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The electronic structure of a surfactant layer: Pb/Cu(1 1 1)

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Abstract

The electronic structure of an incommensurate Pb layer on Cu(1 1 1) is investigated by means of angle scanned ultraviolet photoemission. Despite of the rather complex atomic structure with three competing periodicities, we observe a well defined band structure, reflecting essentially the fundamental (1×1)-periodicity of the adlayer. Comparison with band structure calculations for a free standing Pb-layer shows that all observed bands can be fully attributed to the overlayer.

Keywords: Angle resolved photoemission; Copper; Lead; Low index single crystal surfaces; Metallic films

1. Introduction

Monolayers of Pb have been shown to promote very efficiently the layer by layer growth of epitaxial films on Cu(1 1 1) [1,2]. Recently, the atomistic mechanism of this surfactant effect has been revealed for the homoepitaxial case [3]. A key step is the rapid penetration of arriving Cu atoms through the compact Pb layer. The second important ingredient of the surfactant system is that the buried Cu adatoms can diffuse below the Pb layer by concerted exchange processes with other Cu atoms, both on flat terraces and across steps on the Cu(1 1 1) surface. In order to fulfill these requirements the Pb layer must have the properties of a highly elastic skin which is only weakly coupled to the substrate. This renders the system interesting from a second point of view. Low dimensional metallic systems grown on semiconducting [4] or metallic [5] substrates can exhibit a number of exotic physical phenomena such as Peierls-like instabilities and surface charge-density waves.

In this paper we present a detailed photoemission study of the electronic structure of one compact Pb layer forming an incommensurate quasi (4×4) structure on Cu(1 1 1). The experiments are compared with band structure calculations of a free standing Pb-layer.

2. Experiment

The growth of Pb on Cu(1 1 1) is well characterized by LEED and STM studies [6–9]. At the initial stage of room temperature adsorption Pb atoms decorate step sites on the otherwise flat surface. Simultaneously a disordered alloy forms, where randomly distributed Pb atoms are incorporated in the first Cu layer at substitutional sites [7]. For relative atomic coverages higher than ~0.2

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monolayers (ML) surface alloying stops, and large close packed Pb islands of monatomic height evolve with the same crystallographic orientation as the substrate. The islands initially show a lattice constant clearly above the bulk nearest neighbor distance [8]. Upon completion of the monolayer, the film compresses by $\approx 3\%$ to reach a in plane lattice constant of 3.39 Å, slightly below 4/3 of the room temperature Cu surface lattice constant (3.40 Å) [8]. The detailed LEED analysis of Müller et al. revealed a considerable buckling of 0.2 Å in the Pb-layer and an even larger but inverted corrugation of the first substrate layer [9]. In the intermediate (4×4) phase nine Pb atoms are accommodated in the (4×4) supercell containing 16 Cu atoms. Within the accuracy of our experiment it is sufficient to assume the same coverage for the complete wetting layer. Further deposition of Pb leads to the formation of large 3D islands on the wetting layer, a behaviour known as Stransky–Krastanov growth. We have used the changing substrate and adsorbate self-damping in X-ray photoelectron spectra (XPS), associated with the transition from 2D to 3D growth to calibrate the Pb/Cu intensity ratio in XP-spectra. The relative atomic coverage of 9/16 ML has been defined as the crossing point of linear extrapolations to the elastic peak intensities in the low- and high coverage regimes.

The experiments have been performed in a VG ESCALAB 220 spectrometer, modified with a computer controlled two-axis sample goniometer [10]. All UV-photoemission data were taken at room temperature using He Iα radiation. The energy/angle resolution was set to 40 meV/1° (full width at half maximum (FWHM)). A mechanically polished Cu(1 1 1) single crystal was prepared by standard sputter/anneal cycles. A good surface quality can be deduced from the width of the Shockley surface state, which was measured in normal emission below 70 meV FWHM with the above resolution parameters. Lead was evaporated from a resistively heated molybdenum crucible with the sample held at room temperature. The background pressure during evaporation was kept below 3×10^{-10} mbar. Oxygen and carbon contaminations in the film were checked by X-ray photoelectron spectroscopy and were found to be below the detection limit of ~ 0.01 ML.

