PHYSICAL REVIEW B **66**, 073405 (2002)

First-principles identification of quasi-two-dimensional Fermi surface nesting on a metallic $c(2\times2)$-In/Cu(001) surface

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(Received 8 February 2002; revised manuscript received 16 April 2002; published 2 August 2002)

The first-principles all-electron linearized augmented planewave film method in the local density functional approximation is employed to investigate the band structure of the In/Cu(001) surface. A square-shaped, quasi-two-dimensional Fermi surface within the projected bulk Cu band gap due to the mostly in-plane In induced bonding band is identified for the bilayer $c(2\times2)$-In adsorption. The nesting Fermi wave vector along [001] direction is at 0.38–0.41 Å^{-1} from $\overline{\Gamma}$, consistent with the experimental measurements, and is expected to drive a Peierls transition which has distortion doubling the lattice period. Another surface band is identified as In p_z state, which was observed in the low-temperature phase.

DOI: 10.1103/PhysRevB.66.073405 PACS number(s): 71.18.+y, 73.20.At, 68.35.Bs

The exotic physical properties discovered in the systems of reduced dimensions have been one of the central issues of condensed matter physics. Because of the simple Fermi surface in reduced dimensions, electrons near the Fermi level are unstable against a lattice distortion. This instability leads the materials to a Peierls transition at finite temperature and reduced symmetry appears at low temperature.[1] In this Peierls transition, the Fermi surface nesting manifests itself as periodic lattice distortion (PLD) or charge density wave (CDW). Solid surface is a suitable candidate for the study of the physics in reduced dimensions, since surface atoms form localized electronic structure and often exhibit peculiar low-dimensional characteristics. However, there are only a few surfaces which invoke intrinsic Peierls transition or CDW's. Recently the origin of this transition for various systems has been actively investigated experimentally.[2–5] For example, self-assembled linear chains of metallic In atoms on semiconducting Si(111) surface are shown to undergo a temperature induced reversible phase transition.[6] Nakagawa *et al.*[7] reported a Fermi surface nesting and structural transition in a metallic ultrathin In film adsorbed on Cu(001) by scanning tunneling microscopy (STM), low-energy electron diffraction, and angle resolved photoelectron spectroscopy (ARPES). According to their experiments, a surface band approaches and crosses E_F in the high temperature (HT) phase, but in the low-temperature (LT) phase this band does not cross E_F but disperses back to higher binding energies with very large dispersion. In order to investigate the mechanism of the structural phase transition and identify the orbital character of the observed surface bands, theoretical calculations are made to investigate the band structure of this In/Cu(001) surface.

In this paper the first-principles all-electron linearized augmented plane wave (LAPW) film method[8] with the Von Barth-Hedin exchange-correlation term is employed to carry out the calculation of the band structure. According to the experiment,[7] In adsorption at monolayer coverage [defined as the surface atom density of Cu(001), 1.53×10^{19} m^{-2}], form a bilayer structure, one interface and one surface layer, and both layers have $c(2\times2)$ structure with respect to Cu(001) surface. To simulate this structure, a slab consisting of five Cu(001) layers ideally cut from a bulk fcc Cu crystal ($a_0=3.61$ Å) and In layers adsorbed symmetrically on both sides is used in the present calculation. The z distance between the interface In and Cu layer varies with respect to different In adsorption site, i.e., atop, hollow and bridge sites (see Fig. 1), but the nearest neighbor (NN) In-Cu atom distance is set as 2.90 Å, the average of the NN distances of Cu and In crystals, 2.55 and 3.25 Å, respectively. For the bilayer In adsorption, each surface In atom has four NN In atoms in the interface layer below, and the z distance between surface and interface In layers is set as 2.01 Å so that the NN In-In atom distance is the same as in an In crystal. For this bilayer system, there are 14 atoms in one 2D unit cell, basis size

