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First-principles calculation of the atomic and electronic structure of the surface alloy Cu(001)$c(2\times2)$-Pd

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The first-principles all-electron linearized augmented plane wave film method in the local density functional approximation is employed to investigate the total energy and the electronic structure of the Cu(001)$c(2\times2)$-Pd ordered surface alloy. Our energy calculations show that the slight buckling of the Pd atoms is less than 0.1 Å, which is in accord with low-energy electron diffraction and scanning tunneling microscopy observations. This slight buckling can be well understood by considering the metallic bonding between the deposited Pd and the interface Cu atoms. In addition, according to the calculated densities of states and the energy bands of Cu(001)$c(2\times2)$-Pd, three features due to the incorporation of Pd are found at −3.8, −1.0, and 0.1 eV relative to the Fermi level, in agreement with the observations of the angle-resolved photoemission spectra, allowing an overall energy shift of about 0.7–1.0 eV.

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I. INTRODUCTION

Metal-on-metal growth has attracted much attention for the sake of both fundamental research and the development of applications in recent years. In some cases, such as in Pd/Cu(001), the admetal may combine with the top few layers of the substrate to form surface alloys.[1,2] Due to its catalytic activity[3] and novel structural character, the Pd/Cu(001) surface system has been extensively studied by both experiment[4–21] and theory[22–27] since a Cu(001)$c(2\times2)$-Pd phase was reported by Fujinaga.[28] In early studies, attention had been focused primarily on the growth of 0.5 monolayer (ML) Pd on Cu(001) at 300 K. By means of quantitative low-energy electron diffraction (LEED) intensity analysis, Lu *et al.*[6] and Wu *et al.*[7] proposed a surface alloy model of the Cu(001)$c(2\times2)$-Pd phase. In the model, analogous to Cu(001)$c(2\times2)$-Au,[29] the Pd and Cu atoms in the top layer arranged in an alternating checkerboard pattern, while the Pd atoms in the alloyed surface buckled outwards slightly by 0.02 ± 0.03 Å and the spacing between the mixed top layer and the second pure Cu layer was almost the same as the interlayer spacing of bulk Cu(001) (1.807 Å). More surface sensitive techniques, including reemitted-positron spectroscopy,[11] medium-energy ion scattering (MEIS),[14] low-energy ion scattering (LEIS),[17] scanning tunneling microscopy (STM),[15] and positron-annihilation-induced Auger electron spectroscopy[10] (PAES) have been used to study the atomic structure of Pd/Cu(001). For the Cu(001)$c(2\times2)$-Pd phase, using STM the corrugation heights are measured to be approximately 0.12 Å (Ref. 30) or 0.15 Å.[15] This supports the LEED results and indicates that the origin of the corrugation is due to the electronic structure rather than the geometric structure of the surface. In addition, when 1 ML of Pd was deposited on the Cu(001) substrate, the experiments[14,15,17,19,21,27] agree on the formation of a bilayer surface alloy. Although there might still be some debate about the actual atomic arrangement in the first layer and about the *p4g* or *p2gg* structure of Pd/Cu(001), agreement has been established on two points: (1) the clock-rotation PdCu alloy layer has been observed and (2) the outermost two interlayer spacings are found to be expanded by about 6% compared with that of bulk Cu. Both phenomena are due to the size mismatch between Pd and Cu atoms. This implies that we should consider the validity of the hard-sphere model when we study the buckling of Pd in the Cu(001)$c(2\times2)$-Pd surface alloy.

In the simplest cases, both types of atoms on the surface of a surface alloy may maintain the planar position of the bulk with only different relaxation perpendicular to the surface.[31] The difference of the perpendicular relaxation leads to buckling. For most surface alloys, including Cu(001)$c(2\times2)$-Pd, it is well established that the buckling of the outermost layer is smaller than what is expected on the basis of the sum of the incorporated atomic (metallic) radii.[32] For example, the expected buckling of Cu(001)$c(2\times2)$-Pd should be about 0.713 Å according to the atomic metallic radii of Cu atom and Pd atom. Even if the radius of Pd atom is taken to be the same as that in the Cu_3Pd bulk alloy (1.340 Å), the expected buckling is still as large as 0.569 Å. Despite the well established experimental observations, the theoretical interpretation is not clear yet. Brown *et al.* thought that the reduction of the adsorbate-substrate nearest-neighbor (NN) distance in the outermost layer was related to the charge (mainly *s*-, *p*-like) spill-out into the vacuum on the surface,[33] which had also been used to interpret the relaxation and buckling in NiAl and Ni_3Al alloy surfaces.[34,35] Recently, Quinn observed that within the surface alloy layer of Ni(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb the Pb atoms are 0.73 ± 0.05 Å higher above the Ni atoms subplane.[36] Compared to the buckling of 1.67 Å expected from a simple hard-sphere model based on bulk metallic radii, they thought that there was a strong reduction of the atomic radii in this surface alloy. However, it is difficult to understand how the charge spill-out can result in so strong reduction of the atoms radii in surface alloy.

