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Atomic Relaxations on Cu(210)

Handan Yıldırım and Sondan Durukanoğlu
Department of Physics, Istanbul Technical University, 34469 Maslak, Istanbul,Turkey
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We report the results of calculations for multilayer and atomic relaxations around steps on Cu(210), using many-body interaction potential extracted from the embedded atom method (EAM). Relaxations are found to extend several layers into the bulk with an oscillatory behavior of (-,-,+,-,+,+). Unlike the recent low energy electron diffraction (LEED) data, the calculated multilayer relaxations reveal a nonuniform damping magnitudes in interlayer relaxations. We, furthermore, investigate the local atomic relaxations around steps and trace the changes to the modifications in the associated local force fields, relative to the bulk.

Keywords: Copper, embedded atom method, surface relaxation and reconstruction, vicinal crystal surfaces, surface Structure.

1. Introduction

Studies involving the structure of vicinal or so-called, regularly stepped, or high Miller-index, surfaces have attracted many surface scientists because not only on any real surfaces steps are unpreventably present but also they represent excellent examples of the systems with defects and reduced symmetry. Unlike the flat-low Miller-index-surfaces, vicinal surfaces consist of a periodic array of terraces separated by atomic steps. Existence of these defects (steps) on the surface is expected to alter the local electronic and ionic structures around the steps, thus in turn might lead to modification of the force fields in these vicinities. As a result, atoms near and at the surface are expected to relax to new equilibrium positions which will minimize the energy of the system. Hence, on the stepped surfaces in addition to relaxation of the whole surface layer, local relaxations of the atoms around steps are expected.

Advances in atomic scale experimental techniques, supplemented by enhanced computational power, have led to a surge in the studies of structural properties of high Miller-index (or vicinal) surfaces. Although there exists a variety of possible experimental methods [1], the brunt of experimental data have come from the low energy electron diffraction (LEED) techniques. For example in the recent experimental LEED work, Ismail et al., [2] have studied the structure of Cu(210) and found the oscillation of the interlayer relaxations to be (-,-,+,+,-) with uniformly damping magnitude away from the surface into the bulk. Here - stands for a contraction for interlayer spacing between two consecutive layers, whereas + represents an expansion. However, the LEED observation associated with the uniform damping in magnitudes of multilayer relaxations contradicts the experimental work on Al(210), where a significant interlayer relaxation has been found for the neighboring layers away from the surface into the bulk[3]. In this experimental work for Al(210), the magnitude of interlayer relaxation for d_{34} is found to be larger than d_{23} which is surprising as d_{23} is closer to the surface compared to d_{34}. Similar trend has been reported for the interlayer relaxations of Cu(211) and Cu(511), examples of vicinals of Cu(111) and Cu(100), respectively, with close packed step edges [4]. In addition, in the recent theoretical work on Pd(320)[5], based on the first principles electronic structure method, Makkonen *et al.* have predicted that the magnitude of interlayer separations, relative to the bulk, leads to the following observation: $|d_{45}|>|d_{23}|>|d_{34}|$, where $d_{i,i+1}$ is the percentage wise change, relative to the bulk, in the interlayer spacing between layer i and layer $i+1$.

Let us remind that while an $fcc(320)$ consists of three atomic chains of $fcc(100)$ terraces separated by (100) monoatomic steps, an $fcc(210)$ is a vicinal of $fcc(100)$ with (110) microfacetted steps. One, therefore, can attribute these different characteristics in the multilayer relaxations to the varying geometries of these two separate surfaces. On the other hand in a separate study on the structure of Cu(410)[6], which is in the same family as Cu(210) with a distinction that it

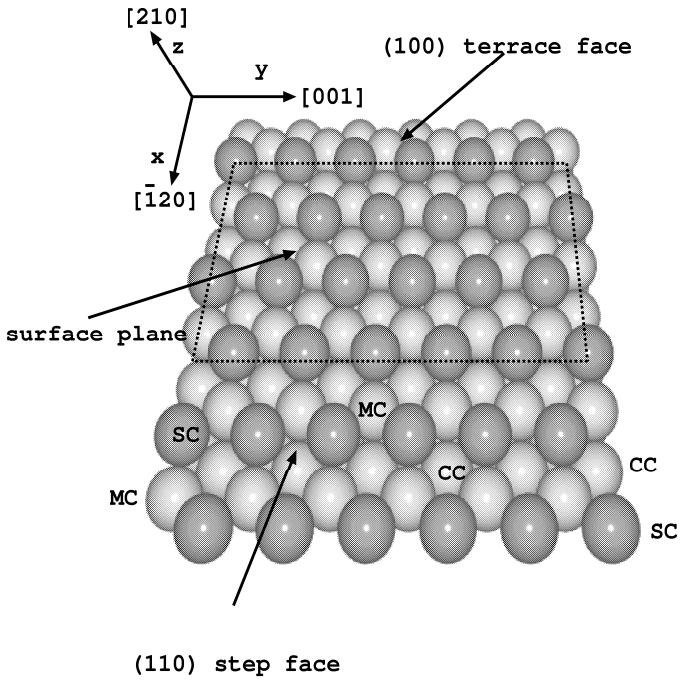

Figure 1. Front view of fcc(210). Here x, y, z are the Cartesian coordinate axes.

