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Abstract
The atomic structure of a monolayer of Pb on Cu(111) was investigated by an *in situ* combination of low-energy electron diffraction, scanning tunnelling microscopy and Auger electron spectroscopy. The pronounced (4 × 4) super-structure observed is found to be due to a (in surface projection) hexagonally close-packed but vertically buckled Pb layer which induces a substantial complex restructuring of the first three Cu layers. In this interface to the copper bulk no intermixing of Pb and Cu atoms is observed. Surprisingly, the overall buckling amplitude of the first Cu layer is even larger than that of the lead layer and the positional height of Pb atoms residing on top of Cu atoms is lower than for all other atoms. The structural results agree qualitatively with recent effective-medium-theory calculations. The reconstruction induced by the lead adatoms shows that the substrate reacts in a structurally flexible way to their presence. It is proposed that this might be related to the surface-active ('surfactant') role that Pb plays in homogeneous and heterogeneous epitaxial growth on Cu(111).

1. Introduction

Recent years have seen intensive research on the epitaxial growth of ultrathin metallic films on single-crystal surfaces. The motivation for this stems mainly from the possibility of producing materials with extraordinary magnetic properties due to the reduced dimensionality, to the new lattice parameters imposed by the substrate chosen or to the new periodicities (superlattices) artificially achieved as a result of the chosen growth sequence of the films. As a consequence, scientific efforts have concentrated on the properties of the film and less on the modification of the substrate induced by its presence. Yet, it is well known that an adsorbate can significantly change the electronic and geometric properties of a substrate, and the initial growth of new materials may be strongly influenced by this modification. The use of such surface-active species ('surfactants') has long been known to play an important role in crystal growth [1].

It can stabilize a certain growth mode, in particular layer-by-layer growth, and this may be connected with the surfactant-induced substrate restructuring in epitaxial growth. The latter scenario is the main motivation for the present paper. We concentrate here on the structural modification induced by the adsorption of Pb on a Cu(111) surface. As is well known, Pb plays the role of a surfactant in the growth of Co on Cu(111) [2–5], which system exhibits the technologically important phenomenon of giant magnetoresistance [6–9] associated with oscillatory magnetic coupling [10, 11]. Lead was found to be surface active also in the homo-epitaxial growth of Cu on Cu(111) [12]. This is interesting, because homoepitaxy represents a simplified case where kinetic aspects of growth can be studied free from the thermodynamical complications arising from the presence of two different materials. In the above-mentioned work, a change in the mechanism of diffusion of Cu adatoms caused by the presence of Pb was proposed as the origin of the surfactant activity leading to layer-by-layer growth by 2D nucleation [12, 13].

A rather complex interplay of electronic and structural properties might determine the surface activity of Pb. Consequently, a detailed and quantitative determination of the structure of Pb/Cu(111) may allow an important step towards the understanding of the surfactant's role at the atomic scale in homoepitaxial and heteroepitaxial systems. Previous investigations have already shown that the adsorption system Pb/Cu(111) is rather complex structurally. The initial state of adsorption is characterized by Pb atoms decorating surface steps and, with further increasing coverage, the formation of a disordered alloy in the top layer is observed [14–16]. For coverages higher than about 0.4 monolayers (ML) the alloying is largely stopped, though some randomly distributed Pb atoms remain within the top copper layer. As shown by detailed spot profile analyses using low-energy electron diffraction (SPALEED) [17], hexagonally close-packed Pb islands develop whose lattice is incommensurate with the substrate and exhibits a lattice parameter slightly larger than that in bulk lead. Approaching 1 ML coverage, the lead lattice starts to compress, forming an incommensurate floating layer [17, 18] whereby— still below the total full-monolayer coverage—an intermediate (4×4) diffraction pattern appears, as already observed many years ago [19]. In this commensurate phase, nine Pb atoms are accommodated in the (4×4) superstructure cell containing sixteen Cu atoms per layer. This is equivalent to a *relative* atomic coverage of 9/16 and a ratio of the lattice parameters of 4/3. We define this as (local) 1 ML coverage with the density of Pb atoms equal to $(\frac{3}{4})^2 = \frac{9}{16}$ times the atomic density in the Cu(111) surface. Though the phase is frequently considered to be commensurate due to the equidistant arrangement of diffraction spots, one should keep in mind that it is an intermediate structure in a sequence of incommensurate structures that appear during the compression of the lead layer. Also, one should keep in mind that the phase is not uniform but consists of (4×4) islands with some domains still consisting of uncovered copper in which some randomly distributed lead atoms are incorporated. At full total coverage (1 ML), the compression of the Pb layer is at its maximum with the position of the diffraction spots again indicating an incommensurate structure [17]. We also mention that the precise values of total coverage necessary for the development of the practically commensurate (4×4) superstructure are rather sensitive to details of the preparation parameters such as deposition and annealing temperatures.

