Inverse corrugation and corrugation enhancement of Pb superstructures on Cu(111) and (110)

C. Nagl, M. Schmid, P. Varga *

Institut für Allgemeine Physik, Technische Universität Wien, A-1040 Wien, Austria

Received 16 February 1996; accepted for publication 24 June 1996

Abstract

Contrary to intuitive expectation, a monatomic hexagonal close-packed Pb film on Cu(111) shows an "inverse" corrugation, i.e. the Pb atoms in on-top adsorption sites appear lowest in scanning tunneling microscopy (STM) images, as well as in effective medium theory (EMT) simulations. On small subsurface Cu islands on a Pb(111) substrate, which are also covered by a monatomic Pb film, the corrugation of this film was found to be strongly dependent on the thickness of the Cu island (the thinner the island, the larger the corrugaion). EMT simulations reproduce this enhanced corrugation qualitatively and thus further confirm the formation of these subsurface Cu islands. On a p(8×1) superstructure of Pb/Cu(110), similarly, the lowest coordinated Pb atoms also show the lowest apparent height in STM images.

Keywords: Adatoms; Copper; Lead; Metal–metal nonmagnetic thin film structures; Nucleation; Scanning tunneling microscopy; Single crystal surfaces; Superstructure

1. Introduction

The structure of metallic monolayers on metal substrates is a complex interplay of electronic, stress and geometric effects, all related to each other. Equilibrium as well as kinetically limited structures therefore show a variety of often surprisingly complex structures. The substrate has also been shown to be considerably influenced by the film and strongly interact with the film in many cases. Recently, Mottet et al. [1] and Foiles [2] have found by numerical simulations (extended tight-binding quenched molecular-dynamics and embedded atom method, respectively) a moiré pattern that is due to an unexpected relaxation of an Ag monolayer on Cu(111). It has been shown that the film surface exhibits a depression in low coordinated sites, i.e. in on-top sites. Experimental observations, supported by numerical simulations of this effect, have been reported for Ag on Ru(0001) [3] and Au on Ni(111) [4]. For Ag on Cu(111) and Ag on Ru(0001), Foiles and co-workers examined this feature in more detail. They showed that the depression is due to a strong relaxation of the topmost substrate layers beneath the film atom in on-top and bridge locations, respectively, in order to reduce the bond length between film and next-nearest neighbour substrate atoms [2,3].

In this paper we present a scanning tunneling microscopy (STM) study on the same phenomenon, found for close-packed Pb films on Cu(111) and a Pb superstructure on Cu(110). A reduced
3. Corrugation of Pb films on various Cu substrates

3.1. (4 × 4) superstructure of Pb on Cu(111)

Fig. 1a shows an STM image of a hexagonal close-packed Pb film on Cu(111) at a coverage of 0.6 ML Pb [5]. The ratio of bulk lattice constants of Pb and Cu is 4.11/3; the lattice constant of the Pb film, however, is dependent on the coverage [11]. The Pb film can therefore be understood as an incommensurate floating solid. At the coverage at which the STM image has been taken, the lattice constant corresponds almost exactly to 4/3 of the Cu lattice constant. This results in large areas that show perfect (4 × 4) periodicity, as can be seen in Fig. 1a. A model of this superstructure is presented in Fig. 1c. One Pb atom per unit cell is on top of a Cu atom, and two are in hollow sites (one in an fcc site, the other in an hcp site). The unit cell of the superstructure in the STM image exhibits one dark atom per unit cell, and all the other atoms appear almost equal (for quantitative values see below and Table 1). To preserve the symmetry and the correspondence with the model, the dark atom, i.e. the atom that is imaged deeper, has to be in an on-top site. In other words, the atom that should appear higher in a hard sphere model appears lowest. This is the same behavior as has been described in Refs. [1,2]. Experimental obser-
Fig. 2. (a) EMT result of a Pb film on an eight layer thick Cu(111) slab. The greyscale represents the height of the Pb atoms. The white dots indicate the Cu atoms of the layer beneath. (b)–(d) Topmost three Cu layers. The height difference between the brightest and the darkest atom in (a)–(d) is 7, 25, 13 and 7 pm, respectively. The greyscale of the Pb film in (a) is exaggerated by two times compared to the three Cu layers.