has five chains of atoms on a terrace instead of three as it is for Cu(210), Durukanoğlu and Rahman found similar characteristic in multilayer relaxations, with $|d_{56}|>|d_{45}|$ in magnitude. In the view of these reported findings, atomistic calculations on the structure of Cu(210), using realistic many-body interaction potentials, are expected to provide further insights for conceiving the nature of the multilayer relaxation of this specific surface.

In this work, we present a study of multilayer and atomic relaxations of Cu(210), using many-body potentials based on the Embedded Atom Method[7]. Among the issues investigated are multilayer relaxations, local relaxations of atoms around steps, and the changes in the force fields in the vicinitiy of steps relative to the bulk. The paper is organized as follows. While the structural characteristics of the surface with some computational details are presented in Section 2, Section 3 contains the results and discussion. The concluding remarks are presented in Section 4.

2. Surface Geometries and Computational Details

Vicinal surfaces can be obtained by cutting the crystal at an angle away from the lower-index crystal planes (i.e., (110), (100), and (111) planes). We are, in this report, interested in the $fcc(210)$ surface which is a vicinal of $fcc(100)$ created by slicing the crystal at an angle of 26.5^0 away from the (100) plane towards the [010] direction. Our calculations for Cu(210) are performed using a 48-layer super cell which is thick enough so that the top and the bottom surface do not interact. The surface super cell dimensions of $N_x \times N_y$, where N_x is the number of terraces and N_y is the number of atoms along the step direction is chosen as 8x6 (i.e., 8 terraces with 6 atoms along each chain) so as to diminish the size effects in the direction parallel and perpendicular to the step edge. As shown in Fig.1 , x and y lies in the surface plane, being along the line joining the consecutive steps and parallel to the step, respectively, while z is along the surface normal. We also label the surface atoms as step-chain (SC), middle-chain (MC), and corner-chain (CC) atoms as displayed in Fig.1 . In the simulations, periodic boundary conditions are applied along the x and y directions, while no such a constraint is imposed along the z-direction.

To describe the interactions between the atoms in the model system, we use a semi-empirical and many-body type potential based on the Embedded Atom Method. These potentials have so far found to be realiable in the study of Cu flat and vicinal surfaces, in particular [8, 9]. After being constructed in its bulk terminated structure, the system is let relax to its minimum energy (0K equilibrium) configuration, through the standard conjugate gradient method. Atomic force constants are then calculated from analytical expressions for the partial second derivatives of EAM potentials.

3. Results and Discussion

While the broken symmetry normal to the surface, introduced by the existence of the surface, results in relaxations of atomic planes inward or outward perpendicular to the surface (interlayer relaxations), the presence of steps at the surface, breaking the symmetry along the direction perpendicular to the step-edge (x), yields lateral relaxations of the surface atoms (in-plane or reg-

Table 1
Calculated and experimental percentage change in interlayer relaxation $d_{i,i+1}$ for Cu(210). Here $d_{i,i+1} = 100 \times [(z_i - z_{i+1}) - d_b]/d_b$ where d_b is the bulk interlayer spacing and equal to 0.808$\mathring{A}$.

Relaxation	Cu(210)-EAM	Cu(210)-LEED
d_{12}	-12.13%	-11.12±2.0%
d_{23}	-1.29%	-5.68 ±2.3%
d_{34}	+3.07%	+3.83 ±2.5%
d_{45}	-3.38%	+0.06 ±3.0%
d_{56}	+0.41%	-0.66 ±3.5%
d_{67}	+0.82%	
d_{78}	-0.69%	
d_{89}	+0.17%	