In spite of there having been a number of investigations of the (4×4) phase (or phases very close to it), the knowledge about its detailed crystallographic structure is still rather incomplete. There is evidence from scanning tunnelling microscopy (STM) [14] and helium-atom scattering (HAS) [20] that the Pb layer exhibits a considerable corrugation. Experimental information about the structure of the substrate, however, is lacking. Calculations using effective-medium theory (EMT) [14] indicate that the copper substrate is considerably reconstructed leading to an inverse corrugation of the lead layer; i.e. Pb atoms residing on top of Cu atoms appear

lower than other atoms. This surprising behaviour is known also from Ag films epitaxially grown on Cu(111) [21] and so seems to be of more general importance. As mentioned above, it could be correlated with the adsorbate's surface activity in epitaxial growth, in particular as it indicates that the substrate reacts in a structurally rather flexible way to the adsorbate. So, the experimental determination of the full adsorbate structure, which must include the adatom positions *and* the structure of the first few substrate layers, is highly desirable. Besides, by comparison of the results with those of the EMT simulations, a check of the accuracy of the latter is possible.

In the following we therefore present a quantitative structure determination of (4 × 4)-Pb/Cu(111) by means of the measurement and full dynamical analysis of low-energy electron diffraction (LEED) intensity versus energy spectra, $I(E)$, complemented by STM investigations of the film. Whilst the latter method provides an image of the actual surface and information about the quality of the film, the LEED analysis gives access to the structure of the full surface extending into the substrate by several layers. By means of Auger electron spectroscopy (AES), independent information about the lead coverage is obtained.

## 2. Sample preparation and data collection

The experiments were carried out in a standard UHV chamber equipped with a home-made STM and a commercial rear-view four-grid LEED optics which simultaneously served as a retarding-field spectrometer for AES. The sample holder allowed *in situ* transfer from the LEED optics to the STM head. The Cu(111) sample was cleaned by repeated argon-ion sputtering followed by annealing. Eventually, no impurities could be detected by AES and sharp LEED diffraction spots were observed, whose $I(E)$ spectra correspond to published data [22]. With the sample at room temperature, lead was deposited at a rate of about 0.15 ML min^{-1} by evaporation from a resistively heated Pb reservoir of 4N purity. To allow for ordering, the films were annealed at 420 K for about one minute. With increasing coverage the initial (1 × 1) LEED pattern transforms into a superstructure showing practically ideal (4 × 4) symmetry. The coverage was monitored by AES using both the Cu peak at 61 eV and the Pb peak at 94 eV. As displayed in figure 1, both signals exhibit clear breaks after about 7 min deposition time. This is a manifestation of the Stranski–Krastanov mode of growth of Pb on Cu(111) [13]: initially, a single flat Pb ML covers the Cu surface and further deposition leads to the formation of large, well separated 3D Pb clusters on the wetting layer. Therefore, we identify the breaks in the AES signals with the completion of the first ML and this allows us to calculate the Pb coverage in a precise way. It turns out to be 0.8 ML in our experiment.