In the present paper, the first-principles calculation is employed to investigate the Pd buckling's effect on the total energy and the core-level eigenenergy of the Pd and Cu atoms, and then to discuss the mechanism of the slight buckling of the Cu(001)$c(2\times 2)$-Pd ordered surface alloy. Both our energy calculation and our phenomenological explanation indicate that the energy of the system is lowest when the buckling of the Pd atoms is less than 0.1 Å, in good agreement with the LEED (Refs. 7, 13, 14, and 20) and STM (Refs. 15 and 30) observations. Our result suggests that in addition to four NN surface Cu atoms (Cu_S), the deposited Pd atoms also interact significantly with four NN interface Cu atoms (Cu_I). The slight buckling of the CuPd surface alloy can be well understood by considering the metallic bonding between Pd and Cu_I. In this work we also study the core-level eigenenergy shifts of the Pd and Cu atoms as the Pd buckling is varied from 0.713 to -0.2 Å, which can be well explained by the charge transfer between the Pd and Cu atoms and the theory of surface core-level shift given by Citrin *et al.*[37]

In addition to the atomic structure of the Cu(001)$c(2\times 2)$-Pd system, the electronic structure has been probed by angle-resolved ultraviolet photoemission spectroscopy (ARUPS).[4–7] The result reveals that the incorporation of Pd in the Cu(001) surface gives rise to three photoemission peaks at -0.7, -1.7, and -4.8 eV below the Fermi level.[6–8] The latter two peaks have also been observed for the Cu-rich bulk Cu_3Pd alloy.[38] In this paper, we report three features due to the incorporation of Pd, which are all consistent with experimental observations though there is an energy shift of about 0.7–1.0 eV.[39]

The paper is organized as follows. In Sec. II we present the total energy and the core-level eigenenergy shifts of the Pd and Cu atoms as the Pd buckling decreases from 0.713 to -0.2 Å, and then discuss the origin of the slight Pd buckling using a phenomenological model. In Sec. III the electronic structure for that buckling with the lowest total energy are presented and discussed. Finally, a summary is given in Sec. IV.

II. EFFECT OF THE PD BUCKLING

Self-consistent calculations of the Cu(001)$c(2\times 2)$-Pd system are performed for a slab consisting of five substrate layers of Cu atoms with two Cu atoms per layer in the planar unit cell representing the Cu(001)$c(2\times 2)$ substrate as shown in Fig. 1. On top of each Cu surface of this slab, Pd and Cu atoms are arranged in a checkerboard structure simulating the Cu(001)$c(2\times 2)$-Pd surface alloy. The system we calculate contains 14 atoms in one unit cell. The first-to-second interlayer spacing of Cu atoms, d_{12} in Fig. 1, is set equal to 1.707 Å (-0.1 Å relaxation), 1.807 Å (without relaxation), and 1.907 Å (+0.1 Å relaxation) in turn to look for the energy minimum with respect to possible buckling. For each first-to-second interlayer spacing d_{12}, the height of the Pd atoms subplane relative to the Cu atoms subplane in the surface alloy layer varies from -0.2–0.713 Å. The buckling optimized total energy minimum is 0.136 and 0.381 eV/cell larger for -0.1 Å relaxation and +0.1 Å relaxation than that without relaxation, respectively, which is in agreement with the experimental observations.[6,7] So, we will deal with only the case with $d_{12}=1.807$ Å in following discussion.The first-principles all-electron linearized augmented plane wave (LAPW) film method[40] is used in our calculation with the Von Barth–Hedin exchange-correlation term. The basis size used in solving the eigenvalue problem is more than 60 LAPWs per atom; and 100 k points in the 2D Brillouin zone are used to generate the charge density in the self-consistence process. Since this calculation uses a film code which gives full consideration of the vacuum region, there is no need of multiple k_z points as usually used in usual supercell calculation. All the muffin-tin circumferences are taken to be adjacent. The convergence measured by the rms difference between input and output is better than 0.03 me/a.u.^{3} for charge density. The total energy converges to better than 0.4 mRy per unit cell.