Table 1

<table>
<thead>
<tr>
<th>Number of Cu layers ($n_{Cu}$)</th>
<th>Pb film, STM</th>
<th>Pb film, EMT</th>
<th>Cu first layer</th>
<th>Cu second layer</th>
<th>Cu third layer</th>
<th>Pb, uppermost substrate layer</th>
<th>Pb–1, substrate layer</th>
<th>Pb–2, substrate layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\infty$</td>
<td>5–10</td>
<td>7</td>
<td>25</td>
<td>13</td>
<td>7</td>
<td>14–36</td>
<td>14–33</td>
<td>14–60</td>
</tr>
<tr>
<td>3</td>
<td>5–10</td>
<td>15–19</td>
<td>30–73</td>
<td>55–68</td>
<td>14–60</td>
<td>8–14 20–38</td>
<td>6–9 11–13</td>
<td>0–3 4–6</td>
</tr>
<tr>
<td>2</td>
<td>~15</td>
<td>30–57</td>
<td>86–130</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>~75</td>
<td>10–16</td>
</tr>
<tr>
<td>1</td>
<td>~30</td>
<td>~100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Corrugations within the (4 × 4) unit cell for structures with one Pb overlay on Cu(111) ($n_{Cu} = \infty$) and Pb-covered Cu islands on Pb(111) with one, two and three Cu(111) layers; the corrugations of the deeper layers are results of EMT calculations; all values are given in pm.

Table 2

<table>
<thead>
<tr>
<th>Number of Cu layers ($n_{Cu}$)</th>
<th>Pb film, STM</th>
<th>Pb film, EMT</th>
<th>Cu first layer</th>
<th>Cu second layer</th>
<th>Cu third layer</th>
<th>Pb, uppermost substrate layer</th>
<th>Pb–1, substrate layer</th>
<th>Pb–2, substrate layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\infty$</td>
<td>5–10</td>
<td>7</td>
<td>25</td>
<td>13</td>
<td>7</td>
<td>14–36</td>
<td>14–33</td>
<td>14–60</td>
</tr>
<tr>
<td>3</td>
<td>5–10</td>
<td>15–19</td>
<td>30–73</td>
<td>55–68</td>
<td>14–60</td>
<td>8–14 20–38</td>
<td>6–9 11–13</td>
<td>0–3 4–6</td>
</tr>
<tr>
<td>2</td>
<td>~15</td>
<td>30–57</td>
<td>86–130</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>~30</td>
<td>~100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Corrections of this phenomenon have been reported in Ref. [4] for an Au monolayer on Ni(111), for Ag on Ru(0001) in Ref. [3] and for a Pb superstructure on Cu(110) in Ref. [12] (see also below). The observed moiré patterns and corrugations of the Pb film on the Cu(111) substrate, as well as on the Cu islands, were found to be independent of tunneling conditions. Though the STM contours correspond rather to LDOS than to the pure geometry, this independence should allow us to compare the corrugation in the STM images with atomic positions.

Fig. 2a shows an EMT simulation of a Pb film with (4 × 4) periodicity on an eight-layer Cu(111) slab. A comparison with the STM image shows good agreement. The superimposed Cu lattice from the topmost Cu substrate layer (visible as white spots) again shows that the dark Pb atoms, i.e. the deepest, are exactly on top of Cu atoms. The height difference between the dark (= on-top Pb atom) and the brightest atom (= hollow site) is about 7 pm. This is exactly the same value as in the STM image (Table 1). As in the case of Ag on Cu(111) [2], in our case the “inverse” corrugation is also caused by the Cu substrate since the on-top Pb atom is 0.302 nm above the nearest Cu atom, whereas the Pb atom in the hollow site is 0.284 nm above the Cu atom next to it when comparing the difference in height normal to the surface (nevertheless, the bond length of the on-top Pb atom is 20 pm smaller than that of the Pb atom in the three-fold hollow location). Hence the modulation has to be much stronger for the substrate than for the film. Indeed, whereas the corrugation of the Pb film is only 7 pm, it is 25 pm for the topmost Cu layer, 13 pm for the second layer, and 7 pm for the third layer (Figs. 2b–2d). These values are, however, half as much as in the case of an Ag monolayer [2]. The reason for this may be the smaller unit cell (twice as small) on the one hand, and a weaker bonding of the Pb film to the Cu substrate on the other.