LEED $I(E)$ spectra were measured for the (4 × 4) superstructure using a video-based and computer-controlled technique for automated data acquisition described in detail elsewhere [23]. All data were recorded with the sample at room temperature and at normal incidence of the primary beam. This was adjusted by R-factor comparison of the spectra of symmetrically equivalent beams, whereby the Pendry R-factor [24] was applied. The data were collected in the energy range 50–400 eV in steps of 0.5 eV. The intensity levels of integer-order diffraction beams appeared to be reduced compared to those of the clean Cu(111) surface, obviously mainly due to the appearance of the numerous fractional-order spots. Nevertheless, we were able to record a data set consisting of the spectra of nine symmetrically inequivalent beams (five integer-order and four fractional-order spots). In order to improve the signal-to-noise ratio, each intensity was measured several (8 or 16) times and spectra of symmetrically equivalent beams were averaged off-line according to the threefold rotational symmetry of the substrate. This procedure also reduces the influence of some possible residual sample misalignment and inhomogeneities of the luminescent screen.
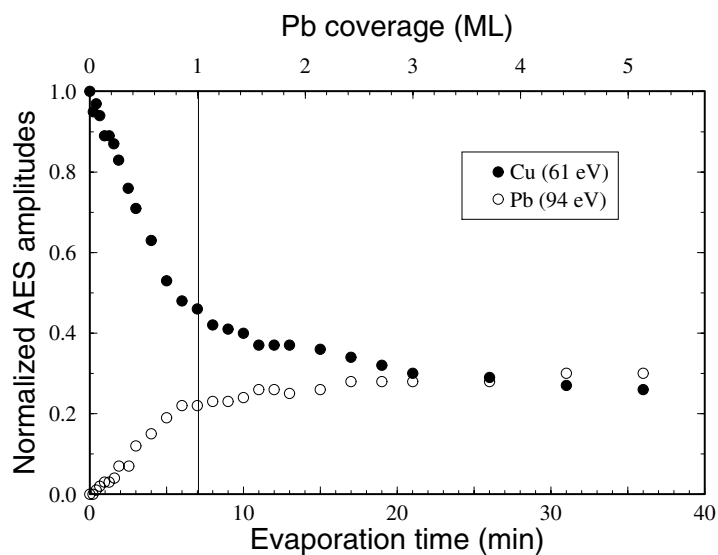
Figure 1. Auger peak-to-peak amplitudes of Pb and Cu as a function of evaporation time. The break indicated by the vertical full line is identified with the full-monolayer (ML) coverage.

STM images were recorded in the constant-current mode at room temperature, where the tip was a polycrystalline tungsten wire. The piezodrives were calibrated laterally by means of images at atomic resolution and vertically by the step height of the clean Cu(111) surface. Figure 2 displays the image of the (4×4) phase with atomic resolution. The quasi-hexagonal arrangement of Pb atoms shows up clearly and the (4×4) superstructure (with nine Pb atoms per cell) is also indicated by a weak moiré pattern.
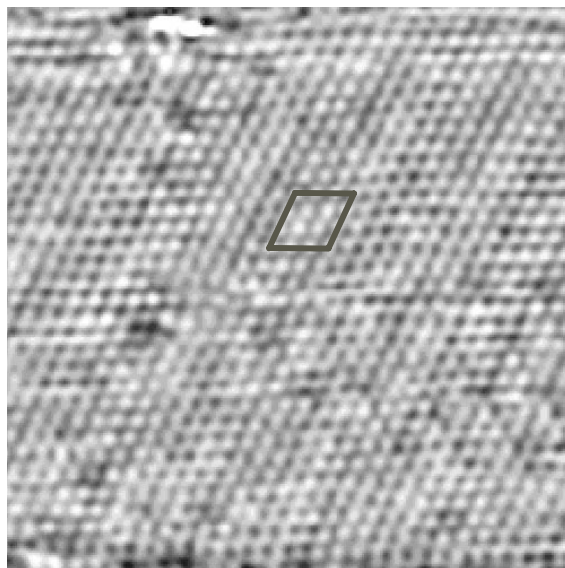
Figure 2. An STM image of about 1 ML Pb on Cu(111) at atomic resolution (100×100 Å^2). The (4×4) superstructure cell is indicated.