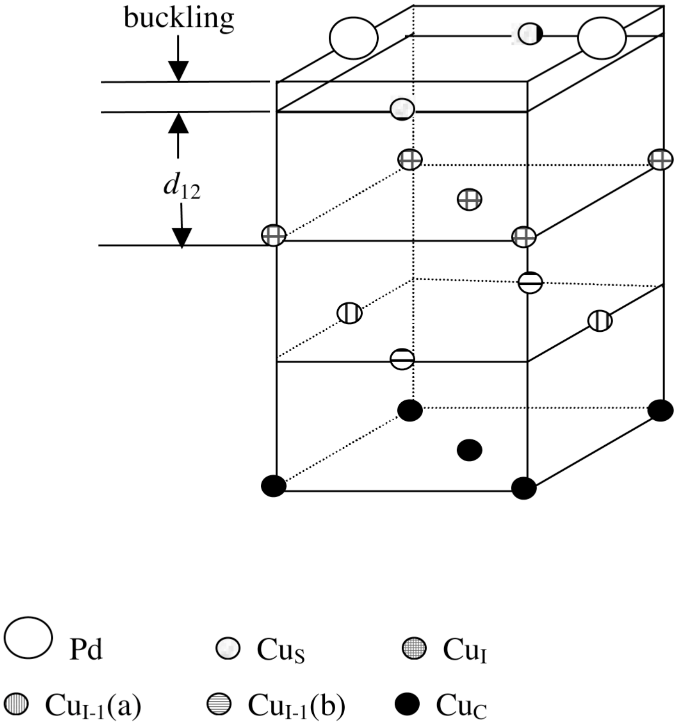

FIG. 1. Schematic structure model of the Cu(001)$c(2\times 2)$-Pd ordered surface alloy.

In order to investigate the effect of the buckling of the Pd atoms on the total energy and the surface core-level eigenenergy, we let the buckling vary from 0.713 to -0.2 Å. The positive (negative) value means the Pd atoms are buckled outwards (inward) from Cu_S, and zero means that the Pd and Cu_S atoms are located in the same plane. The values of 0.713 and 0.569 Å correspond to two cases where the Pd radii are taken as those in Pd bulk (1.375 Å) and in the Cu_3Pd bulk alloy (1.340 Å), respectively. In Table I we give the total valence electron number of all types of atoms within their muffin-tin spheres for various buckling cases. Whatever the case, the incorporation of Pd hardly affects the center (Cu_C) and the subinterface Cu atoms (Cu_{I-1}). However, the total number of valence electrons of the Pd, Cu_S, and Cu_I atoms

TABLE I. The total valence electron number inside the muffin-tin spheres of the Pd and Cu atoms in the Cu(001)$c(2\times2)$-Pd surface alloy for different bucklings. Subscripts S, I, $I-1$, and C denote the mixed, interface, subinterface and center layer, respectively. Two column values under Cu_{I-1} correspond to the atoms under surface Pd and Cu atoms, respectively.

Buckling (Å)	Cu_C	Cu_{I-1}		Cu_I	Cu_S	Pd	R_{Pd} (Å)
0.713	10.372	10.372	10.375	10.285	10.200	8.902	1.3753
0.569	10.372	10.370	10.375	10.294	10.228	8.800	1.3403
0.500	10.372	10.369	10.374	10.300	10.239	8.753	1.3262
0.400	10.372	10.368	10.375	10.312	10.253	8.698	1.3089
0.300	10.371	10.366	10.373	10.328	10.267	8.665	1.2953
0.200	10.370	10.365	10.372	10.353	10.274	8.652	1.2856
0.100	10.370	10.364	10.372	10.376	10.279	8.661	1.2797
0.000	10.369	10.363	10.370	10.408	10.282	8.694	1.2777
−0.100	10.368	10.361	10.367	10.445	10.281	8.361	1.2080
−0.200	10.366	10.359	10.363	10.488	10.275	8.006	1.1405

are significantly changed. As the buckling decreases, the number of valence electrons of the Pd atom markedly decreases, and on the contrary, those of Cu_S and Cu_I increase. We note that when the buckling is less than 0.1 Å, the number of valence electrons remains almost unchanged for Cu_S as the buckling is reduced, but even further increased for Cu_I.

