system. Solid circles in SB sites represent oxygen atoms; empty squares in HL sites represent added copper atoms; empty circles represent copper atoms on the subsurface just below the topmost copper layer.



**Figure 5.** The atomic pattern of oxygen atoms on the Cu(110) surface varies with relaxation time for the HL system. The square, circle and triangle in the figure represent the oxygen position at the relaxation step of 0, 400 and 800 respectively.

at 300 K. The results obtained by MD simulation are shown in figures 5 and 6, which display the changes of atomic positions of oxygen atoms and added copper atoms before and after MD relaxation, respectively.

Similarly to the LB system, the oxygen atoms in the HL system shift a little from their original HL sites corresponding to the topmost layer by MD simulation, as shown in figure 5. On the other hand, figure 6 indicates that the added copper atoms move quickly from their original HL sites, then to LB sites, and at last to other HL sites near the positions of oxygen atoms, corresponding to the subsurface, along the  $[1\bar{1}0]$  direction. The AR reconstruction has also been formed at last.



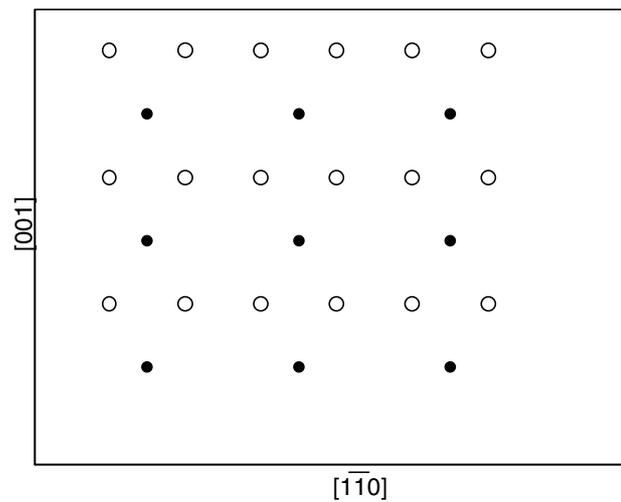
**Figure 6.** The atomic pattern of added copper atoms on the topmost layer varies with relaxation time for the HL system. The square, triangle and circle in the figure represent the position of added copper atoms at the relaxation step of 0, 400 and 800 respectively.

Liem *et al* [21] indicate that the absorption sites for copper atoms in the Cu(110) surface are given in the order of HL, LB, SB and TP in decreasing preference by first principles calculation. In fact, HL sites are also a favourable location for the next layer of copper atoms in bulk material. In this work, we find that the added copper atoms can diffuse easily between HL and LB sites in the troughs parallel to the  $[1\bar{1}0]$  direction at very high speed, which agrees with the first principles calculation [21]. This process is similar with the description of the ‘jump’ mechanism, in which an added atom jumps from one adsorption site to a nearby adsorption site. First principles calculation [27] shows that there exists an energy difference of 250 meV between HL and LB sites. Considering the strong activity of added atoms at room temperature and attractive interactions with the nearby oxygen atoms, the small energy barrier of only 250 meV cannot affect greatly the diffusion, while the diffusion of added copper atoms along the  $[001]$  direction has been greatly limited by the strong energy barrier of 1 eV between HL and SB sites. Therefore, we obtain that the pathway along the  $[1\bar{1}0]$  direction is preferable and added atoms can diffuse easily from one site to another which is just like a ‘jump’ by MD simulation at room temperature.