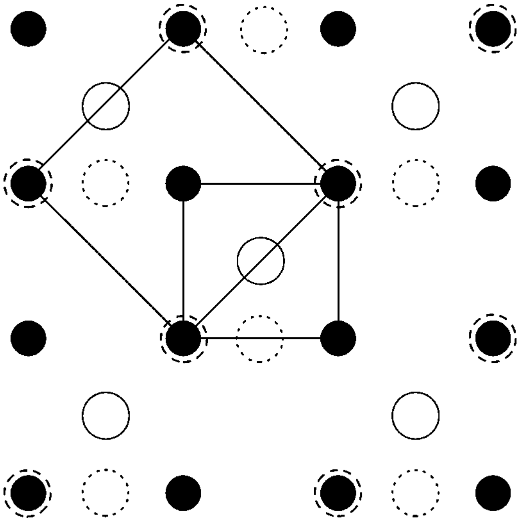

FIG. 1. Top view of the Cu(001) showing interface In and Cu atoms for $c(2\times2)$-In/Cu(001) structure. The solid circles represent Cu atoms, and the open circles with solid, dash, and dotted borders represent the interface In atoms locating at the hollow, atop and bridge sites, respectively.

TABLE I. Total energy (relative to the bilayer hollow site adsorption) and work function.

System	Total energy (eV/cell)	Work function (eV)
Pure Cu(001)		5.02
Single $c(2\times2)$-In, hollow		5.30
Bilayer $c(2\times2)$-In, hollow	0	5.52
Bilayer $c(2\times2)$-In, bridge	1.1	5.40
Bilayer $c(2\times2)$-In, atop	1.6	5.15

used in solving the eigenvalue problem is more than 50 LAPW's per atom, and 36 $\bar{k}$ points in the 2D Brillouin zone are used to generate the charge density in the self-consistency process. The convergence measured by the r.m.s. difference between input and output is better than 0.04 me/a.u.^{3} for charge density. The total energy is converged to better than 0.1 mRy per unit cell. A system of single $c(2\times2)$-In layer adsorption has also been calculated, and results are presented below for comparison.

First, in order to investigate the stable In adsorption sites on the Cu(001) surface, the total energy and work function are calculated for different In adsorption sites. From the results listed in Table I, we can see that when the interface In atoms locate at the hollow sites, the system is energetically favorable, in qualitative agreement with previous theoretical results of adsorption of In atoms on Cu (001) surface,[9] and has the highest work function. In following discussion, we focus on the system that interface In atoms locate at the hollow sites. The value of work function for the clean Cu film is in good agreement with experiments,[10] and earlier self-consistent calculations.[11,12] Electron transfer at interface is expected to happen from Cu to In which is confirmed by our calculated data, and thus the adsorption is expected to increase the work function, though there is no experimental report about the work function of In/Cu(001) available for comparison.

As a check of above postulated adsorption geometry, a relaxation was made in the CASTEP approach. The structure of the hollow $c(2\times2)$ In on Cu(100) was optimized for a system consiting of 7Cu + In slab (single or bilayer) + 15 A empty space. In this geometry relaxation, the density functional formalism is GGA, and used are ultrasoft pseudopotential, planewave basis with 350 eV energy cutoff, and 10 k point in the 2D-IBZ. For $c(2\times2)$ In single layer case, the relaxed In-Cu interatomic distance is 2.83 Å (in contrast to the above postulated 2.90 Å). For $c(2\times2)$ In bilayer case, the relaxed In-In interatomic distance is 3.31 Å (in contrast to the above postulated 3.25 Å) while the In-Cu distance is 2.78 Å (in contrast to the above postulated 2.90 Å). The Cu layers are also allowed to relax and it is found that their relaxation is extremely small (0.5%). Thus, the geometry relaxation confirmed again the hollow site adsorption, and all changes of the interatomic distance are found less than 4%. To show the effect of this relaxation on the exact magnitude of the nesting Fermi wave vector, for the bilayer In adsorption, calculations were made for both unrelaxed and relaxed system, and the results were plotted together for a clear comparison.