We list in Table II the total energy (relative to the case of 0.1 Å buckling) as the buckling of the Pd atoms is varied from 0.713 to −0.2 Å. Since the charges in Cu_{I-1} and Cu_C are hardly affected with the change of buckling, the change in total energy should reflect mainly the change in the bonding energies of Pd-Cu_S and Pd-Cu_I. The total energy of the system decreases first with a decrease of the buckling from 0.713 to 0.1 Å, and continues to decrease, but very slowly, as the buckling decreases from 0.1 to 0.0 Å, then it begins to increase after the Pd atoms are buckled inwards due to the strong repulsive interaction between the Pd and Cu atoms. Since involving only a small range of buckling, in Fig. 2 we fit the five data points near the total energy minimum simply by quadratic curve to determine the position of minimum energy. The buckling corresponding to the lowest total energy is calculated as 0.10 ± 0.03 Å, as compared to the value of 0.02 ± 0.03 Å obtained from the LEED data,[7,13,20] 0.04–0.08 Å obtained from the MEIS data,[14] and 0.12 (Ref. 30) and 0.15 Å (Ref. 15) observed by STM.

Table III lists the orbital decomposition of the valence electrons inside the muffin-tin spheres of Pd, Cu_S, and Cu_I. We can see that the decrease in total electrons of the Pd atom is mainly due to its *d*-like component, and the increases in total electrons of Cu_S and Cu_I are mainly due to their *p*- and *d*-like components.

Table IV lists core-level eigenenergy of different atoms in the Cu(001)$c(2\times2)$-Pd surface alloy for different bucklings with the $2p_{3/2}$ eigenenergy of central Cu as reference. From Table IV it can be seen that the core-level eigenenergies of Cu_{I-1} are almost the same as that of Cu_C for buckling range from 0.713 to −0.2 Å. This suggests that the subinterface layer is already bulklike. Since the *d* electrons are more localized, any change in *d* electrons has stronger influence on the core-level eigenenergy than the change in the *s* electrons.[41] Thus it is easy to understand an eigenenergy decrease (1.15 eV) of the Pd $3d_{5/2}$ core level with the buckling decreasing from 0.713 to −0.2 Å. Both Cu_S and Cu_I have higher core-level eigenenergy than Cu_C, and the core-level eigenenergies (relative to that of Cu_C) of Cu_S and Cu_I decrease from 1.02 and 0.31 eV to 0.89 and 0.13 eV, respectively, with the buckling decreasing from 0.713 to −0.2 Å. Considering 3*d* electrons of Cu_I and Cu_S increasing with the reduction of buckling, it is not so evident to understand the increases of Cu $2p_{3/2}$ core-level eigenenergies. This result will be discussed later.

Brown *et al.* have compared the NN distance between adsorbate and substrate atoms of some surface alloys with the sum of atomic radii in bulk metal and noted that for a range of surface alloys the NN adsorbate-substrate distances are noticeably smaller than the sum of their metallic radii and are closer to the sum of covalent radii.[33] It is well established that the valence charge density at unreconstructed elementary metal surface is lower than that in bulk due to the spill over of the valence charge into the vacuum, which will result in a tensile stress in the surface or will make the effective radii of the atoms at the surface reduced.[42] If some fraction of the atoms in such a surface is substituted by an-

TABLE II. Total energy (relative to that of 0.1 Å buckling) of the Cu(001)$c(2\times2)$-Pd ordered surface alloy for different bucklings of the Pd atoms.