3. LEED intensity calculations and the strategy of analysis

The large unit cell with nine Pb atoms and sixteen Cu atoms in substrate layers together with the need to allow for the reconstruction of several substrate layers as indicated by the EMT simulations [14] practically prevents the application of standard LEED computer codes [25, 26]. Instead, the perturbation method Tensor LEED (TLEED) [27–29] was applied. A special program package was used [30] which also allows for a check on possible intermixing between Pb and Cu by application of chemical TLEED [31, 32] based on the average t-matrix approximation [33, 34]. In the calculation of reference structures, layer diffraction matrices were obtained by matrix inversion with reconstructed layers treated as composite layers. A maximum of 847 symmetrically inequivalent beams were considered in the layer stacking procedure applying the layer-doubling method. All calculations were restricted to a maximum energy of 360 eV in order to save computer time. For both lead and copper, a total of eleven relativistically calculated and spin-averaged phase shifts were used. They were corrected for isotropic thermal vibrations using the bulk Debye temperature of copper (343 K). The corresponding value for lead atoms was used as a fitting parameter and was determined to be 110 K. The electron attenuation was simulated by a constant imaginary part of the inner potential, $V_{0i} = 5.0$ eV, whilst the real part was adjusted in the course of the theory–experiment fit as usual. For the structural search an automated algorithm based on a frustrated simulated annealing procedure and guided by the Pendry R-factor [24] was applied [35]. The variance of the R-factor:

$$\text{var}(R_p) = R_p^{min}\sqrt{8V_{0i}/\Delta E}$$

allows an estimation of the limits of errors of the model parameters determined. Here ΔE is the energy width of the database. In the present case ΔE amounts to $\Delta E^f = 650$ eV and $\Delta E^i = 800$ eV for the subsets of fractional- and integer-order spots, respectively, giving a total of $\Delta E = 1450$ eV.

With the total number of reconstructed atomic layers initially unknown, the analysis was performed in several steps, allowing in each subsequent step one more, i.e. deeper, layer to reconstruct. So, the first step assumed only the lead layer to reconstruct, i.e. all copper layers to remain flat and only their spacings to vary. In the last step as many as four layers (the Pb layer plus three copper layers) were allowed to reconstruct. In order to avoid landing only in a local minimum of the R-factor, two different starting TLEED reference calculations were used in each step. In one of them all layers were flat with interlayer spacings according to the atomic hard-sphere radii. The second was based on the best-fit structure of the preceding step with only the additional copper layer (the lead layer in the first step) assumed to be flat. However, if the movement of atoms during the structural search made TLEED go beyond its validity range, a new reference calculation was carried out. This procedure required up to four reference calculations in each step until convergence was achieved. Eventually, the best-fit structure was confirmed by a conventional full dynamical calculation.

An additional difficulty of the structure analysis arose from the fact that the surface is not fully covered by lead, i.e. integer-order peak intensities are affected by contributions from uncovered areas. As STM and AES tell us that about 20% of the surface contributes in this way, a possible way of proceeding could have been by means of the corresponding mixing of integer-order spot intensities, as the structure of clean Cu(111) is well known. Yet, as mentioned above, the intensity level of the latter is much higher than that of the lead-covered surface, leaving the mixing rather critical as regards the correct domain weight being considered. Also, because of the dominance of contributions from the uncovered surface, there would be only little additional information about the reconstruction phase. Additionally, the uncovered area

is disturbed by random point defects caused by some Pb atoms that are still incorporated. Therefore, we decided to use only fractional-order spot intensities for the structural search. For a final check, however, we also compared integer-order spot spectra for the structure retrieved, adding contributions from uncovered copper.