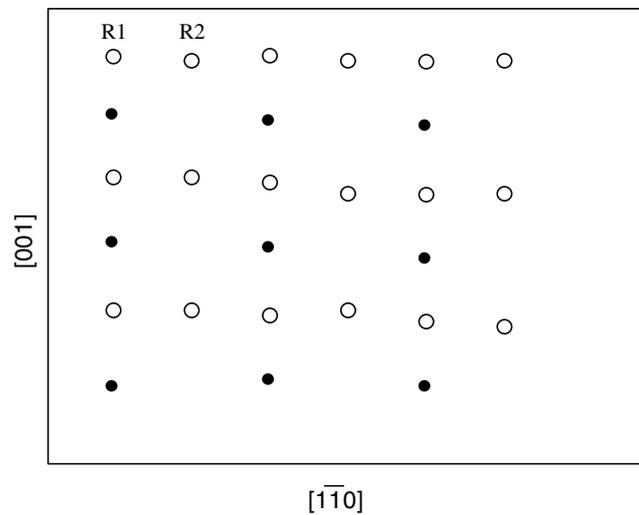
For oxygen atoms, it is very difficult for them to shift because of the strong interactions with copper atoms in both subsurface and topmost layers. In addition, the most favourable sites for their location, HL sites, also limit their diffusion on the surface in the present case.

### 3.2. BR reconstruction of Cu(110) surface

In order to compare with the above mentioned case, we present a model which has oxygen atoms covering the normal Cu(110) surface without added copper atoms on the surface in this section. We call this the PO system in this work. The original projected atomic arrangements for the PO system along the  $[110]$  direction are shown in figure 7. The copper atoms (empty circles in figure 7) occupy their usual positions on the Cu(110) plane. Then the oxygen atoms (solid circles in figure 7) lie on the HL sites on the copper surface for the reason we mentioned in section 3.1.2. The MD simulations have been performed for 1000 time steps to obtain equilibrium at 300 K. The results obtained by MD simulation are shown in figure 8.



**Figure 7.** The original atomic arrangement on the surface of the PO system. The solid circles stand for oxygen atoms, empty circles for copper atoms.



**Figure 8.** The relaxed atomic arrangement on the surface of PO system after 1000 time steps. The solid circles stand for oxygen atoms, empty circles represent copper atoms.

As shown in figure 8, the copper atoms on the surface diffuse easily along the  $[1\bar{1}0]$  direction. There is little change for the relative positions of copper atoms on the surface, which indicates that the HL sites of surface copper atoms corresponding to the subsurface are very stable for copper atoms at room temperature; while the oxygen atoms relax from original HL sites to LB sites in MD simulations, corresponding to the diffusing copper atoms on the Cu(110) surface. The corresponding surface structure after MD relaxation is just the same as the BR model.

In section 3.1, the similar AR reconstruction is obtained with added copper atoms by MD simulation, though the original positions of oxygen atoms are different in the two systems.

In fact, the difference of the original positions of oxygen brings different structural parameters of the obtained AR reconstruction, which we have studied extensively in [26], recently. According to results of the statistical XRD [4] and our TBMD [26], we conclude that the HL sites of oxygen atoms corresponding to the surface structure are the most possible places for them to locate originally before surface reconstruction. In section 3.2, BR reconstruction but not the AR model was obtained, though we originally put the oxygen atoms in the same place as those in section 3.1.2.