3. Results and discussion

In Fig. 1, we compare the experimental Fermi surface maps of Cu(1 1 1) and (4×4) Pb/Cu(1 1 1) with density functional (DFT) calculations. The calculations have been performed for the Cu bulk structure and for a free standing planar Pb layer using the *Wien*97 DFT-package [11]. The experimental Fermi surface maps represent the He Iα excited photoemission intensity, measured for more than 10^4 angular settings over the full hemisphere above the sample [12]. In the Cu(1 1 1) Fermi surface map shown in Fig. 1(a), we readily identify direct transition lines, forming the bone shaped hole orbits, separated by necks, which are characteristic for the Cu bulk Fermi surface. The contours are well reproduced by a spherical cut through the calculated bulk Fermi surface (Fig. 1(c)), as it was shown earlier by Aebi et al. [13]. The most intense circular feature centered at $\overline{\Gamma}$ is due to the free electron like Shockley surface state [14], which is not reproduced in the bulk calculation.

In the data from the lead covered surface shown in Fig. 1(b), the surface state is either quenched or pushed above the Fermi level. Instead, bright features in the shape of eyebrows appear in a sixfold symmetric arrangement in the second Brillouin zone of the overlayer 1×1-periodicity. These features appear to be completed to small triangular pockets by weaker structures in the first BZ. Besides the remaining intensity from the Cu bulk Fermi surface, we further observe a weak regular hexagon centered at $\overline{\Gamma}$ with its sides parallel to the SBZ and measuring about half its linear dimension. Both features are surprisingly well reproduced in the calculated Fermi surface of a free standing Pb layer (Fig. 1(d)). Closer inspection of the experimental Fermi surface map reveals also indications of the umklapps of the inner hexagon with reciprocal lattice vectors of the fundamental 1×1-periodicity. The striking similarity of the adlayer electronic structure with the Fermi surface calculated for a free standing Pb layer shows that adsorbate and substrate electronic systems are largely decoupled. This might surprise, since the Fermi surface of bulk fcc lead is constituted by p-states [15,16], for which we

