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First principles calculations of relationship between the Cu surface states and relaxations*

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In this paper the relationship between the surface relaxations and the electron density distributions of surface states of Cu(100), Cu(110), and Cu(111) surfaces is obtained by first-principles calculations. The calculations indicate that relaxations mainly occur in the layers at which the surface states electrons are localized, and the magnitudes of the multilayer relaxations correspond to the difference of electron density of surface states between adjacent layers. The larger the interlayer relaxation is, the larger the difference of electron density of surface states between two layers is.

Keywords: surface states, relaxations, first-principles calculation
PACC: 7320A, 3330B

1. Introduction

With the development of nano-science and nano-technology, the scale of all kinds of electronic apparatus is smaller and smaller. So the effect of the surface on the metal properties could no long be neglected.[1−5] Surface relaxations and reconstructions are very basic properties of the surface and affect many physical and chemical processes, such as surface reactions, surface adsorptions of ad-particles, and surface growth. The microscopic knowledge of surface relaxations and reconstructions[6−14] is very important to the surface science due to the influence of the surface structure on many physical and chemical processes.

Multiscale modelling methods such as first-principles calculations, semi-empirical molecular dynamics, and Monte Carlo simulations have been used extensively for the understanding of surface structures. Recently, the relaxations of different surfaces, for example, the multilayer stepped Cu surfaces as well as the Cu(331) surface, were investigated for their undistinguishable relaxations and paradoxical results of different methods.[6−8] The rules of surface relaxations attracted strong interest.[9−11] Very recently, Vasile and Hellsing revealed that surface states had a crucial role for understanding the surface relaxations.[15] They verified that the signs and magnitudes of the relaxations of topmost atomic layer were mainly determined by the rearrangements of the charges of the surface states in view of the *ab initio* calculations of Al slabs with different number of layers.

Though there are many experimental and theoretical researches on surface relaxations and surface states, the roles of surface states in surface relaxations are scarcely presented. For further understanding the effects of surface states on the relaxations of multilayer near the surfaces and the relaxations mechanisms, we performed systematic density-functional theory (DFT) calculations of Cu(100), Cu(111), and Cu(110) surfaces. Different from the Vasile and Hellsing calculations only including the surface states close to special bands in the surface Brillouin zone (SBZ), our calculations include the whole contributions of all surface states and discuss the relationship between the Cu surface relaxations and surface states.

2. Methods and computational details

Our calculations are performed based on DFT, employing the plane wave basis and projector aug-

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mented wave pseudopotential method (PAW). The results reported in this paper are obtained by using the Vienna *ab initio* simulation package (VASP).[16−18] The exchange–correlation effects are treated with the generalized gradient-corrected exchange–correlation functions[19−21] and energy cutoff of 400 eV is used. The repeated slabs with eleven atomic copper layers separated by a vacuum region are used for the model surfaces. A two-dimensional Monkhorst–Pack k-mesh (13×13), (9×13), and Gamma centred grid k-mesh (15×15) for the Cu(100), Cu (110), and Cu (111) surfaces are adopted to do the SBZ integrations respectively.

In order to calculate the valence electron density distribution $\rho_t(z)$, we firstly calculate the partial electron density $\rho(E(\boldsymbol{k}), x, y, z)$ with an eigenvalue $E(\boldsymbol{k})$, then calculate the integral of the $\rho(E(\boldsymbol{k}), x, y, z)$ over the planar plane paralleled to the surface for a given z to obtain the plane-averaged valence electron density $\rho(E(\boldsymbol{k}), z)$, and finally get the valence electron density distribution $\rho_t(z)$ by adding up all of $\rho(E(\boldsymbol{k}), z)$ with different eigenvalue $E(\boldsymbol{k})$. In order to divide the surface electron states from the total electron states which include the bulk states, we use a widespread quantitative criterion, and calculate the valence electron density of surface states $\rho_{\rm s}(z)$.[22,23] For numerical comparisons between the electron density distributions of surface states in different layers, we sum $\rho_{\rm s}(z)$ of each layer to get the i-th layer's electron density of surface states ρ_{si}.

3. Results and discussions

Firstly we calculate the equilibrium properties of the bulk copper and the comparisons of the experimental and calculated values are tabulated in Table 1. The excellent agreement of the present calculating results with the experimental data underpin the DFT study of Cu surfaces in this paper.