Whereas repulsive interactions can be localised rather easily in the EMT data, attractive interaction can be studied only in an indirect way. Some insight into the driving forces for the inverse corrugation can be gained, however, by comparing an unrelaxed (flat) structure with the relaxed one. In the unrelaxed case, the overlap of the on-top Pb atom with the Cu atom beneath is rather large, resulting in a large repulsion. An outward relaxation of the Pb atom would decrease the binding energy drastically. Therefore, the seven Cu atoms beneath form a concave dimple, thereby decreasing on the one hand the repulsive interaction between the on-top Pb atom and the Cu atom beneath; on the other hand, the binding energy is increased by the six surrounding Cu atoms. This is supported by the fact that about one third of the electron density of the on-top Pb atom that comes from Cu is coming from the six nearest-neighbour Cu...
atoms. The strong relaxation of the Cu layers might be promoted by an additional effect: the Cu atoms that are beneath on-top Pb atoms are somewhat under-coordinated compared to the neighbouring atoms, i.e. they might tend to relax inward. This line of reasoning is in agreement with Foiles [2], who studied isolated adatoms to explain this inverse corrugation.

3.2. Layer-dependent corrugation of Pb films on Cu islands

In two recent papers we have reported on the deposition of Cu on Pb(111) [6,13]. 3D Cu islands form, most of which are orientated with their (111) planes parallel to the substrate. These Cu islands are about 10 nm in diameter and between one and 11 layers thick. The Cu islands immerse several layers deep into the substrate and they are covered by a monatomic Pb film. This unexpected behavior results from the considerably different surface energies of Cu and Pb. Figs. 3a and 3b show one of these Cu islands. The numbers on the different parts correspond to the estimated number of Cu layers beneath the Pb film, as determined from an analysis of the step height [6,13]. The Pb film covering this island shows different corrugation on several parts of the island. Whereas in the upper part in Fig. 3a the corrugation is rather small – similar to that on the pure Cu(111) substrate – it is much more pronounced on the lower lower part. A comparison with the number of Cu layers beneath indicates that this enhanced corrugation occurs when there are only one or two Cu layers beneath the Pb film. A detailed analysis shows that the corrugation within the (4×4) superstructure unit-cell increases from 5 pm when there are three or more Cu layers beneath to 15 pm on the Cu island terrace with two layers, and finally to 30 pm when there is only one Cu layer left (Table 1).

3.2.1. Three Cu layers on Pb(111)

In order to simulate this behavior, a seven-layer thick Pb(111) slab with a unit cell of 35×35 atoms has been built up on which 48×48 Cu atoms with the corresponding number of layers has been placed. This assembly has then been covered with a monatomic Pb film with 36×36 atoms to achieve
Fig. 4. (a) Model of the unit cell used in the EMT simulations. On seven Pb(111) layers, two of which are fixed, consisting of $35 \times 35$ atoms, each three Cu(111) layers with $48 \times 48$ atoms have been placed. On this assembly a Pb(111) film with $36 \times 36$ atoms has been placed. (b) EMT result of the Pb film. The greyscale corresponds to the height difference, which is about 25 pm between the brightest and darkest atoms. (c) Total energy per $(4 \times 4)$ unit cell of the first six layers. The energy difference between maxima and minima is about 0.4 eV. The cross marks the same point in both images.

a $(4 \times 4)$ superstructure (Fig. 4a). The different numbers of Pb atoms in the film and the substrate layers account for the reduced interatomic distance of the Pb film observed on a Cu(111) substrate [11], as well as on Cu islands [6].