Of course, this cautious strategy reduces the width of the database which in turn raises the question of how many structural parameters, i.e. the reconstruction of how many layers, can be determined safely. For the consideration of the layer reconstructions we assumed that—due to the superstructure being commensurate—the mirror-symmetry plane present for the unperturbed substrate (indicated by the straight line in the left-hand panel in figure 3) is present also for reconstructed layers. As a consequence, only four out of nine Pb atoms per (4×4) unit mesh are symmetrically inequivalent, as labelled in the left-hand panel: two of them reside in fcc and hcp hollow sites (1 and 3, respectively), one in a near bridge site (2) and one in an atop site (4). As indicated in the right-hand panel of figure 3, similar arguments reduce the number of symmetrically inequivalent atoms to five in reconstructed Cu layers. Each of them is differently coordinated to neighbouring lead atoms or corresponds to different sites with respect to the next copper layer, as displayed by different degrees of shading in figure 3. Additionally to the assumption of mirror symmetry, we allowed only vertical displacements of atoms (the LEED analysis would be rather insensitive to small in-plane displacements anyway). As a consequence, there are four structural parameters describing the Pb layer and five parameters for each reconstructed Cu layer. Their variation also covers the top three (average) interlayer spacings $d_{i,i+1}$ ($i = 1, 2, 3$). For n reconstructed layers this yields a total of $N = 4 + 5(n - 1)$ structural parameters to be determined. This varies from $N = 4$ for only the lead layer reconstructed to as much as $N = 19$ (14) for four (three) reconstructed layers. As each energy window of width $\delta E = 4V_{0i} = 20$ eV in a spectrum is supposed to provide independent structural information [24], the total number of parameters for which independent information is provided is $\nu = \Delta E^f / \delta E \approx 33$. Yet, one must additionally consider some redundancy factor which is in the range 2–3, so no more than about 16 parameters can be determined safely. The case of three reconstructed layers ($N = 14$) is within this limit.
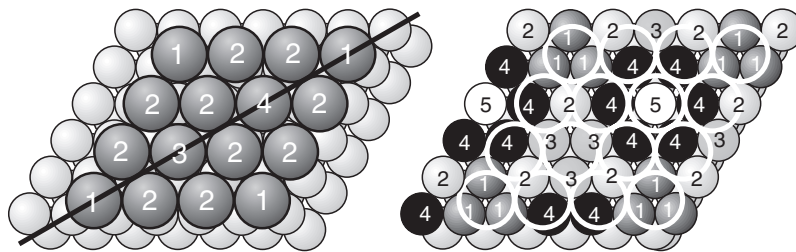
Figure 3. A top-view ball model for (4×4)-Pb/Cu(111) with symmetrically different Pb atoms (left) and Cu atoms (right) labelled. The black line marks the assumed mirror plane.

4. Results

Application of the above strategy for the structure determination produces the following results and consequences:

- With only the lead layer reconstructed, the Pendry R-factor for the subset of fractional-order beams is only $R_p^f = 0.42$ and that of integer-order spots is also at that level even when contributions from the uncovered surface are considered. Also, the relative weight of

fractional-order relative to integer-order (energy-averaged) intensities $r = \langle I_{frac} \rangle / \langle I_{int} \rangle$, which, like the R-factor, is a sensitive check for the correct model [36], is much lower than the experimental value, $r_{exp} = 26\%$. This is in spite of substantial buckling of the lead layer (overall amplitude 0.62 Å). As a consequence, this model can be clearly ruled out.

- When both the lead and top copper layers are allowed to reconstruct, the R-factor decreases to $R_p^f = 0.32$. Additional to that in the lead layer there is now also substantial buckling in the copper layer with an overall amplitude 0.74 Å. This value is too large by far, as the next, i.e. second, copper layer could be flat, as assumed in this second-step model. Together with the still modest level of the R-factor, this demands that we extend the reconstruction to the next layer.

- With three layers reconstructed, there is a further considerable drop of the R-factor, namely to $R_p^f = 0.18$. The overall buckling amplitudes are 0.20, 0.24 and 0.20 Å for the first to third atomic layers. The R-factor for the integer-order spot intensities is $R_p^i = 0.18$ when contributions of 20% of the uncovered surface are considered. The ratio of relative intensities, $r_{calc} = 26\%$, is not far from the experimental value. Yet, the still considerable buckling of the second copper layer makes us suspicious that the next layer is reconstructed, too. Therefore, as a test we decided to also allow the atoms of this layer to move, though knowing that our database definitely is not broad enough to determine as many as 19 parameters safely.