Table 1. The comparisons of experimental and calculated equilibrium properties of FCC Cu, where a_0, B, and $E_{\rm c}$ are lattice constant, bulk modulus, and cohesive energy per atom, respectively.

	a_0/(Å)	B/(Mbar)	$E_{\rm c}$/(eV/atom)
Expt.[24]	3.610	1.370	3.49
Calc.	3.638	1.370	3.679

3.1. Results of relaxations

The surface relaxations of our calculations and comparisons with available theoretical and experimental results[22,23,25−30] are presented in Table 2.

Table 2. Multilayer relaxations of the Cu(100), Cu(110), and Cu(111) surfaces. N indicates the number of the layers in the slab. The + and – signs mean expansion and contraction of the interlayer spacing respectively. LEED and MEIS are respectively the experimental results of low energy electron diffraction and medium-energy ion scattering. FLAPW, PPPW, PAW are respectively the density functional theory calculations by all-electron full-potential linearized augmented plane-wave method, pseudopotential plane-wave method, and present projector augmented waves method used in this paper.

Surf.	N	Methods	$E_{\rm cut}$/eV	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	Δd_{56}
(100)		MEIS[22]		− 2.4	1			
		LEED[23]		− 1.2	0.9			
	11	FLAPW[25]	220	− 2.92	0.70	0.45	0.12	− 0.02
		PPPW[26]		− 3.02	0.08	− 0.24		
	11	PAW*	400	− 2.70	1.16	0.22	− 0.01	− 0.02
(110)		MEIS[27]		− 7.5±1.5	2.5±1.5			
		LEED[28]		− 9.5	2.6			
	11	FLAPW[25]	220	− 9.74	3.64	− 1.17	0.40	− 0.09
		PPPW[27]		− 9.24	2.77	− 1.08		
	11	PAW*	400	− 9.94	4.02	− 0.03	0.45	− 0.21
(111)		MEIS[29]		− 1.0	− 0.2			
		LEED[30]		− 0.3±1				
	11	FLAPW[25]	220	− 0.60	− 0.18	0.12	0.40	0.38
		PPPW[26]		− 1.27	− 0.64	− 0.26		
	11	PAW*	400	− 1.05	− 0.27	0.20	0.19	0.08

*this work

In this table, the interlayer relaxations, $\Delta d_{i,i+1}$, are defined as

$$\Delta d_{i,i+1} = (d_{i,i+1} - d_{\text{bulk}})/d_{\text{bulk}} \times 100,$$

where $d_{i,i+1}$ denotes the interlayer distance between i-th and $(i+1)$-th layers of the relaxed surface, and d_{bulk} denotes the bulk interlayer distance.

For the Cu (100) surface, Table 2 shows that the $\Delta d_{1,2}$ is '$-$' and $\Delta d_{2,3}$ is '+', and our results are in general agreement with experimental and other theoretical results except LEED result which has a small magnitude of $\Delta d_{1,2}$. Compared with the results of MEIS experiment, our calculations are much more acceptable than other theoretical calculations.

For the Cu (110) surface, our results of the first two interlayer relaxations are in good agreement with that of LEED and theoretical results of FLAPW, and in general agreement with that of MEIS. Table 2 shows that the relaxation patterns are '$-$ + $-$ + $-$' for the Cu(110) surface. The alternating oscillatory behaviour is also found by using FLAPW calculations, but is not found by experiments of LEED and MEIS since only first two interlayer relaxations have been detected by LEED and MEIS experiment.

For the Cu(111) surface, Table 2 shows that the $\Delta d_{1,2}$ and $\Delta d_{2,3}$ is '$-$', while the $\Delta d_{3,4}$, $\Delta d_{4,5}$, and $\Delta d_{5,6}$ is '+', which are similar to FLAPW results, while our calculations are more agreeable with the results of MEIS experiment than other theoretical calculations.

Table 2 also shows a little inconsistent of the results of calculation obtained by different *ab initio* method. We attribute these to the calculation details such as the choices of energy cutoff and the K-points sampling for BZ integration.