istry relaxations). On the other hand, relaxations along the step-edge (y-direction in Fig.1) are forbidden by symmetry. Our calculated percentage interlayer spacing and registries for Cu(210) together with the available LEED data are summarized in Table 1, and 2, respectively. As seen in Table 1, the largest interlayer relaxation occurs for d_{12} as expected, since layer 1 and layer 2 are both exposed to the vacuum (See Fig. 2). Note that such trend in the first interlayer spacing have been reported for several metal vicinal surfaces. In addition, interlayer relaxations are found to extend several succesive layers into the bulk. As it is clear from Table 1, our calculated values for the multilayer relaxations of Cu(210) are in qualitative agreement with the available LEED data. However, contrary to the LEED data, where the measured magnitude of interplanar relaxation is uniformly damped (see Table 1), results from our calculation for the relaxations of interlayer spacing reveal an oscillatory behavior of (-,-,+,-,+) with a nonuniform damping . While the first and the second interlayer spacings (d_{12}, d_{23}) are contracted (-) by 12.13% and 1.29%, respectively, the next interplanar spacing (d_{34}) is expanded (+) by 2.47%, relative to the corresponding bulk interlayer spacings. Note that the percentage change for interlayer spacing d_{34} is larger than that for d_{23}. Such a nonuniform damping trend in multilayer relaxations has also been reported for several other metal vicinal surfaces, including Pd(210) [10] . As for the comparison of our calculated intralayer (in-plane) relaxations for Cu(210) to the LEED data, both the calculated and measured relaxations are found to be consistent with each other within the error bars of the experiment (See Table 2).

We have also examined the changes in the interatomic distances (bond-lengths) of a SC-atom to its nearest neighbors, relative to the bulk values, along the x-, y-, and z-directions and presented our predicted values in Table 3. Evidently, the existence of the surface leads a pronounced shortening in the z-component of the bond-lengths, as expected. The 12.17% shortening in the z-component of the interatomic distance between SC- and MC-atom is followed by a 6.74% contraction and a 3.47% dilation in the same component of bond-lengths of SC-atom to CC-atom and BNN-atom, respectively. In addition, the broken symmetry along the x-direction yields a 4.4% increase in the x-component of the interatomic separation between SC-atom and CC-atom, a 2.9% and 0.7% decrease in the same component of the bond lengths of SC-atom to BNN- and to MC-atom, respectively, as compared to the corresponding bond-lengths components in the bulk.

To have a better understanding of the interlayer relaxations and the change in the interatomic distances between SC-atom and its nearest neighbors, we have also investigated the relaxations of individual atoms at/near the surface and plotted them together with the corresponding layer definitions in Fig. 2. As seen in the figure, among the downward relaxations of the surface atoms, that of SC-atom is pronounced the most. Interestingly, the downward relaxation of SC-atom -towards the remainder of the bulk- is accompanied by a downward relaxation of BNN-atom (layer 4 atom) and an upward relaxation

Table 2
Calculated and experimental percentage change in registry relaxation $r_{i,i+1}$ for Cu(210). Here $r_{i,i+1} = 100 \times [(x_i - x_{i+1}) - r_b]/r_b$ where r_b is the bulk intralayer spacing and equal to 1.616$\mathring{A}$.

Relaxation	Cu(210)-EAM	Cu(210)-LEED
r_{12}	-0.77%	-1.83±3.0%
r_{23}	-1.44%	-2.51±3.2%
r_{34}	+0.74%	+1.68±3.5%
r_{45}	0.00%	-0.48±3.7%
r_{56}	-0.15%	+0.06±4.0%
r_{67}	+0.29%	
r_{78}	-0.07%	
r_{89}	-0.04%	

Table 3
Interatomic distances in $\AA$ along the x-, y-,and z-direction between a step atom and its nearest neighbours for the relaxed and bulk terminated structure of Cu(210).

Atoms	Surface			Bulk		
	d_x	d_y	d_z	d_x	d_y	d_z
SC-MC	1.604	1.807	0.710	1.617	1.808	0.808
SC-BNN	0.784	0.000	2.341	0.808	0.000	2.425
SC-CC	0.844	1.807	1.508	0.808	1.808	1.617

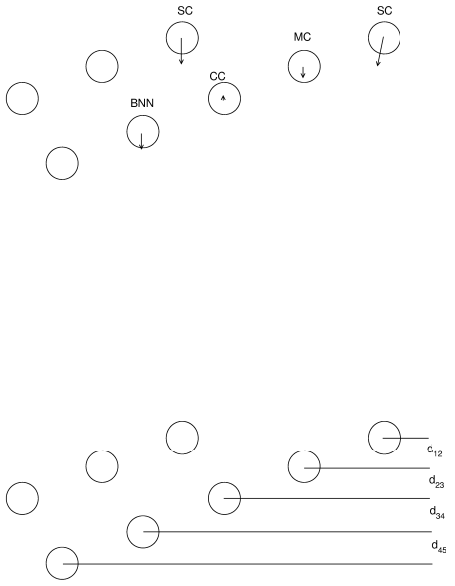

Figure 2. The relaxation patterns of the atom at and near the surface and associated layer definitions for fcc(210).Here the atomic displacements from the bulk terminated positions are magnified by a factor of 20. Arrows indicate the corresponding atomic relaxations.