- Surprisingly, the reconstruction of four layers leads to only a small further decrease of the R-factor ($R_p^f = 0.17$). The overall buckling of the fourth layer is only modest and there is no or only little change in the amplitudes of the others (sequence from the top: 0.20, 0.24, 0.18, 0.09 Å). The average interlayer spacings also remain unchanged ($d_{12} = 2.44$ Å, $d_{23} = 2.24$ Å, $d_{34} = 2.16$ Å). The intensities of integer-order beams also compare very favourably with experiment when, with the structure for the lead-covered area fixed, fitted to contributions from the uncovered surface with variable weight. The best fit ($R_p^i = 0.17$) is obtained for exactly 20% uncovered surface, which is in quantitative agreement with the AES data. Also, the corresponding intensity ratio is $r_{calc} = 22\%$ compared to $r_{exp} = 26\%$, a small difference which can easily be explained by some disorder in the uncovered surface, e.g. caused by the Pb point defects. We also mention that no intermixing of lead and copper is found in the (4 × 4) phase. This is within an error margin of only 10% due to the rather different scattering strengths and characteristics of Pb and Cu.

In summary we can state that (i) the low (and equal) R-factors for both the fractional- and integer-order beams, (ii) the reproduction of the ratio of fractional-order to integer-order spot intensities and (iii) the agreement between LEED and AES concerning the weight of the uncovered surface give a high degree of confidence in the reliability of the structure determination. This is even though for four reconstructed layers it is based on a database that is possibly too small to allow for the safe determination of all atomic coordinates. Also, the variance of the R-factor, $\mathrm{var}(R_p) = 0.04$, is too large for one to safely deduce that the fourth layer is reconstructed, too. Yet, two features make us confident that the structural search procedure involving four reconstructed layers has not led to a wrong, i.e. only local, minimum of the R-factor hyperface. First, the reconstruction of the fourth layer is comparably weak and follows the generally expected attenuation towards the bulk. Second, limitation to only three reconstructed layers produces a very similar structure for the layers involved. We also emphasize that a buckling amplitude of 0.20 Å deduced for the third layer (in the three-layer case) makes it unlikely that the fourth layer remains unreconstructed. Of course, we must concede rather large error limits with respect to the coordinates of individual atoms. Their

estimation via the variance of the Pendry R-factor yields errors of ± 0.03 to ± 0.08 Å for atoms in the first to fourth layers. However, due to (not considered here) correlations between parameters, the errors are certainly even larger. The best-fit values of the atomic coordinates as well as the overall buckling amplitudes (vertical distances between highest and lowest atoms) are given in table 1.

Table 1. Vertical displacements of atoms with respect to the average plane and overall buckling amplitudes in the four reconstructed layers. The numbering of atoms is according to figures 3 and 5. Positive (negative) coordinates denote outward (inward) displacements relative to the average plane of the layer.

	Vertical displacements (Å) for atom No					
	1	2	3	4	5	Overall buckling (Å)
Pb layer	+0.04	0.00	+0.06	−0.14	—	0.20
First Cu layer	−0.02	+0.12	−0.02	0.00	−0.12	0.24
Second Cu layer	−0.10	−0.03	+0.02	+0.08	−0.02	0.18
Third Cu layer	0.00	−0.01	−0.05	0.00	+0.04	0.09

