Submonolayer growth of Pb on Cu(111): surface alloying and de-alloying

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Received 15 June 1994; accepted for publication 8 September 1994

Abstract

In spite of the immiscibility of Pb in bulk Cu, atomically resolved scanning tunneling microscopy reveals surface alloy formation of Pb deposited on Cu(111), even at 300 K. Due to kinetic limitations at room temperature, the incorporation of Pb is restricted to advance from step edges, while after annealing to 470 K or higher, embedded Pb atoms are found to be randomly distributed over terraces. At low tunneling voltages, standing waves of surface-state electrons scattered by embedded Pb atoms could be observed. The maximum packing density of the surface alloy is about 40% (= 0.4 ML) of a close-packed Pb overlayer. Thus, deposition above 0.4 ML and subsequent annealing results in hexagonal close-packed Pb regions, whereas on the non-annealed surface hexagonal close-packed Pb islands are already found at 0.2 ML. Eventually, at 1 ML the surface alloy is entirely replaced by a Pb overlayer.

1. Introduction

Surface alloying of thin metallic films has become a well-known phenomenon and has been proved through various experimental techniques in the last years. Besides surface alloying of Au deposited on Cu(100) [1] or Au on Ag(110) [2], where Cu–Au and Au–Ag are miscible in bulk, mixing in the first monolayer of immiscible metals like Au on Ni(110) [3] or Ag on Pt(111) [4] has been recently revealed by scanning tunneling microscopy (STM). The latter result has also been confirmed by X-ray photoelectron spectroscopy (XPS) and CO thermal desorption spectra [5]. Neugebauer and Scheffler [6] examined Na and K on Al(111) – also immiscible in the bulk – theoretically by means of density functional theory total-energy calculations. They found the substitutional site to be energetically most favourable. Stampfl et al. [7] verified these results by low-energy electron diffraction (LEED).

The system chosen for our study – Pb on Cu(111) – adds a new aspect to the discussion of surface alloys: in contrast to the systems studied previously, the size difference between Pb and Cu (Pb is 37% larger) is much larger than in most other surface alloy systems studied previously. Only K and Al, studied by Stampfl et al. and Neugebauer et al., have a larger size difference, which is still not comparable to Pb and Cu, since the atomic radius of K is strongly dependent on the coordination number and the degree of ionicity [6,7]. Furthermore, Al has a rather low vacancy formation energy compared to Cu [6,19]. Therefore, the formation of a Pb/Cu surface alloy on the close-packed Cu(111) could not be anticipated even after it has become clear that surface alloying is a common phenomenon.
There have been studies on the growth of ultra-thin Pb films on Cu for the last two decades. In 1972, Henrion and Rhead reported about LEED studies on Pb films with a thickness up to several monolayers on low-index faces of Cu [8]. LEED and Auger electron spectroscopy (AES) studies were performed by Barthès and Rhead in 1979 [9]. The oxidation of submonolayer Pb films was examined by Ocal et al. [10]. A more detailed LEED analysis of Pb deposited on Cu(111) was done by Meyer et al. [11], who determined the average Pb–Pb distance in a close-packed overlayer under various conditions. Their results were interpreted as an incommensurable Pb overlayer with a lattice constant being dependent on coverage and temperature. Thermal energy atom scattering (TEAS) experiments at 140 K by Hinch et al. [12] were interpreted as the growth of the layer being influenced by a quantum size effect.

In our studies, Pb was deposited in the coverage range of 0.05 to 1.1 ML and investigated with STM. To examine surface alloying under thermodynamic equilibrium conditions we also performed annealing experiments up to 573 K.