3.2. The effects of the surface states on the relaxations of multi-layer

For investigating the relationship of the surface states and multilayer relaxations, we calculate the valence electron density distribution $\rho_t(z)$ for Cu(100), Cu(110) and Cu(111) surfaces respectively, the results are shown in Fig.1, Fig.2, and Fig.3 (dotted lines). The figures show that the valence electron densities of the topmost layers are smaller than that of the internal layers. This means that the valence electron densities of the topmost layers are decreased in comparison with the valence electron densities of the bulk Cu. This decrease of valence electron densities comes from the emergences of the surface states. As showed in Fig.1, Fig.2, and Fig.3, the valence electron densities of surface states $\rho_s(z)$ (solid lines) are mainly localized in the first three layers and the proportions of the electron densities in first three layers to the total electron densities of the surface states is 74.21%, 69.4%, and 73.2% for Cu(100), Cu(110) and Cu(111) surfaces respectively. On the other hand, by observing the relaxation results of the three surfaces, the surface relaxations mainly appear in the topmost layers as showed in Table 2. The surface contracting relaxations obviously occur in the layers at which the surface states electrons are localized. This result is consistent with the conclusion of Ref.[14]. The surface relaxation is strongly influenced by the surface states. The degree of surface relaxations is determined by the location of the surface states.

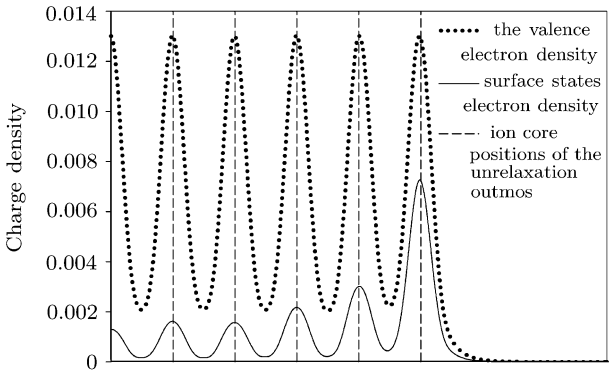


Fig.1. The valence electron density (dotted line) and electron density of surface states (solid line) for the Cu(100) surface. The dashed lines represent the ion core positions of the unrelaxed uppermost five layers.

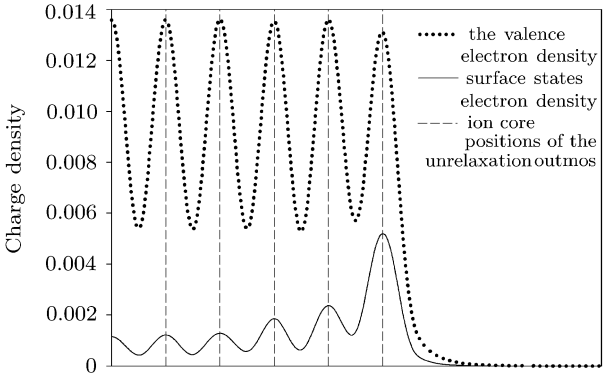


Fig.2. The valence electron density (dotted line) and electron density of surface states (solid line) for the Cu(110) surfaces. The dashed lines represent the ion core positions of the unrelaxed uppermost five layers.

For more quantitative discussion about the relationship of surface relaxations and surface states, we calculate $\Delta_{i,i+1}$ which is defined as the difference of electron density of surface states between $(i+1)$-th and i-th layer, i.e. $\Delta_{i,i+1} = \rho_{si+1} - \rho_{si}$, and the relaxation magnitudes of each interlayer $|\Delta d_{i,i+1}|$. The tendencies of the changes of $\Delta_{i,i+1}$ and $|\Delta d_{i,i+1}|$ are presented respectively in Fig.4(a) and Fig.4(b). One can find from the figures that the consistent trends of relaxation magnitudes $|\Delta d_{i,i+1}|$ and the difference of electron density of surface states $\Delta_{i,i+1}$. For Cu(100), Cu(110), and Cu(111) surfaces, the trend of multilayer relaxations is consistent with the decrement of surface state electron between adjacent layers. The larger difference of electron density of surface states between adjacent layers results in the larger magnitude of surface relaxation between these adjacent layers and *vice versa*.

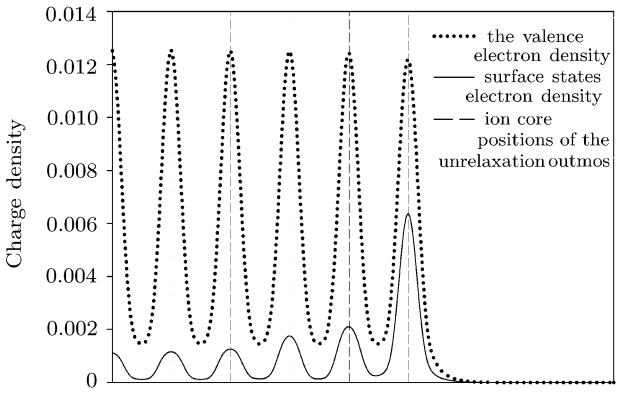


Fig.3. The valence electron density (dotted line) and electron density of surface states (solid line) for the Cu(111) surface. The dashed lines represent the ion core positions of the unrelaxed uppermost five layers.