Figure 4 displays experimental and calculated best-fit spectra for a selection of beams. As expected from the small R-factor, they also compare very well visually. Figure 5 displays a schematic view of the corresponding best-fit model eventually retrieved for the lead-covered area, whereby the interlayer distances and the overall buckling amplitude for each layer are given. The view corresponds to a vertical cut through the surface along the symmetry plane indicated by the straight line in the left-hand panel of figure 3. Atoms both cut by the plane and touching it are displayed. The numbering of atoms is according to figure 3. Vertical displacements of individual atoms with respect to the centre-of-mass plane in each layer are given in table 1. The layers are strongly buckled and, consequently, the average interlayer spacings ($d_{12} = 2.44$ Å, $d_{23} = 2.24$ Å and $d_{34} = 2.16$ Å) are significantly expanded compared to the value resulting from hard-sphere radii or known for the copper bulk ($d_0 = 2.09$ Å).
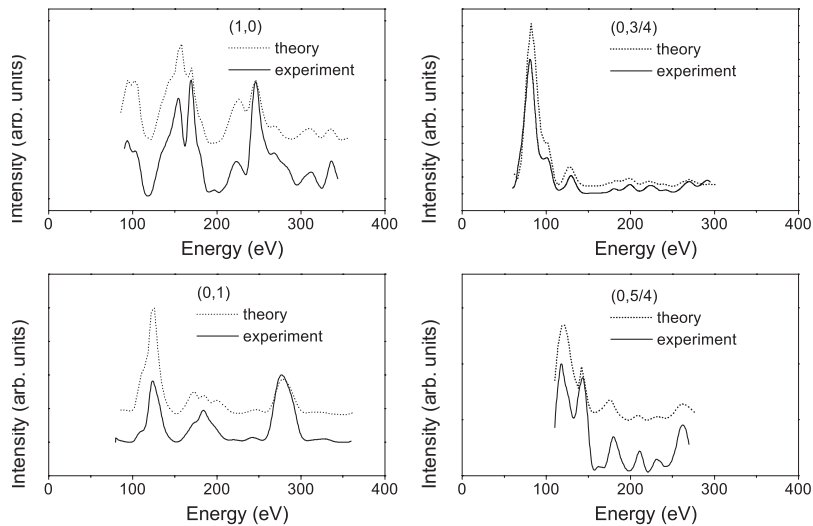
Figure 4. Comparison between experimental and calculated best-fit model spectra for some selected beams of (4×4)-Pb/Cu(111).
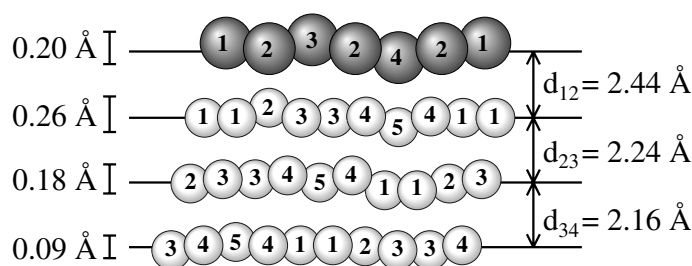
Figure 5. A surface cross section along the mirror plane. Atoms cut by the plane and atoms touching it are displayed. The mirror plane and numbering of atoms are according to figure 3.

Surprisingly, the total buckling amplitude in the lead adlayer is smaller than that in the top copper layer. As expected, however, the buckling decreases with increasing depth. The third-copper-layer buckling amplitude is only 0.09 Å, so it is justified—as assumed—to treat deeper layers as unreconstructed. We can conclude that the interface between the lead adlayer and the copper bulk is a slab made up of three considerably reconstructed copper layers.

5. Discussion and conclusions

The above-described combined application of STM, AES and quantitative LEED has revealed that the Cu(111) surface is nearly completely covered by a quasi-hexagonally close-packed Pb layer exhibiting a considerable vertical modulation and causing a pronounced (4 × 4) superstructure. Simultaneously, the lead layer induces a substantial reconstruction of the copper substrate extending as deep as three layers towards the bulk. Interestingly, among all Pb atoms, the one positioned on top of a copper atom (No 4 in figure 3 or 5) and which therefore should be higher than all others if the substrate is unreconstructed, resides in the lowest site, which feature has been called *inverse corrugation* [14]. Of course, this is due to the reconstruction induced in the substrate which allows the lead layer to be less buckled than the top copper layer. Reinspection of figure 5 shows that there is a kind of wave-like reconstruction embedding the on-top Pb atom in a kind of 'Cu valley'.