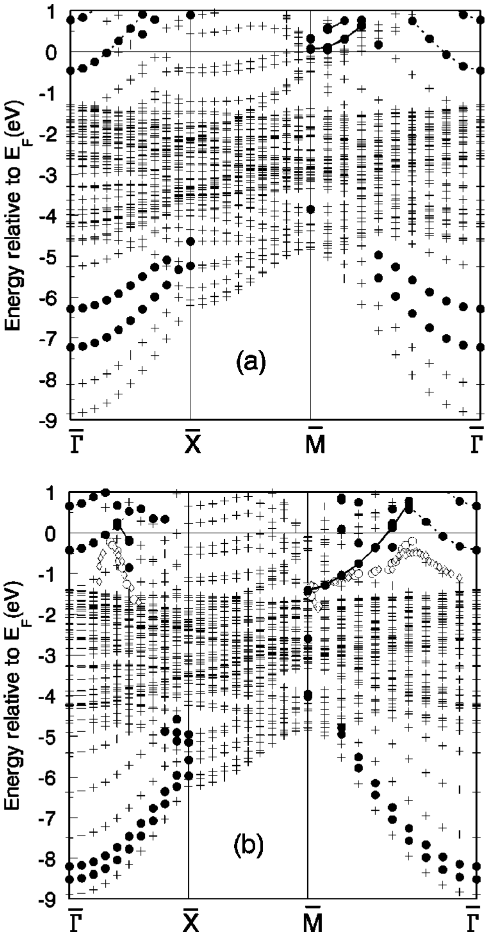

FIG. 2. Valence bands of $c(2\times2)$-In/Cu(001) surface, (a) single In layer and (b) bilayer In adsorption. Solid circles are In induced bands obtained by present calculations. Open circles are experimental ones for high temperature phase, and the open diamonds for the low temperature phase (Ref. 7). The bands linked by solid lines are of $p_{x,y}$ symmetry, and the bands linked by dotted lines are of p_z symmetry.

In Fig. 2 the calculated energy bands of the In/Cu(001) surface are plotted along the high symmetry directions of the $c(2\times2)$ surface Brillouin zone, which is half in area and rotates 45° with respect to the Brillouin zone of Cu(001). The In-induced surface resonance states, which have, as defined, their largest layered projection on one of the In layers, are marked by solid circles. Figure 2(a), plotted for comparison, is for single layer In adsorption, and Fig. 2(b) is for the bilayer In adsorption on Cu(001). Present calculation is made for a finite thickness slab, and thus all surface bands should be nearly doubly degenerate. Their splitting is a measure of the penetration of the wave function of these surface states towards the substrate interior. The two In-induced bands at low energy below -6.0 eV are s states, and they split 0.94 eV at $\bar{\Gamma}$ point for the single In layer adsorption, but only 0.32 eV in the bilayer case, showing strong bonding character between interface and surface In atoms in the bilayer structure. The high-lying (above -2.0 eV) In-induced bands are mainly p character and only partially filled. With more detailed symmetry analysis of these p bands, two groups of bands with different symmetry are identified. The bands connected by dotted lines in both Figs. 2(a) and 2(b) are contributed mostly by p_z orbitals of In atoms, which show minimum at $\bar{\Gamma}$, but are mostly above the Fermi energy. These states not only have more charge spilled out into the vacuum region, but also penetrate into Cu bulk. The splits due to interaction between their top and bottom surface states are, at $\bar{\Gamma}$, 1.23 eV for single layer In adsorption, and 1.09 eV even for bilayer In adsorption, showing that the surface In p_z state also has rather strong mixing with Cu substrates.

The bands connected by solid lines in Fig. 2 are contributed mostly by $p_{x,y}$ orbitals of In atoms, directed in the film plane for single layer In adsorption, or directed along the NN pairs between interface and surface layer in bilayer In adsorption system. For the single $c(2\times2)$-In layer system (Fig. 2(a), the $p_{x,y}$ bands have energy above Fermi level due to weak interaction, because all In atoms are far separated. So there is no Fermi surface nesting at all in this system, and thus no Peierls transition is expected to occur. In contrast, for the bilayer In adsorption system, bonding is formed between the two NN In atoms, one in the interface and the other in the surface layer. The strong bonding brings the lowest energy of thess bands well below E_F at $\bar{M}$ [Fig. 2(b)] when going away from $\bar{M}$. However, the energy of these bonding bands increases when going away from $\bar{M}$, and crosses the E_F level. These bonding states are very localized ones, which have negligibly small spill both to the vacuum and to the Cu bulk. The solid circles connected by solid lines in Fig. 2(b) consists, in fact, of two almost degenerate (only split about 0.03 eV) bands on both top and bottom surfaces due to vanishing interaction. The scattered solid circles in Fig. 2(b) are other p character states, e.g., antibonding σ or nonbonding π, of In atoms on both interfaces and surfaces, and they have consequently strong mixing with substrate states.