Buckling (Å)	0.713	0.569	0.500	0.400	0.300	0.200	0.100	0.000	−0.100	−0.200
Total energy (ev/cell)	1.77	1.03	1.00	0.65	0.42	0.11	0.00	0.01	0.45	1.22

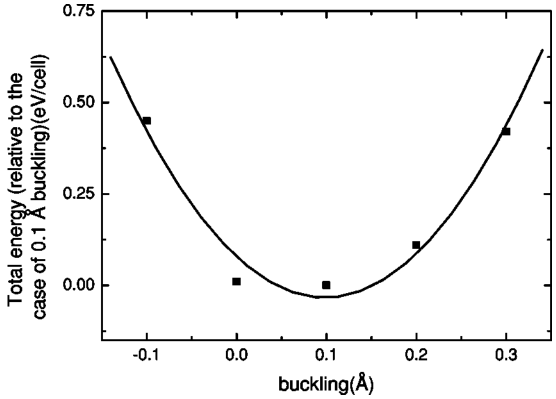

FIG. 2. The total energy (relative to that of 0.1 Å buckling) of the Cu(001)$c(2\times2)$-Pd ordered surface alloy when the buckling of the Pd atoms varies from −0.1 to 0.3 Å. The total energy curve is obtained by fitting five calculated results (solid squares) between bucklings of −0.1−0.3 Å with the quadratic curve.

other kind of atoms with a larger radius, it is clear that the buckling at outermost mixed layer will be less than what expected from the sum of metallic radii of adsorbate and substrate atoms.[33]

It seems to us that the intrinsic tensile stress can reduce the effective radii of atoms in a metal surface and can partially interpret the slight buckling of surface alloys. However, it is difficult to accept that the atomic radii in surface alloys are close to covalent radii. Here, by means of a simple phenomenological model, we will show that the smaller buckling in surface alloys is easy to understand if we take the metallic bonding between the absordate atoms and their NN atoms on the subsurface layer into account.

When the atoms deviate from their equilibrium positions, the energy change of the system depends on the change of bond length, and can be expressed as

$$\delta E = \frac{k}{2}\sum_i (\delta l_i)^2 + \text{higher order terms}, \tag{1}$$

where k and l_i are the force constant and the bond length of the ith bond. Here we suppose that the bonds between Pd and its NN Cu atoms on both surface and subsurface plane have the same force constant, the change of energy per Pd atom can be written as

$$\delta E = \frac{k}{2}[4(R_{\text{Pd–Cu}_S} - R_{\text{Pd–Cu}})^2 + 4(R_{\text{Pd–Cu}_I} - R_{\text{Pd–Cu}})^2] \tag{2}$$

in which $R_{\text{Pd–Cu}_S} = \sqrt{h^2 + a^2/2}$ and $R_{\text{Pd–Cu}_I} = \sqrt{h^2 + ah + a^2/2}$ are the distances from the Pd atom to the NN Cu_S and Cu_I atoms when the buckling of the Pd atoms is h. $R_{\text{Pd–Cu}}$ is the equilibrium length of the Pd−Cu bond; and a is the lattice constant of copper. Assuming that (1) the interlayer distance between the Cu_S and Cu_I layers is equal to the Cu(001) bulk interlayer spacing supported by LEED studies and (2) $R_{\text{Pd–Cu}}$ is equal to the length (2.618 Å) of the Pd−Cu bond in Cu_3Pd bulk alloy, equilibrium condition reaches when the buckling is 0.0916 Å. In this case, the Pd−Cu_S distance $R_{\text{Pd–Cu}_S} = 2.557$ Å is less than $R_{\text{Pd–Cu}}$, so a repulsive force exists between the Pd atoms and Cu_S, but for the Cu_I atoms, $R_{\text{Pd–Cu}_I} = 2.621$ Å is slightly larger than $R_{\text{Pd–Cu}}$, and an attractive force exists between the Pd atoms and Cu_I. At this buckling, the repulsive force reaches equilibrium with the attractive force and the total energy is minimized.

Turning to the expressions of $R_{\text{Pd–Cu}_S}$ and $R_{\text{Pd–Cu}_I}$, we can see that their changes depend on the second-order and first-order of the buckling h, respectively. Therefore, the second term in the formula of total energy—i.e., the interaction between the Pd and the interface Cu atoms—dominates the change in total energy when the buckling is small. Based on this simple model, the occurrence of small buckling, obtained by experiments and theoretical calculations, can be well understood. In previous studies a larger buckling was expected because only the bonding between the Pd atoms and their NN surface Cu atoms are considered, but the bonding between the Pd atoms and their NN interlayer Cu atoms are omitted.[32]

This simple phenomenological model should be general. It can also be applied to other surface alloy systems such as Cu(001)$c(2\times2)$-Au. With the equilibrium bonding length of 2.658 Å in Cu_3Au, we estimate the buckling of

TABLE III. Orbital decomposition of the total valence electron number inside the muffintin spheres of Pd, Cu_S, and Cu_I for the Cu(001)$c(2\times2)$-Pd surface alloy, for different bucklings of the Pd atoms.