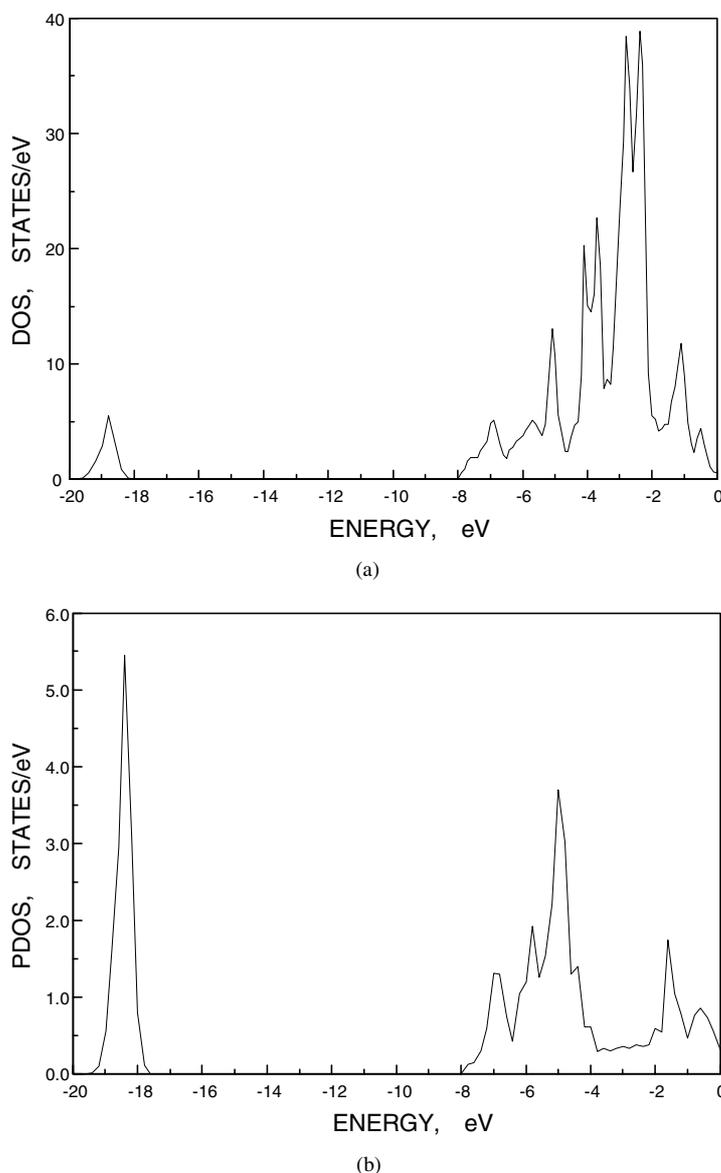
Comparing the descriptions in section 3.1 and section 3.2, the only difference between them is whether the added atoms exist or not. At room temperature, AR reconstruction will be produced with the added copper atoms on the surface; on the other hand, BR reconstruction will be obtained without the existence of added copper atoms. Regarding the above, we conclude that the added copper atoms are essential to the O/Cu(110) surface reconstruction. In another word, the formation of the AR model or BR model depends on the existence of added atoms. In addition, our MD simulation [27] shows that the added copper atoms are more active than the normal atoms on the surface. Thus, the Cu–O–Cu chains can be formed easily with the active added copper atoms. In contrast, the copper atoms on the normal Cu(110) surface without added atoms with lower activities take more time to form Cu–O–Cu chain labelled R1 in figure 8. It should be noted that the nearest-neighbour pure copper rows, labelled R2 in figure 8, cannot disappear but still occupy their HL sites and form the BR reconstruction. However, the AR model has been proved by various methods and the BR model has rarely been obtained in recent years. We consider that this is because the existence of an ideal Cu(110) surface without terraces is mostly impossible at room temperature according to STM observation [20]. STM observation has shown that the real Cu(110) surface at room temperature always exists as many surface terraces ordering step by step. Our MD simulation [27] shows that the copper atoms at the edge of terraces can remove easily from the terrace and become added atoms. Thus, the formation of the BR reconstruction is greatly limited.

#### 4. Electronic properties of AR reconstruction

Our band calculation is based on the AR structure obtained by MD relaxation mentioned in section 3.1.2, whose projected structure along the [110] direction is similar to that shown in figure 2. The topmost copper layer is displaced outward by 0.21 Å from its original place along the [110] direction and the oxygen atoms are located 0.16 Å below the topmost copper layer.

The total density of states for AR reconstruction and the partial density of states for oxygen layer is shown in figures 9(a) and (b) respectively, which is similar to those obtained by LAPW calculation [12]. We first focus on the PDOS for the oxygen atoms. The peak at about  $-19$  eV is due to the O 2s states which contribute little to the bonding. The peak at  $-5$  and  $-1.5$  eV is dominated by O 2p states, which hybridize strongly with Cu 3d states. The strong hybridization between Cu 3d states and O 2p states forms bonding at  $-8$  eV to  $-5$  eV and antibonding states above  $-2$  eV.