In Fig. 2(b) the experimental points given in Ref. 7 are also drawn for comparison with open circles for the bilayer $c(2\times2)$-In/Cu(001) HT phase and open diamonds for the $(9\sqrt{2}\times2\sqrt{2})R45°$ LT phase. From this experiment,[7] the calculated mostly $p_{x,y}$ energy bands (connected by solid lines) are easily identified with the surface band going upward from $\bar{M}$ which were observed experimentally for both the $c(2\times2)$-In HT phase and the $(9\sqrt{2}\times2\sqrt{2})R45°$-In LT phase. Present calculation gives correct dispersion in good agreement with the experiment. The calculated mostly p_z bands near $\bar{\Gamma}$ are almost empty for the $c(2\times2)$-In phase. This agrees with the fact that there are not bands clearly observed for HT phase with similar dispersion around $\bar{\Gamma}$ in the ARPES experiments. However, in the $(9\sqrt{2}\times2\sqrt{2})R45°$-In LT phase, the suface band disperses back to higher binding energy when going further to near $\bar{\Gamma}$ in the experiment.[7] Comparing with our calculation, we prefer not to identify this part of surface band as the same band which is observed in HT phase, but assume it is another surface band bearing p_z character from its dispersion. Its energy has been decreased to below E_F due to PLD at LT, and then appears clearly in ARPES measurements. Though, unfortunately, because of the too large unit cell of $(9\sqrt{2}\times2\sqrt{2})R45°$-In/Cu(001) structure, calculation of this system has not been made in present work.

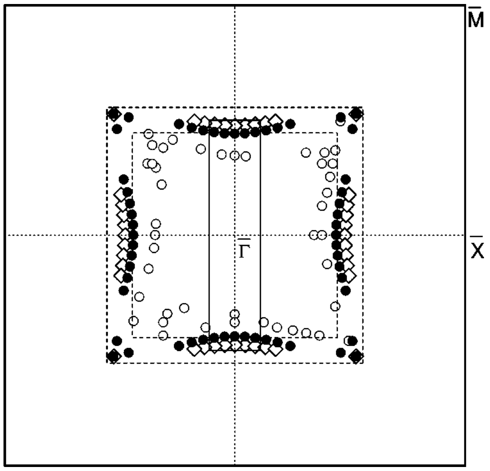

FIG. 3. Nesting of the Fermi surface of the surface $p_{x,y}$ bonding bands of the bilayer $c(2\times2)$-In/Cu(001). The large square (edge length $2\pi/a_0=1.74$ Å^{-1}) represents the surface Brillouin zone of $c(2\times2)$-In and the small rectangle represents the surface Brillouin zone of $(9\sqrt{2}\times2\sqrt{2})R45°$-In. The dashed lines show the range of the nesting Fermi wave vector. The open circles are experimental results (Ref. 7), and the solid circles and open diamonds represent our calculated results for the unrelaxed and relaxed adsorption system, respectively.

The caluclated In induced $p_{x,y}$ bonding band forms a nesting Fermi surface in the bilayer $c(2\times2)$ system as shown in Fig. 3 drawn within the $c(2\times2)$-In surface Brillouin zone (solid circles and open diamonds for unrelaxed and relaxed adsorption system, respectively). It is in very good accordance in shape with the experimentally determined one (open circles in Fig. 3). The nesting Fermi wave vector k_F, along [100] and [010] is located at $k_F=0.38$ Å^{-1} from $\bar{\Gamma}$ for unrelaxed system, or 0.41 Å^{-1} for the relaxed one, which is in reasonable agreement with the experimental detected value 0.30 Å^{-1}. The surface Brillouin zone boundary of the $(9\sqrt{2}\times2\sqrt{2})R45°$-In/Cu(001) structure along [100] and [010] is, respectively, $Q_1=2\pi/9a_0=0.19$ Å^{-1} and $Q_2=2\pi/2a_0=0.87$ Å^{-1} (the smallest rectangle in Fig. 3). Here, $Q_2\approx2k_F$, which is consistent with a simple nesting condition for driving a Peierls transition doubling the lattice period with respect to the $c(2\times2)$ structure. Thus the origin of the experimentally observed PLD, at least along one direction, can reasonably be attributed to this nesting. In contrast, the long wavelength distortion, $Q_1=2\pi/9a_0=0.19$ Å^{-1}, along the other direction can not be simply explained by this argument. We noticed that both our calculated and experimental results show that the Fermi surface is not exactly a square and there is a distribution around $k_F\approx\frac{1}{2}Q_2$, as shown by the dashed line frame having width from $4\pi/9a_0$ to $5\pi/9a_0$ in Fig. 3. This distribution of k_F will lead to a long wave length modulation superposed on the short wavelength PLD of period $Q_2\approx2k_F$. The STM image[7] does show such superposition, and the $Q_1=2\pi/9a_0$ does manifest itself as a modulation upon short wavelength PLD.