Buckling (Å)	Pd			Cu_S			Cu_I		
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*d*
0.713	0.315	0.155	8.411	0.520	0.319	9.331	0.512	0.414	9.326
0.569	0.307	0.158	8.314	0.531	0.330	9.336	0.512	0.422	9.326
0.500	0.304	0.159	8.268	0.535	0.335	9.337	0.512	0.427	9.326
0.400	0.303	0.165	8.209	0.541	0.343	9.334	0.514	0.436	9.326
0.300	0.304	0.172	8.166	0.546	0.347	9.338	0.517	0.446	9.328
0.200	0.311	0.182	8.135	0.547	0.350	9.339	0.523	0.460	9.331
0.100	0.320	0.192	8.122	0.549	0.350	9.342	0.529	0.471	9.334
0.000	0.333	0.206	8.125	0.546	0.348	9.348	0.537	0.486	9.338
−0.100	0.281	0.168	7.889	0.540	0.343	9.359	0.546	0.503	9.334
−0.200	0.234	0.137	7.616	0.537	0.337	9.362	0.557	0.520	9.352

TABLE IV. The core-level eigenenergy of different atoms in the Cu(001)$c(2\times2)$-Pd surface alloy for different bucklings. The energy reference is taken as the $2p_{3/2}$ eigenenergy of the central Cu. Two column values under Cu_{I-1} correspond to the atoms under surface Pd and Cu atoms, respectively.

Buckling (Å)	Cu_{I-1} $2p_{3/2}$ (eV)		Cu_I $2p_{3/2}$ (eV)	Cu_S $2p_{3/2}$ (eV)	Pd $3d_{5/2}$ (eV)
0.713	0.00	0.02	0.31	1.02	585.85
0.569	−0.01	0.04	0.30	0.95	585.67
0.500	−0.02	0.04	0.29	0.92	585.59
0.400	−0.01	0.06	0.29	0.87	585.48
0.300	−0.01	0.07	0.27	0.83	585.36
0.200	−0.02	0.08	0.24	0.80	585.27
0.100	−0.02	0.08	0.22	0.79	585.18
0.000	−0.02	0.08	0.19	0.82	585.12
−0.100	−0.02	0.08	0.16	0.89	584.98
−0.200	−0.02	0.08	0.13	0.89	584.70

Cu(001)$c(2\times2)$-Au to be 0.153 Å, which is very close to the value of 0.1 Å given by experiments.[29]

According to the decrease of the Pd 4*d* electrons, we can well understand the eigenenergy decrease of the Pd $3d_{5/2}$ core level when the buckling of the Pd atoms decreases from 0.713 to −0.2 Å. In principle the increase in 3*d* electrons of Cu_S and Cu_I should lead to an increase in the $2p_{3/2}$ eigenenergy. However, we still obtain a decrease of 0.13 and 0.18 eV for Cu_S and Cu_I, respectively. In Ref. 37, Citrin *et al.* obtained that the density of states of surface Cu atoms becomes narrower and shifts to the Fermi level in comparison with the bulk Cu atoms. This means that the eiengenergy of the bulk Cu atoms is lower than that of the interface and surface Cu atoms. In the Cu(001)$c(2\times2)$-Pd system the hybridization of Cu_S and Cu_I with Pd gradually increases with a decrease in the Pd buckling, thus Cu_S and Cu_I gradually possess the characteristics of the bulk Cu atoms, and the eigenenergy of Cu_S and Cu_I $2p_{3/2}$ core-level should decrease. This boost to the $2p_{3/2}$ eigenenergy overcompensates the increase caused by the additional valence electrons of Cu_S and Cu_I and results in a net decrease in $2p_{3/2}$ eigenenergy.