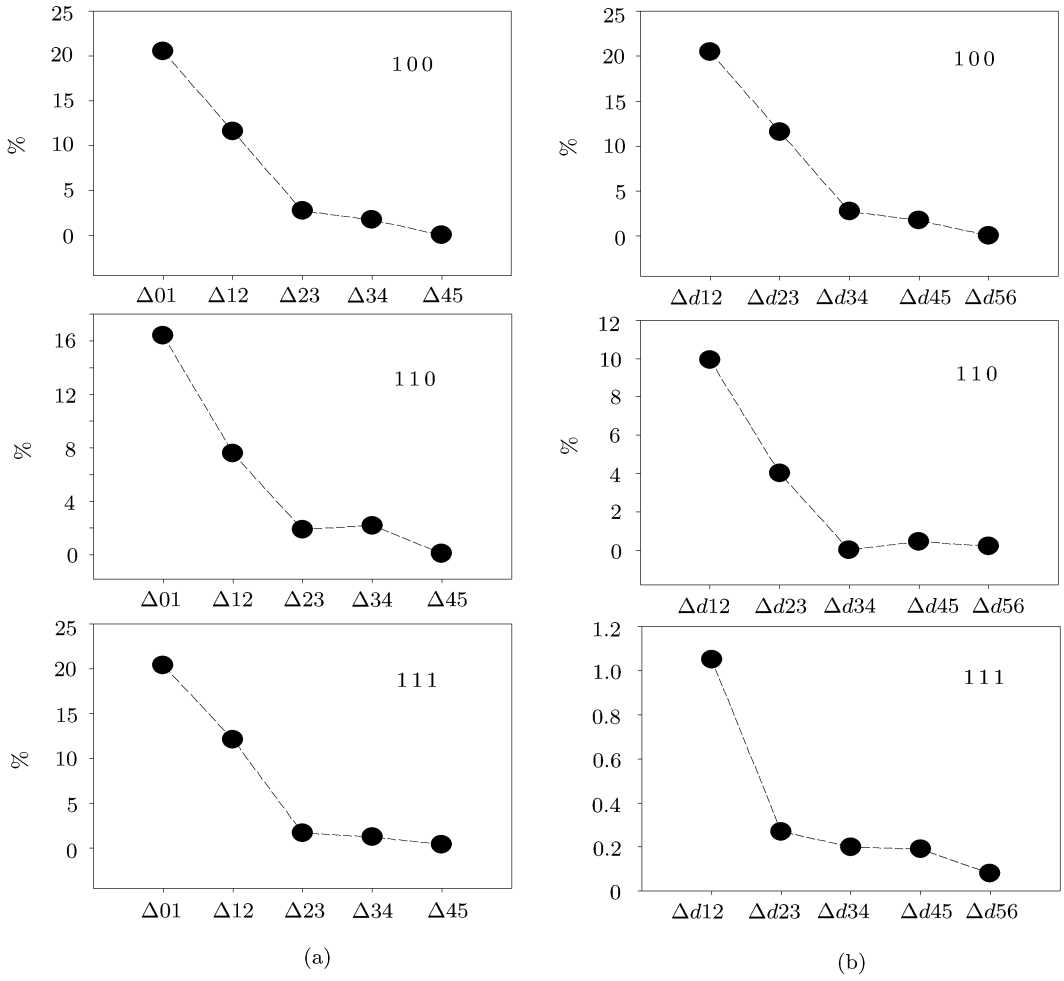


Fig.4. (a) The difference of electron density of surface states between adjacent layers $\Delta_{i,j}$ (b) Interlayer relaxations $|\Delta d_{i,i+1}|$. Filled circles are calculated results and the dashed line serves as a guide for the eye.

In this paper we calculate the surface relaxations, the valence electron density distribution, surface state electron density distribution of the Cu(100), Cu(110), and Cu(111) surfaces, and we have investigated in detail the relationship of the relaxations between the surface electron density distribution and the multiplayer relaxation. We find that for the different surfaces the larger the relaxation is, the larger the change of the electron density near the surface is. The relaxations mainly occur in the layers at which the surface state electrons are localized. Further investigations show that the magnitudes of the multilayer relaxations are sensitive with differences of electron density of surface states in the same surface. The larger the difference of the surface state electron density between layers is, the larger the interlayer relaxation is.

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