2. Experimental

The STM experiments were carried out in a UHV chamber with a commercial scanning tunneling microscope (Omicron Micro-STM). All STM images were obtained in constant-current mode with the sample negative. The pressure in the STM chamber was below $5 \times 10^{-11}$ mbar. Sample preparation (sputter-cleaning, annealing and deposition) was done in a separate preparation chamber with a base pressure in the low $10^{-10}$ mbar region. The Cu(111) (99.999%) single crystal was cleaned by cycles of 1 keV Ar$^+$ bombardment and annealing to 773 K until no contamination could be detected with AES.

Pb (99.999%) was deposited with an Omicron EFM3 electron-beam evaporator at deposition rates of 0.2 to 1 ML/min (1 ML Pb(111) = $9.43 \times 10^{14}$ atoms/cm$^2$; 1 ML is defined as a complete overlayer with Pb bulk lattice constant). The increase in pressure during evaporation was below $1 \times 10^{-10}$ mbar. Due to the electrons heating the crucible of the evaporator, about 0.5% of the evaporated Pb atoms are ionised in the evaporator. These Pb$^+$ ions are accelerated by the crucible voltage to a kinetic energy of 800 eV. Therefore, the sample is bombarded by energetic Pb ions during evaporation unless a bias voltage is applied to the sample to repel the Pb ions. The amount of energetic Pb ions neutralised in the Pb gas after acceleration was estimated to be negligible.

Prior to deposition on the Cu single crystal, the evaporation rate was checked by a quartz crystal microbalance. Comparison of the quartz microbalance measurements with AES signal versus coverage plots showed excellent agreement. The inaccuracy in Pb deposition was estimated to be less than 3% for coverages above 0.2 ML. Before deposition, the Cu(111) single crystal was cooled down to a temperature that was at most 3 K above room temperature (RT). All STM experiments were performed at RT.

3. Results and discussion

3.1. Surface alloying at low coverages (0.05 ML Pb)

After deposition of 0.05 ML Pb on a clean Cu(111) surface, a typical STM image exhibits Pb atoms as bright spots on the unresolved Cu surface (Fig. la). The Pb atoms are situated at two clearly distinguishable adsorption sites, namely on the terrace and directly at the step edge. The first type is represented by a group of 10 Pb atoms on the right part of Fig. la and a seam of Pb atoms on the upper part of the monatomic step approximately parallel to the step edge in Figs. la and lb. The second type of adsorption site is the Cu step itself, which is decorated with Pb atoms (Fig. la). A section through Fig. la shows that the Pb atoms parallel to the step and in the group exhibit a corrugation of only 0.07 nm above the Cu plane, which is substantially less than the height of a Pb(111) step and a close-packed 2D Pb island (0.28 nm). However, the height of the Cu step in Fig. la agrees very well with the bulk interlayer spacing of 0.21 nm. The Pb atoms at the step appear a bit lower, but also 0.02 nm higher than the Cu plane. Additionally, the atomic arrangement of the Pb atoms remains stable during several STM scans, whereas a high diffusivity of Pb can be deduced from the growth of very large close-packed 2D Pb islands with a rather round and “frizzy” shape at higher coverage (see, e.g., Fig. 6). Furthermore, under special tip conditions with a small tip–surface
Fig. 1. STM topographs of the Cu(111) surface after deposition of 0.05 ML Pb. Pb atoms are visible as bright spots. (a) On the right margin a group of embedded Pb atoms, caused by the impact of an energetic Pb ion, is visible. Single embedded Pb atoms are situated near a monatomic Cu step. The step itself is also decorated with Pb. A section (taken along the line) shows a monatomic Cu step with an adsorbed Pb atom and four embedded Pb atoms (Cu itself is not atomically resolved) (5×10 nm²). (b) When the energetic Pb ions are suppressed by a retarding voltage, no more groups of embedded Pb atoms are visible. However, there are still some single Pb atoms embedded in the terrace (20×20 nm²).
Fig. 2. Atomically resolved STM topograph (10 × 10 nm²) of the Cu(111) surface showing 20 Pb atoms embedded in Cu (0.05 ML Pb deposited). Although the Pb atoms appear distorted due to tip-sample interaction at the close tunneling distances used, one can see that the Pb atoms occupy substitutional sites, where one Pb atom replaces one Cu atom. The Pb atoms are separated from each other by at least one row of Cu atoms.