of CC-atom (layer 3 atom). It is obviously this particular pattern of relaxations that causes the 3.07% expansion for the interlayer spacing d_{34} and 6.74% shortening in the z-component of interatomic distance between SC- and CC-atom. It is also clear from the figure that the contraction in the interlayer separation of d_{23} is due to the downward relaxation of MC-atom (layer 2 atom), coupled with the upward relaxation of CC-atom (layer 3 atom). From the relaxation patterns of surface atoms, we find that the z-component of the bond-length of SC-atom to MC-atom and, correspondingly, the interlayer spacing d_{12} is contracted because the downward relaxation of SC-atom (layer 1 atom) is more pronounced than that of MC-atom (layer 2 atom).

We have also calculated the modifications in the local force fields around the step atoms, as compared to those in the bulk, so that we can better analyze the changes in the atomic distances. The calculated force constant matrices $k_{\alpha\beta}$, where α and β stands for Cartesian components, x, y, z, between the atoms in the vicinity of step, together with those corresponding bulk values are presented in Table 4. The force constant k_{zz} between the SC-atom and MC-atom is found to be stiffened 70%. It is, evidently, this stiffening that yields a contraction in the z- component of the corresponding bond-length. While k_{zz} element of the force constant matrix between BNN- and SC-atom is stiffened 54%, the same force constant matrix element for CC-atom and SC-atom is stiffened 31%. We also observe dramatic effects on off-diagonal elements of the force constant matrices. For example, the k_{zx} between BNN- and SC atom is stiffened 54%. Remember that the k_{zx} between BNN- and SC-atom is the force per unit mass in the z-direction on BNN-atom resulting from unit displacement of SC-atom in the x-direction. So when SC-atom moves along the x-direction during the relaxations process, the BNN-atom experiences a great deal of increase in the z-component of the force due to this particular movement of SC-atom. In addition, we find the k_{zx} element of the force constant matrix for SC- and MC-atom is softened 33%. So as the position of SC-atom is displaced along the x-direction, MC-atom experiences a decrease in the z-component of the force resulting from the SC-atom displacement, which might be the explanation for why MC-atom has a less pronounced z-component relaxation. One must, however, bear in mind that atoms in a solid relax collectively. Therefore, change in a local force field around an atom is not the only factor in describing the relaxation of that particular atom.

4. Conclusions

In summary, we have reported the multilayer and atomic relaxation of Cu(210), and traced these relaxations to the modifications in the local force fields around the steps, and compared

Table 4
Force constant matrices between a step atom and its nearest neighbours for the relaxed surface and the corresponding ones in the bulk for Cu(210).

Atoms		Surface			Bulk		
		x	y	z	x	y	z
	x	-0.798	-0.948	-0.584	-0.735	-0.925	-0.420
SC-MC	y	-0.927	-1.006	-0.647	-0.923	-0.945	-0.462
	z	-0.279	-0.313	-0179	-0.420	-0.462	-0106
	x	-0.159	-0.585	0.459	-0.106	-0.462	0.420
CC-SC	y	-0.599	-1.146	0.990	-0.462	-0.945	0.924
	z	0.599	1.264	-0.960	0.420	0.924	-0.735
	x	-0.155	0.000	-0.857	-0.120	0.000	-0.619
BNN-SC	y	0.000	0.160	0.000	0.000	0.104	0.000
	z	-0.952	0.000	-2.726	-0.619	0.000	-1.771

the calculated multilayer relaxations with recent low energy electron diffraction (LEED) data and available calculations on the relaxation of vicinal surfaces. The most striking feature in the calculated relaxation trend of Cu(210) is pronounced expansion of interlayer distance between the 3^{rd} and the 4^{th} layers which leads to a nonuniform damping magnitude in the multilayer relaxations of Cu(210). Our results on the multilayer relaxation of Cu(210) are in qualitative agreement with the recent LEED data, albeit different magnitudes. From the results of interatomic distances of a step and its nearest neighbors, we find that relaxation in the bond length showed the most shortenings along the z-direction. We also find that the relaxations around the step can be traced to the local force fields modifications in the vicinity of step. The work using *ab initio* electronic calculations is on the way to put our understanding of the nature in atomic relaxations of Cu(210) on a firmer footing.

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