Whilst most interatomic bond lengths are consistent with the atomic hard-sphere radii or are only slightly larger, we have to note that two Pb/Cu pairs come considerably closer than expected from the value calculated from their radii (3.02 Å). This holds for Pb/Cu pairs Nos 4/5 and 2/4, for which the distances are only $l_{4,5} = 2.42$ Å and $l_{2,4} = 2.58$ Å, respectively. The latter might to a certain extent come closer to the hard-sphere values when lateral relaxations were allowed (to which LEED is less sensitive and which would have blown up the parameter space), but certainly some considerable discrepancy would remain. This raises the question of whether these values are an artifact of the multi-parameter structure determination. However, reinspection of this point in the analyses involving only one and two reconstructed copper layers reveals that the small Pb–Cu spacing is practically invariant (e.g. $l_{2,4} = 2.49$ Å for the case of two reconstructed copper layers); i.e. it always shows up. This is also independent of the starting reference structure; i.e. the feature also develops when atomic distances consistent with the atomic hard-sphere radii are chosen as the initial structure. Obviously, there are features in the $I(E)$ spectra which strongly demand these special small bond lengths. Yet, they are not reproduced by the EMT calculations [14]. Interestingly, however, recent (still preliminary) calculations involving density functional theory (DFT) in the local density approximation (LDA), which are much more accurate than EMT ones, produce

similarly small Pb–Cu spacings [38]. Apparently, the energy cost involved is overcompensated by the total atomic relaxation in the (4×4) unit cell. The value derived here for the average spacing between the lead and top copper layer, $d_{12} = 2.44$ Å, also differs substantially from the corresponding result from EMT (3.02 Å). Again, however, the preliminary DFT result is very close to the experimental value (within 0.02 Å). Also, roughly speaking, the relatively small value of d_{12} and the value of d_{23} being increased over the layer spacing in the copper bulk (2.08 Å) fit the general layer relaxation pattern of metal surfaces according to which the first spacing is contracted and the second is expanded.

We also note that the corrugation of the lead layer determined in the present LEED analysis (0.20 Å) is considerably higher than that found by STM ($\simeq 0.07$ Å), both in the present investigation and in earlier work [14]. However, this can be easily interpreted on the basis of the fact that the STM is sensitive to electronic states rather than to the atomic positions. Yet, the EMT simulations [14] also with a value of 0.07 Å also underestimate the buckling of the lead layer. On the other hand, for the copper layers—to which the STM is blind—the underestimation by EMT is less pronounced. The overall buckling amplitudes determined by means of LEED in the present work and EMT [14] compare rather well, i.e. 0.24 Å versus 0.25 Å, 0.18 Å versus 0.13 Å and 0.09 Å versus 0.07 Å for the first three copper layers, respectively. Our experimentally determined bond lengths between copper atoms are in the range 2.54–2.76 Å, i.e. rather close to the hard-sphere value (2.55 Å). They would possibly come even closer when lateral relaxations were allowed.

As mentioned already in the introduction, the precoverage of Cu(111) by about 1 ML Pb changes the growth mode of Cu or Co films from 3D island growth to layer-by-layer growth; i.e. Pb acts as a surfactant in this sense. With the detailed structure of the interface at hand, we are in the position to speculate about its role in the homoepitaxial growth and in the early stages of heteroepitaxial growth. Recent studies of the homoepitaxial growth of Cu/Cu(111) in the presence of lead, applying STM, thermal energy atom scattering (TEAS) and Monte Carlo (MC) simulations [12], suggest that the main effect of the surfactant is to modify the mechanism of atomic diffusion on the terraces of Cu(111). It is found that arriving Cu adatoms quickly get buried below the Pb layer where they diffuse by exchanging sites with other Cu atoms from the substrate. It was already speculated in reference [12] that this crucially important exchange process might be favoured by the 'considerable distortion on the Cu surface'. These latter distortions from the ideal hexagonal structure of layers have been quantified in the present paper and imply a reduction of the atomic coordination at the surface. In fact, there are EMT calculations on the (111) and the more open (100) and (110) surfaces of Cu showing a trend towards diffusion by the exchange mechanism as the degree of coordination on the surface diminishes [37]. Our results demonstrate that the copper substrate is indeed rather structurally flexible in the presence of lead, so exchange processes might be facilitated. Additionally, we have another and impressive example of adsorbate-induced surface reconstruction that shows that substrates in general do not behave as inert entities but are important elements participating in surface processes. We further suggest that substrate restructuring by the surfactant might be a general phenomenon occurring not only in metals but possibly also in semiconductor surfaces. Additional studies are under way intended to qualify this suggestion and correlate the structure in the first layers with the atomistic modification of the diffusion mechanism induced by the surfactants.

Acknowledgments

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