In summary, the first-principles all-electron linearized augmented plane wave film method in the local density functional approximation has been applied to investigate the surface band structure and Fermi surface nesting properties of $c(2\times2)$-In/Cu(001) surface. Calculated results confirm the nesting of the quasi-2D Fermi surface which was postulated to drive the phase transition. The band dispersion of the bonding In $p_{x,y}$ bands is in good agreement with experimental results. Another surface band, which are clearly observed only for $(9\sqrt{2}\times2\sqrt{2})R45°$ LT phase in the experiment,[7] are presumably identified as p_z states. For the HT phase, it is almost above the Fermi surface and thus can not be clearly observed in ARPES. Its existence is not a result of the Peierls distortion, but its energy has certainly been decreased below the Fermi energy after the distortion and it appears clearly for the LT phase.

This work was supported by the National PAN-DENG Project No. G19990328-02 and the National Natural Sciences Foundation of China under Grant No. 19874003. The authors are grateful to Professor Ru-qian Wu of the University California-Irvine for his helpful suggestions, critical reading, and checking the geometry using the CASTEP approach.

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[1] G. Gruner, *Density Waves in Solids* (Addison-Wesley, Reasing, MA, 1994).

[2] R. Liu, C.G. Olson, W.C. Tonjes, and R.F. Frindt, Phys. Rev. Lett. **80**, 5762 (1998); T. Valla, A.V. Fedorov, p.D. Johnson, J. Xue, K.E. Smith, and F.J. DiSalvo, *ibid.* **85**, 4759 (2000).

[3] J.M. Carpinelli, H.H. Weitering, E.W. Plummer, and R. Stumpf, Nature (London) **381**, 398 (1996).

[4] A. Mascaraque, J. Avila, J. Alvarez, M.C. Asensio, S. Ferrer, and E.G. Michel, Phys. Rev. Lett. **82**, 2524 (1999).

[5] C.S. Chang, W.B. Su, C.M. Wei, and T.T. Tsong, Phys. Rev. Lett. **83**, 2604 (1999).

[6] H.W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C.M. Lee, S.D. Kevan, T. Ohta, T. Nagao, and S. Hasegawa, Phys. Rev. Lett. **82**, 4898 (1999).

[7] T. Nakagawa, G.I. Boishin, H. Fujioka, H.W. Yeom, I. Matsuda, N. Takagi, M. Nishijima, and T. Aruga, Phys. Rev. Lett. **86**, 854 (2001).

[8] H. Krakauer, M. Posternak, and A.J. Freeman, Phys. Rev. B **19**, 1706 (1979); M. Posternak, H. Krakauer, A.J. Freeman, and D.D. Koelling, *ibid.* **21**, 5601 (1980); Ding-sheng Wang, A.J. Freeman, H. Krakauer, and M. Posternak, *ibid.* **23**, 1685 (1981).

[9] M. Jiang, Y.J. Zhao, and P.L. Cao, Phys. Rev. B **57**, 10 054 (1998).

[10] G.A. Haas and R.E. Thomas, J. Appl. Phys. **48**, 86 (1977); G.G. Tibbetts, J.M. Burkstrand, and J.C. Tracy, Phys. Rev. B **15**, 3652 (1977).

[11] J.G. Gay, J.R. Smith, and F.J. Arlinghaus, Phys. Rev. Lett. **42**, 332 (1979); Phys. Rev. B **21**, 2201 (1980).

[12] R.Q. Wu and D.S. Wang, Phys. Rev. B **41**, 12 541 (1990).