III. ELECTRONIC STRUCTURES OF Cu(001)$c(2\times2)$-Pd

In this section we investigate the electronic structures of the Cu(001)$c(2\times2)$-Pd system taking the Pd buckling as 0.1 Å, which corresponds to the minimal total energy of the system. The calculated total and layered projected density of states (DOS) of the surface alloy Cu(001)$c(2\times2)$-Pd are presented in Fig. 3, with the results for the clean seven-layer Cu(001) film also shown for comparison. The zero of the energy scale corresponds to the Fermi level. The total DOS of the Cu(001)$c(2\times2)$-Pd is similar to that of clean Cu film, except the former has one extra peak at about −1.0 eV. This notable peak is clearly due to the presence of Pd in the Cu(001)$c(2\times2)$-Pd surface alloy, since it is absent in clean Cu(001). Examining the layered projected DOS of Cu(001)$c(2\times2)$-Pd, we notice a strong peak at −1.0 eV in the DOS of the Pd layer. A weaker peak appears at the same energy in the DOS curve of the Cu_S and Cu_I layers, but it is almost absent from Cu_{I-1} and Cu_C. Therefore, the peak at −1.0 eV is derived mainly from Pd.

In Fig. 4(a) we present the calculated band structure of the ordered Cu(001)$c(2\times2)$-Pd surface alloy. It is shown along the high symmetrical directions of the $c(2\times2)$ surface Brillouin zone, which, with respect to the Brillouin zone of Cu(001), is half as large in area and rotates 45°. In Fig. 4(b) the open and solid circles and the crosses indicate the surface states having weight larger than 55 %, 40–55 %, and 25–40 %, respectively, within the Pd muffin-tin spheres. The states marked by solid circles center around −1.0 eV, which is consistent with the pronounced peak at −1.0 eV found in the total DOS. With more detailed symmetry analysis, we

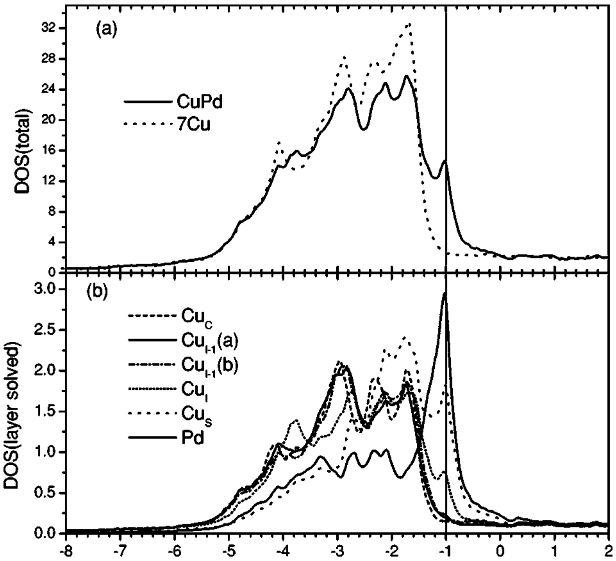

FIG. 3. Total (a) and layered projected (b) density of states (DOS) in unit states/eV of the Cu(001)$c(2\times2)$-Pd ordered surface alloy. The total DOS of the clean seven-layer Cu(001) is also shown in (a) for comparison. The zero of the energy scale corresponds to the Fermi level.