Simple counting of the embedded — and thereby visible — Pb atoms yields only 10–30% of the overall coverage. However, AES shows the whole amount of deposited Pb. The missing Pb cannot be in the bulk since Pb is immiscible with Cu in bulk [13] and we also did not find any indications for distortion of the Cu surface by subsurface Pb atoms. Hence, the Pb atoms have to be elsewhere, e.g., (a) in the 2D adatom gas, (b) in hypothetical close-packed Pb islands, (c) embedded parallel to steps and adsorbed at steps in areas with a high step density. Since a large number of measurements did not reveal any Pb islands and the average step density should be below 10⁻¹ nm⁻¹, we suggest the missing Pb atoms to be mostly in the 2D adatom gas.

This situation changes if the sample is heated to 473 K or higher after RT deposition (Fig. 3). Now also the Pb atoms that were missing at RT are visible. As Fig. 3 shows, the Pb atoms are randomly distributed all over the surface. Counting the Pb atoms proves that each spot corresponds to one embedded Pb atom. Besides, the steps are still decorated with Pb. This annealing experiment shows that the surface alloy is the thermodynamically stable configuration of Pb on Cu(111) in the submonolayer range. In room temperature experiments we see a kinetically limited structure, where the...
barrier for replacement of a Cu by a Pb atom can be hardly overcome. Annealing or the impact of energetic Pb ions can supply the activation energy necessary for forming the surface alloy on flat terraces.

Nevertheless, at room temperature we do already have a surface alloy near steps in the form of rows or a seam of substitutional Pb atoms parallel to the steps (Figs. 1a and 1b). Several mechanisms can cause these structures:

(1) Pb atoms might diffuse from the step edge into the upper terrace.

(2) Pb atoms may be embedded in the surface near a step by pushing a row of Cu atoms one interatomic distance towards the step edge, thereby moving an edge atom onto the terrace. This process was studied by Raeker et al. [14] using simulation calculations for Ni on Cu(111), indicating that this process can occur within 2 or 3 Cu–Cu distances (0.5 to 0.8 nm) from the step edge, whereas we found Pb atoms even in a distance of 2 to 4 nm. In these simulations the Ni atoms were just diffusing towards the step edge while in our case the adsorption energy of a Pb atom near the step edge could be sufficient to push a row of Cu atoms onto the terrace even from larger distances. Additionally, process (2) leads to a short-time roughening of the step edge, which may also facilitate diffusion of Pb atoms from the step edge into the terrace.

(3) Pb adsorbed at the step edge (at the lower terrace) may be buried by Cu atoms diffusing along the step edge. While the mobility of Cu(111) steps at room temperature is normally too low for such a process, adsorption of Pb may possibly lower the relevant barriers.

(4) Surface alloying on the terrace produces Cu adatoms, which will diffuse to a step and may cover the Pb atoms adsorbed there. During deposition, this enables the adsorption of further Pb atoms at the step edge (without forming an overlayer of pure Pb, which would be energetically less favourable). Thereby a mixed Pb + Cu layer, i.e., a surface alloy, can grow from the step edges. Since almost no Pb atoms are embedded in the terrace this mechanism can play only a minor role.

Successive STM images show a sudden appearance of embedded Pb atoms near step edges, as well as growth of the surface alloy by aggregation of atoms to the step edge. Therefore, it is plausible that besides process (2), which should cause the incorporation mainly during deposition, at least one other process contributes to the formation of the surface alloy near step edges at room temperature.