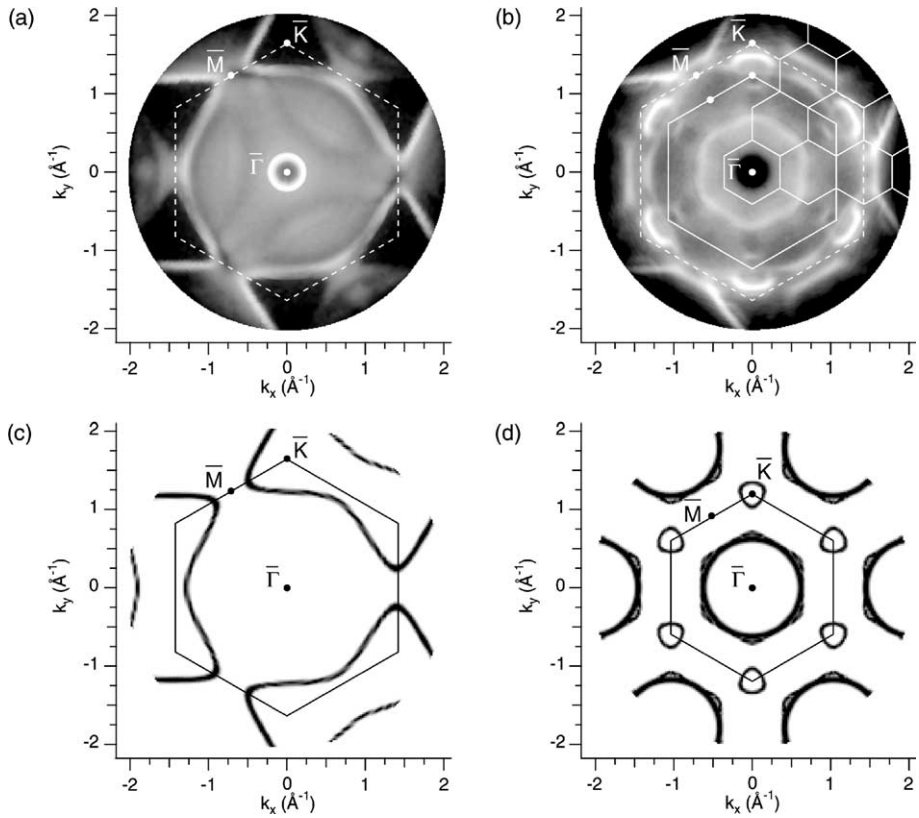

Fig. 1. He Iα excited Fermi surface maps of clean Cu(1 1 1) (a) and (4 × 4) Pb/Cu(1 1 1) (b). The photoemission intensity is shown on a logarithmic gray scale as a function of the two momentum components in the surface plane. Surface Brillouin zones constructed for the Cu (dashed) and Pb (solid line) periodicities are overlined. The smaller hexagons in (b) show the nominal (4 × 4) Brillouin zones. (c) Cu-bulk Fermi surface, calculated on the spherical *k*-space contour, defined by the energy of a free electron like final state. (d) Fermi surface, as obtained from a density functional calculation of a free standing planar Pb layer.

expect a strong coupling to the sp-like Cu Fermi surface and the formation of bonding–antibonding pairs. The reason appears to be the lattice mismatch of ≈33%, which translates into a serious mismatch of the Brillouin zones, relevant inside the Cu(1 1 1) surface and inside the Pb layer. The dominant periodicity in the experimental Fermi surface map is clearly the Pb (1 × 1)-structure. The periodicity of the substrate is not reflected in the adlayer band structure and thus contributes only weakly to the potential felt by the electrons in the Pb film. This might explain the elasticity of the Pb film needed to allow the easy penetration by arriving adatoms, which is a crucial step in the surfactant model of Camarero et al. [1]. The net disappearance of the p_z-like Shockley surface state in the presence of the Pb film can be explained by the outward shift of the vacuum barrier, changing the matching conditions of the surface state wave function with the exponential vacuum tail [17].

An interesting property of the Pb/Cu(1 1 1) system is the considerable corrugation of the substrate which is induced by the overlayer [9]. The restructuring of the first Cu layers can be expected to enhance diffusion by exchange processes considerably and might therefore be crucial for the surface activity of Pb [1,9]. Regarding the pronounced hexagonal structure in the Fermi surface (Fig. 1), one may wonder if the driving reconstruction in the Pb layer might arise from a Peierls instability.

In order to address this question we have measured the dispersion of the bands, constituting the inner hexagon of the Fermi surface along the two high symmetry directions $\overline{\Gamma}\overline{M}$ and $\overline{\Gamma}\overline{K}$ (Fig. 2). Again the different bands are identified from a comparison with the DFT calculation for a free standing Pb layer, shown in Fig. 3. First, we note that the the inner hexagon in the Fermi surface is constituted by two bands with different symmetry. A free electron like band with p_z character and a second $p_{x,y}$-like band, dispersing with a negative effective mass from the zone boundary towards $\overline{\Gamma}$. For a planar Pb film we therefore expect a simple band—crossing, as seen in the calculation (Fig. 3). However, a buckling of the Pb layer can intermix the symmetries, leading to a possible repulsion of the bands at the crossing points. This could provide a way for the adlayer to gain electronic energy, compensating the enhanced elastic energy of the reconstruction. A close inspection of energy distribution curves extracted from the data shown in Fig. 2 indicates indeed the opening of band gaps at the crossing points of the Pb bands along both high-symmetry directions. However, in the $\overline{\Gamma}\overline{M}$ direction, the apparent gap is clearly below the Fermi level. Only along $\overline{\Gamma}\overline{K}$ we find indications for a gap extending over the Fermi level, consistent with the simplest picture of a Peierls transition, where two half filled bands separate in a completely occupied and an empty band. The magnitude of the band gaps is of the order of 200 meV and thus of the same order as the mean field prediction for the Peierls gap [5,18]. It is worth to note that the Pb bands are unusually sharp. An analysis of momentum distribution curves gives Lorentzian linewidths below 0.05 Å^{-1} FWHM, what in turn requires a coherent interaction of the hole state over more than 20 Å, which is larger than the quasi (4×4) unit cell.