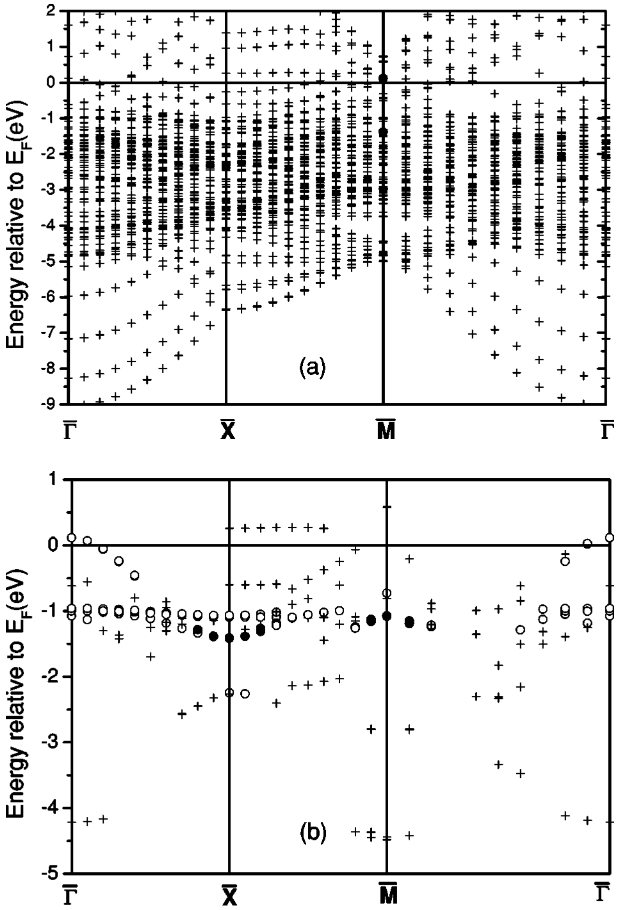

FIG. 4. Valence bands (a) and surface states (b) of the Cu(001)$c(2\times2)$-Pd ordered surface alloy. The open and solid circles and the crosses indicate the surface states, which, respectively, are occupied by more than 55%, 40–55%, and 25–40% of the Pd atoms.

find that those states are contributed mostly by the d_{z^2} orbitals of Pd at the $\bar{\Gamma}$ and $\bar{X}$ points, and by the $d_{x^2-y^2}$ as well as the d_{xy} orbitals of Pd at the $\bar{M}$ points.

In Fig. 3(a) we can see that the incorporation of Pd in the Cu(001) surface gives rise to another peak at about −3.7 eV. Assuming an energy shift of about 1.0 eV which usually exists in single particle calculation,[39] two peaks at −3.7 and −1.0 eV appear consistent with the two peaks at −4.8 and −1.7 eV observed in EDC's from Cu(001)$c(2\times2)$-Pd.[6,7] We notice that these peaks are similar to those observed for the Cu-rich CuPd alloy.[38] As far as the origins of the two peaks are connected, both experiments[6,7] and our calculation agree that the peak at −1.7 eV is due to the incorporation of Pd in the Cu(001) surface and is derived mainly from Pd 4*d* electrons. For the other peak at −3.7 eV, although it is due to the incorporation of Pd in the Cu(001) surface, our calculations indicate that it is derived from the local density of state of Cu$_I$ which has been distorted by hybridization with Pd.

Using ARUPS,[5,7] another peak at about −0.7 eV has been observed. This peak is quite small and difficult to identify, and it can be observed only with special photon energy at a special emission angle (e.g., near the $\bar{M}$ point[5]). If we consider that there is a 1.0 eV difference between the experiment and our calculation, we can expect one peak at about 0.3 eV above the Fermi energy. However, in our calculations, a surface state appears, marked with open circles, at about 0.1 eV above Fermi level at the $\bar{\Gamma}$ point in Fig. 4(b). This state is also derived from the incorporation of Pd, to which the Pd atoms contribute 52% and the Cu (mainly Cu$_S$) atoms contribute 48%. Even though we display it at the $\bar{\Gamma}$ point in the $c(2\times2)$ surface Brillouin zone in Fig. 4(b), it is equivalent to the state at $\bar{M}$ in the Brillouin zone of Cu(001) before alloying, which is used in the experimental work,[5–7] because folding of Brillouin zone will bring them in coincidence. According to the above analysis, we suggest that the surface state at 0.1 eV above the Fermi level corresponds to the peak at −0.7 eV observed in EDC's,[5–7] and it is contributed by both Pd and Cu$_S$.

IV. SUMMARY

The first-principles all-electron LAPW film method in the local density functional approximation has been applied to investigate the effect of the Pd buckling on the total energy of the Cu(001)$c(2\times2)$-Pd ordered surface alloy. Our energy calculation and the phenomenological model indicate that the buckling should be smaller than 0.1 Å for the Cu(001)$c(2\times2)$-Pd ordered surface alloy, which agrees well with the LEED observations. Such slight buckling can be well understood if we consider the metallic bonding between the deposited Pd atom and the interface Cu atoms. In addition, the change of core-level eigenergies of the Pd, Cu$_S$, and Cu$_I$ atoms is well explained by the charge transfer and the theory of surface core-level shift.[37]

We also study the electronic structure of the system with the buckling of the Pd atoms taken as 0.1 Å, which corresponds to the lowest overall energy. The calculations indicate that the incorporation of Pd in the Cu(001) substrate gives rise to three features at −3.7, −1.0, and 0.1 eV (above the Fermi level). If we consider the 0.7−1.0 eV difference between experiment and single particle calculation, our calculated peaks correspond to those photoemission peaks at −4.8, −1.7, and −0.7 eV observed by ARUPS.

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