The incorporation of Pb atoms offers an interesting opportunity to visualise electronic features of Cu(111), i.e., the surface state of Group-Ib metal (111) surfaces [15–17]. While Fe is stabilised on Cu(111) by cooling to 4 K [15], Pb is fixed to a certain site, even at RT, by alloying. Thus – similar to the experiments by Crommie et al. [15] – we were able to image standing waves of surface-state electrons scattered by Pb atoms (Fig. 4). This wave-like structure in Fig. 4 and especially in Fig. 5a is not a topographic effect due to a compressed Cu layer similar to the Au(111) or Pt(111) reconstruction, since it appears only at low tunneling voltages. At these voltages the contributions of different electron energies of the surface state do not smear out the wave-like structure. Additionally, the wavelength agrees with the value expected for the surface state. Besides, standing waves at two impurity atoms that are most likely situated below the surface were also observed (visible on the upper half of Fig. 4). A more detailed discussion will be given elsewhere [18].
3.2. 0.2 ML Pb – structure of the surface alloy

Increasing the coverage to 0.2 ML Pb, an STM image shows the monatomic Cu steps decorated by a seam of disordered Pb atoms (Fig. 5a). As in Fig. 1a, there are groups of embedded Pb atoms in the terrace caused by the impact of single ionised Pb atoms.

The groups of embedded Pb atoms and the disordered Pb seam show the same height as well as identical appearance. For the same arguments that have been given for 0.05 ML Pb coverage above, it is obvious that the Pb atoms in the disordered seam are not adatoms on a flat Cu(111) surface, but are stabilised by Cu atoms between them, forming a surface alloy.

When a Cu lattice is superposed on Fig. 5a, it becomes evident that the Pb atoms in the surface alloy are separated by at least one Cu row. This can also be seen directly from Fig. 2. Although the seam appears
quite disordered, the nearest neighbours are mostly at \((\sqrt{3} \times \sqrt{3})R30^\circ\) or \(p(2 \times 2)\) positions represented in Fig. 5b. In very small areas perfect \((\sqrt{3} \times \sqrt{3})R30^\circ\) or \(p(2 \times 2)\) structures develop, forming locally hexagonal arrangements of the Pb atoms.

The width of the seam of disordered surface alloy is limited to about 2 nm. This upper limit for the seam width must be caused by the formation mechanism of the surface alloy discussed above, namely diffusion and direct incorporation of Pb into the terrace in a region near the step edge. There is no dependence between seam width and terrace width, indicating that diffusing Pb can overcome a possible potential barrier at step edges, even at RT.

The first occurrence of hexagonal close-packed Pb regions adjacent to the disordered Pb–Cu surface alloy can be observed at 0.2 ML (Fig. 6). In contrast to a coverage of 0.05 ML Pb – where no close-packed Pb islands could be found – at 0.2 ML the adatom density is high enough for the formation of these close-packed Pb islands. Annealing to 573 K provides the energy to spread the Pb atoms uniformly over the entire surface.
Fig. 7. 10×10 nm² STM topograph of 0.2 ML Pb on Cu(111) deposited at RT and annealed to 573 K. The Pb atoms are more or less randomly distributed over the surface, embedded in the first Cu layer. (Fig. 7), being embedded in the first Cu layer. No regions of close-packed Pb overlayer can be observed after annealing. This shows once more that the surface alloy is the thermodynamically stable configuration, whereas the close-packed overlayer, observed before annealing, only develops as the amount of deposited Pb cannot be accommodated in the surface alloy due to kinetic limitations. For the \((\sqrt{3} \times \sqrt{3})R30°\) structure, Polatoglou et al. [19] calculated a vacancy formation energy of Cu(111) of 0.92 eV. Hence, the gain in adsorption energy of the substitutional site compared to the dense Pb overlayer must be at least that much higher.