The EMT result of the Pb film on the three Cu layers is shown in Fig. 4b. Two moiré patterns with different unit cells are visible. On the one hand the $(4 \times 4)$ superstructure can be seen, which is due to the 4/3 interatomic distance ratio of the Pb film and the underlying Cu layers. The bright elevation in the center of the $36 \times 36$ unit cell, on the other hand, results from the 35/48 ratio of the interatomic distances of the Pb substrate and the Cu layer and the 35/36 ratio of the Pb atomic radius of the Pb film and the substrate, respectively. In this bright region, which is elevated by about 20 pm, most of the Cu atoms in the layer adjacent to the substrate are neither in on-top nor in hollow sites, but somewhat in between. Fig. 4c shows the
Fig. 5. (a) EMT result for the corrugation of a Pb overlayer on a two-layer subsurface Cu island. The greyscale corresponds to the height difference, which is 80 pm between the brightest and darkest atoms. (b) Total energy per (4 × 4) unit cell of the first four layers. From maxima to minima the energy difference is about 0.25 eV. (c) Total energy of the Pb film and the Cu layer beneath. The cross in (a)–(c) marks the same point.
energy difference of the total energy per \((4 \times 4)\) unit cell averaged over the first six layers (two substrate layers, three Cu layers and the Pb film layer). Obviously the bright elevation in the middle of the \(36 \times 36\) unit cell is energetically least favorable since the energy difference between a dark region in the energy plot and the elevation is about 0.4 eV per \((4 \times 4)\) unit cell. The main contribution to the total variation of energy comes, however, from the interface between the Pb substrate and the Cu island. Except in the two Cu layer region in Figs 3a and b (EMT results – see below), such an elevation has not been observed in the experiment. On the one hand, the average area of a terrace with a certain thickness and without any step is most often smaller than the \(36 \times 36\) unit cell, which has a length of 13 nm. On the other hand, the larger total energy might cause other mechanisms, such as a step or a stacking fault, to prevent the formation of such an elevation.

In qualitative agreement to the STM results, the corrugation was found to be increased for this kind of island. The height difference between the Pb film atoms in on-top and in hollow sites varies between 15 and 19 pm within the \((4 \times 4)\) unit cell (Table 1). The Cu layers show a corrugation of 14–40 pm; the topmost Pb substrate layer is rather flat, the corrugation varies from 8 to 14 pm and then drops to zero within the next few layers. The corrugation of the Pb film derived from EMT simulations overestimates, however, the height differences found in STM images (see Section 3.2.3).

### 3.2.2. Two Cu layers on Pb(111)

The EMT result of the Pb film on the two Cu layer sandwich structure is shown in Fig. 5a. Similar to the three Cu layer structure, a bright elevation can be seen. This elevation is likewise caused by adsorption sites of the Pb substrate and the Cu layer above that are between hollow and on-top sites. The energy plot averaged over the first four layers again shows that this region is the least favorable (Fig. 5b); the energy difference between maxima and minima is about 0.95 eV per \((4 \times 4)\) unit cell. When we look at the energy plot of the Pb film and the top Cu layer separately (Fig. 5c) we can see, however, that for these two layers the bright region in the corrugation plot would be energetically more favorable. The main contribution to the increase of total energy hence comes from the Pb substrate–Cu interface.

The island in the STM image (Figs. 3a and 3b) also exhibits an elevation, visible as a bright strip in the middle (marked by an arrow). The height of the strip is about 40 pm, which is exactly the same value as in the EMT simulation. This correspondence, and the fact that the lattice constant of the Pb film in Figs. 3a and 3b is 3–5% smaller than the lattice constant of the substrate, suggests that the bright strip is a moiré pattern caused by the different Pb lattice constants, as in the simulation. There is, however, a subtle difference between the experimentally observed islands and the simulated structure: the dark stripes, which connect rows of on-top Pb film atoms, are not fixed to a specific row of atoms but change to the row next to it after about 30–40 atoms (visible when Fig. 3b is viewed at a slight angle along a row of atoms). Hence the Pb film has to be rotated by about 0.5° with respect to the underlying Cu layer (a rotation of the Cu island with respect to the Pb substrate would not be visible in the STM image). This rotation might be responsible for the appearance of the elevation as a strip in the STM image and as a bump in the EMT results.

The EMT simulations again reproduce the enhanced corrugation of the two-layer thick island found by STM. The corrugation of the Pb film within the \((4 \times 4)\) unit cell in the computer simulation varies between 30 and 57 pm; in the STM image it is again lower (15 pm) (Table 1). The Cu layers in the simulation show height differences from 50 to 73 pm; the Pb substrate beneath again exhibits less corrugation (20–38 pm in the topmost Pb layer).

### 3.2.3. One Cu layer on Pb(111)

The EMT results of the one Cu layer sandwich structure are quite different. As can be seen in Fig. 6, there are two regions within the \(36 \times 36\) unit cell where the Pb film breaks up and shows a cleft. The larger of these two clefts also proceeds into the Cu layer and the topmost Pb substrate layer. It occurs when a Pb film atom is on top of a Cu atom which itself is on top of a Pb substrate atom. This disadvantageous situation is also reflected by
the fact that the small region in Figs. 3a and 3b is the only one of this kind that has been observed experimentally. Larger regions of a one Cu layer structure tend rather to reconstruct and form a (5 × 5) superstructure [13].