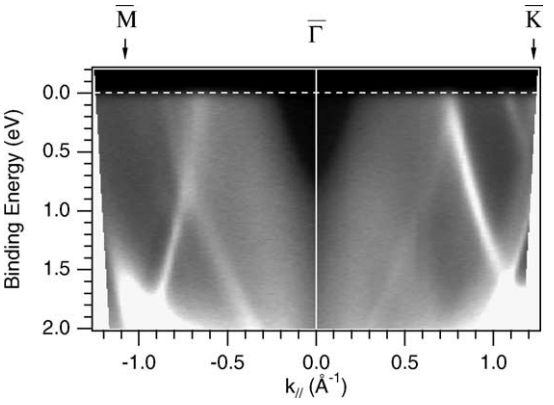

Fig. 2. Band dispersion for quasi (4×4) Pb/Cu(1 1 1) along $\overline{M}\overline{\Gamma}\overline{K}$. The photoemission intensity is shown on a linear grey scale, ranging from black at minimum intensity to white at maximum intensity. Arrows mark the high symmetry points of the adlayer 1×1-periodicity.

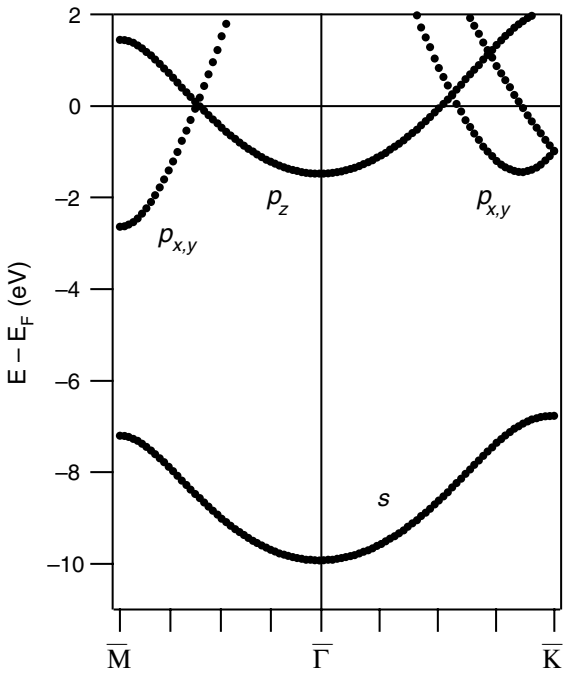

Fig. 3. DFT bands of a free standing planar Pb layer with an in-plane lattice constant equal to the bulk nearest neighbor distance of 3.5 Å. The dominant orbital character of the different bands is indicated.

In conclusion, we have presented a high resolution photoemission study of an incommensurate quasi (4×4) Pb monolayer-film on Cu(1 1 1). We find sharp Fermi surface contours, which reflect the fundamental (1×1) periodicity of the adlayer. The good agreement of the experimental band structure with the electronic structure, calculated for a free standing Pb-layer shows that the film is largely decoupled from the substrate. Energy distribution curves, measured along two high symmetry lines indicate a possible gap opening around

the Fermi level for two (avoided) crossing points. This might be a consequence of the buckling in the Pb layer, but could also be the driving force of the reconstruction.

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