3.3. Maximum density of Pb in the surface alloy

The packing density of the disordered surface alloy (e.g., in Fig. 5a) was found to be restricted to 40% of the close-packed Pb overlayer (coverage 0.22, corresponding to the Cu lattice). The \((\sqrt{3} \times \sqrt{3})R30°\) or \(p(2 \times 2)\) superstructures of the Pb–Cu surface alloy, which have a packing density of 62% or 47% of a close-packed Pb overlayer, respectively, were found to be restricted to very small areas. Neither the packing density nor the regions with \((\sqrt{3} \times \sqrt{3})R30°\) or \(p(2 \times 2)\)
superstructures can be increased by cooling down very slowly from 523 K to RT (Fig. 8). No long-range order can be obtained in this way even if there is enough time for ordering. There are several possible explanations for this limitation in ordering: (a) at the temperature where the structure is frozen during cool-down, entropy prevents the formation of ordered superstructures, or (b) the mechanical distortion of the Cu lattice limits the area of these rather close-packed superstructures; (c) a repulsive adsorbate–adsorbate interaction due to electronic effects could also limit the nearest-neighbour distance. Since there are rather large Pb-free spaces in the surface alloy (Fig. 8) and since the size of the \((\sqrt{3} \times \sqrt{3})\) 30° and p\((2 \times 2)\) domains is very non-uniform, it seems that entropy plays the main role preventing long-range order in the surface alloy.

As the coverage reaches 0.55 – 0.15 ML higher than the disordered Cu–Pb surface alloy – a hexagonal close-packed Pb overlayer is formed besides the surface alloy (Fig. 8).

3.4. Dealloying at higher coverages

Another confirmation of submonolayer surface alloying and an insight into the mechanism of dealloying by increasing coverage is given by the following experiment: after deposition of 0.4 ML, the specimen was annealed to 573 K, thus forming a homogenous Cu–Pb surface alloy of maximum packing density, covering the whole surface. After cooling down to RT, additional 0.4 ML Pb was deposited (Fig. 9). Three clearly distinguishable regions can be seen in Fig. 9. In the layer of the Cu–Pb surface alloy small regions with hexagonal close-packed Pb within the surface alloy and larger ones near the step edge are visible. The close-packed Pb overlayer can be easily recognised by the moiré pattern of the superstructure. The same pattern can also be seen on the islands, which cover about 50% of the surface. The apparent height of the islands is exactly the height of a Cu step (0.21 nm). Hence, it is straightforward to explain the islands as hexagonal close-packed Pb, lying on pure Cu. Since no islands were observed before the second deposition step (0.4 ML Pb onto the surface alloy), the formation of these islands is due to dealloying caused by the additional deposited Pb. We suggest the mechanism for the dealloying and island formation to proceed as follows: proceeding from step edges, the deposited Pb atoms replace Cu atoms of the Pb–Cu surface alloy and form a small area of close-packed Pb embedded in the surface alloy. In contrast to lower coverages (e.g., 0.2 ML), where Cu adatoms formed by this mechanism can diffuse on a pure Cu terrace and adsorb at a Cu step, the upper terraces are now covered by close-packed Pb adjoining the steps, while the whole surface of the lower terrace is covered with the surface alloy. Thus, it is energetically more favourable for the free Cu atoms to push Pb atoms out of the Cu–Pb alloy, thereby creating an area of pure Cu atoms on which the replaced Pb atoms and further deposited Pb atoms can form a close-packed Pb island. Given the density of Pb atoms in the surface alloy, which is 22% with respect to the Cu substrate layer, and the packing density of the close-packed Pb overlayer, which is 56% with respect to the Cu substrate layer, this mechanism can be described in a quantitative way as follows: one Pb atom replaces on an average 2.3 Cu atoms by forming a close-packed Pb island. Since no islands were observed before the second deposition step (0.4 ML Pb onto the surface alloy), the formation of these islands is due to dealloying caused by the additional deposited Pb atoms forming a close-packed Pb region in the surface alloy; these Cu atoms replace 2.3 Pb atoms of the Cu–Pb surface alloy; thereby an area of 10.4 pure Cu atoms is formed on which the 2.3 replaced and 3.6 additional deposited Pb atoms can form a close-packed Pb layer. Given the density of Pb atoms in the surface alloy, which is 22% with respect to the Cu substrate layer, and the packing density of the close-packed Pb overlayer, which is 56% with respect to the Cu substrate layer, this mechanism can be described in a quantitative way as follows: one Pb atom replaces on an average 2.3 Cu atoms by forming a close-packed Pb layer (the non-integer numbers result from the ratio of Cu and Pb atoms in the surface alloy and the Pb atoms in the close-packed Pb overlayer to the Cu substrate, respectively). Expressed in terms of areas, the described mechanism results in an area of about 37.5% Cu–Pb surface alloy, 14% pure Pb in the same layer as the Cu–Pb alloy and 48.5% pure Pb islands on pure Cu, which is in good agreement with the experimentally determined areas. This good agreement also confirms that one Pb atom in the alloy replaces one Cu atom.