The corrugation within a (4 × 4) unit cell is about 100 pm in the EMT simulation. The value found experimentally again is considerably smaller (about 30 pm) (Table 1). Although the general trend of the corrugation enhancement due to a decreasing number of Cu layers is reproduced by the simulation, it is in all three cases (three, two and one layer of Cu) overestimated by a factor of three. This might be caused by several effects: (i) EMT simulations are only an approximation. This is especially true for the EMT potentials of Pb. (ii) STM tips are of finite apex, and large corrugations on small lateral length scales are therefore usually underestimated. (iii) A rotation of the Pb film as observed on the two layer Cu island could also reduce the corrugation.

The corrugation derived by the EMT simulations should therefore be seen in a more qualitative way. Nevertheless, the general trend of the corrugation enhancement is well described. The layer-dependent corrugation furthermore proves that most of the Cu islands described in Refs. [6,13] are indeed thicker than two Cu layers, since these islands do not exhibit the large corrugation shown in Figs. 3a and 3b.

There are two reasons for this strongly enhanced corrugation within the (4 × 4) unit cell of the Pb film in the case of a reduced number of Cu layers. First, the mechanical stiffness is of course reduced in a slab of finite thickness. Second, the Cu layer (or the topmost Cu layer if there are two or more) is modulated by the Pb film and the same layer (or a layer beneath in the case of thicker slabs) is also modulated by the Pb substrate. Due to the different lattice constants of the Pb film and the substrate, this superposition of modulations results in regions with strong and weak corrugations (see Fig. 4, Figs. 5 and 6). For example, in the case of a two layer thick Cu island there is a rather strong corrugation if a Pb substrate atom beneath an on-top film atom is in a hollow site (with respect to the Cu layer above). If the Pb substrate atom is likewise in an on-top site, the effect of inverse
corrugation cancels itself out to some extent, resulting in regions with weak corrugation.

3.3. The p(8 × 1) superstructure of Pb/Cu(110)

Fig. 7a shows the atom-resolved structure of the p(8 × 1) superstructure of Pb on Cu(110), which can be found at a coverage of 0.75 ML \[12\]. The corresponding model is presented in Fig. 7b. The unit cell is terminated by a Pb atom that is substituting a Cu atom (visible as the dark row in the [001] direction; the Pb atoms in these rows are not visible) and five Pb atoms in between. The Pb row in the center appears deeper. A linescan taken along the [110] direction across the atoms shows a depression of about 2 pm. When we compare the STM image with the model it is obvious that this row is in bridge sites, whereas the others are almost in four-fold hollow sites. This suggests that the same mechanism of bond-length shortening and substrate relaxation near less coordinated film-atoms, as described above, also applies to this superstructure. The EMT simulations support this result qualitatively. As in the case of Pb
on Cu(111), the Cu(110) substrate also exhibits a much stronger corrugation within the superstructure unit cell than the Pb overlayer.

4. Conclusion

The corrugation of a hexagonal close-packed Pb film on Cu(111) has been studied by STM and EMT. As has been proposed by Foiles [2], a relaxation of the Cu substrate beneath on-top Pb film atoms causes an “inverse” corrugation, i.e. the on-top atoms appear deeper. This unexpected corrugation has been clearly identified experimentally by STM and reproduced by EMT. Most of the inverse corrugation is caused by a relaxation of the Cu substrate. This is even more pronounced on Cu islands on Pb(111), where the Pb film covering the islands exhibits a corrugation strongly dependent on the thickness of the Cu island.

An inverse corrugation has also been found for a p(8 x 1) superstructure of Pb on Cu(110), where Pb atoms in bridge sites are deeper than the adjacent atoms in hollow sites.

Acknowledgements

We would like to thank K.W. Jacobsen, J.K. Nørskov and P. Stoltze (DTU and CAMP, Lyngby, Denmark) for providing us with the EMT code. This work has been supported by the Fonds zur Förderung der wissenschaftlichen Forschung under project no. P9282 and by the Hochschuljubiläumsstiftung der Stadt Wien.

References