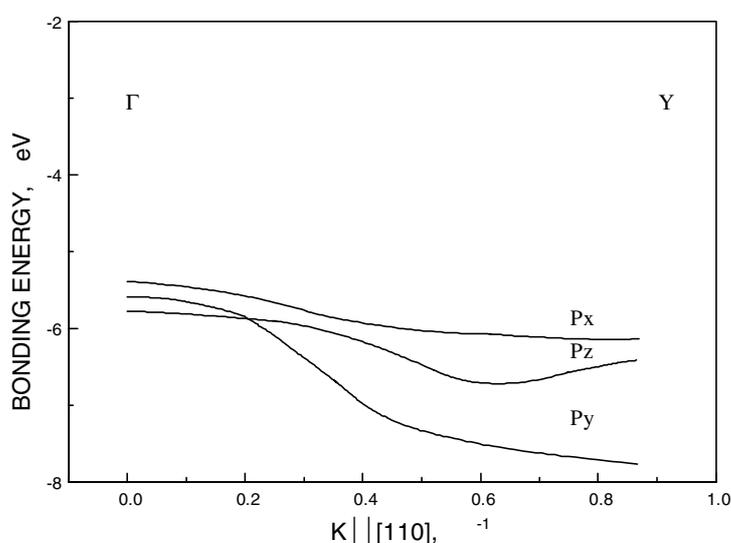
In the present work, we also pay attention to the oxygen-derived 2p bonding band structure along the [001] direction which has been in great controversy. Figure 10 shows the oxygen-derived bonding band structure between  $\Gamma$  and Y, which is in great agreement with the experiments [14]. The  $p_x$  band at  $\Gamma$  is connected with the  $P_x$  band at Y. Between  $\Gamma$  and Y, the  $p_z$  band crosses with the  $p_y$  band. The band order with increasing bonding energy is  $p_x, p_y, p_z$  at  $\Gamma$  and  $p_x, p_z, p_y$  at Y, respectively. Therefore, the TB calculation in this work also reproduces the band crossing of  $p_z$  and  $p_y$  bands which has been found in experiments [14]. In addition, figure 10 also shows that the O  $2p_x$  band disperses fairly little and the O  $2p_y$



**Figure 9.** (a) Total density of states of the O-p( $2 \times 1$ )/Cu(110) AR reconstruction system along the direction of [001]. (b) Partial density of states for the oxygen layer.

band disperses greatly. In the AR model, the O  $2p_y$  orbital and Cu  $3d_{x^2-y^2}$  orbital of the added copper atoms are both directed towards the [001] direction. Thus, the two bands can hybridize very effectively to increase the dispersion of band. Similarly, the small dispersion of the O  $2p_x$  band is ascribed to the weak hybridization between O  $2p$  and Cu  $3d$  along the direction of the  $p_x$  orbital.

In fact,  $p_y$  and  $p_z$  may not cross because their derived states belong to the same irreducible representation of the  $yz$  mirror plane. The necessary condition for band crossing is the existence of interactions between these states. The band structure with no band crossing



**Figure 10.** Plots of the calculated oxygen-derived 2p bonding band structure for the (2 × 1) AR reconstruction along the [001] direction.

calculated by Courths *et al* [30] is based on an isolated and perfect colinear Cu–O–Cu row, and there is no interaction for this ideal model, while the interactions will be present considering both the Cu–O–Cu row and atoms on the subsurface which always interact strongly with the row. Therefore, it is indicated that the function of the atoms on the subsurface just beneath the row cannot be ignored and affects greatly the structure of the surface reconstruction.

## 5. Conclusion

We employed TBMD simulation to examine the formation of Cu(110)-p2 × 1-O reconstruction at room temperature. It is shown that the calculated added-row reconstruction structure is in good agreement with the experimental results.

Furthermore, the buckled-row reconstruction is also obtained by our TBMD simulation. We conclude that the added-row reconstruction will be obtained with the existence of added copper atoms on the surface. While, the buckled-row reconstruction will form with oxygen covering on the normal Cu(110) surface without added copper atoms.

Finally, the band calculation by TB calculation is also performed on the AR reconstruction obtained by MD simulation. The calculated DOS coincides with that calculated by FLAPW [12]. It should be noted that the band crossing between  $p_y$  states and  $p_z$  states is reproduced in this work. In addition, the contribution of atoms on the subsurface to the electronic structure is also focused.

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