Deposition of 1 ML or more leads to a replacement of the surface alloy on the as-deposited as well as on the annealed surface and to the formation of a close-packed Pb overlayer (Fig. 10). The lattice constant of this Pb overlayer is about 3% higher than the lattice constant of a Pb(111) layer [11]. In Fig. 10 there are also some small protrusions visible; these protrusions disappear if the sample is annealed to 380 K or above. The height of these protrusions is about 0.1 nm in contrast to 0.286 nm of a Pb island. The lattice of the Pb overlayer is not disturbed, i.e., these elevations are formed by something beneath the overlayer. These observations lead to the suggestion that this buckling is caused by embedded Pb atoms that are covered by
the growing overlayer. The height of these protrusions also allows us to estimate that the overgrown Pb atoms protrude 0.1 nm from the Cu(111) surface, which is in rough agreement with the STM images of the surface alloy.

4. Conclusion

Although Cu and Pb are immiscible in bulk due to the large difference in atomic radii, a surface alloy can be observed in the submonolayer range, where one Cu atom is replaced by one Pb atom. After RT deposition of 0.05 ML, individual Pb atoms are embedded in the first Cu layer in the vicinity of steps as well as situated at a monatomic step edge. It has been suggested that at least two processes contribute to the formation of the surface alloy.

After increasing the coverage to 0.2 ML, the incorporation of further Pb atoms leads to a seam of Cu–Pb
Fig. 10. 20×20 nm² STM topograph of 1.1 ML Pb grown at RT. The surface alloy has been replaced by the close-packed Pb overlayer. The superstructure, which is close to (4×4), is visible as a hexagonal arrangement of Pb atoms that appear darker. Some single and multiple vacancies are also visible. The bright protrusions are caused by embedded Pb atoms beneath the overlayer (rectangular region). Except the rectangular region the contrast has been enhanced to make the superstructure more apparent.

The maximum packing density of the disordered surface alloy was found to be 40% with respect to a close-packed Pb overlayer (i.e., 22% with respect to the Cu lattice). The surface alloy then consists of small domains of (√3×√3)R30⁰, p(2×2) and more dilute structures. Very slow cooling rates (−0.004 K/s) neither lead to the formation of a higher Pb density nor to long-range order in the surface alloy.

Increasing the coverage above 0.4 ML and subsequent annealing to 470 K or higher, leads to the formation of hexagonal close-packed Pb regions in the surface alloy, eventually replacing all the surface alloy at 1 ML.

By depositing further 0.4 ML Pb on an annealed Cu-Pb surface alloy with maximum packing density (0.4 ML), the kinetics of dealloying has been investigated and a succession of replacement processes has been proposed for the mechanism.

Acknowledgements

The authors would like to thank G. Betz, J. Chladek and A. Biedermann for many helpful discussions. This work has been supported by the “Fonds zur Förderung der Wissenschaftlichen Forschung” (Austrian Science Foundation) under Project No. P9282.
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