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Subsurface islands and superstructures of Cu on Pb(111)

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Abstract

A new growth mode, namely subsurface island growth, has been identified by means of scanning tunneling microscopy . When Cu is deposited on Pb(111), 3D-Cu islands with a thickness between 1 and 11 layers are immersed several layers deep into the Pb substrate. The Cu islands, which can be classified in four different types, are furthermore covered by a monatomic Pb film. On flat Cu islands, this Pb film shows a corrugation that is strongly dependent on the number of Cu layers beneath. Single Cu layers were found to form a new type of Cu–Pb superstructure islands.

Keywords: Copper; Epitaxy; Lead; Low index single crystal surfaces; Metal–metal nonmagnetic thin film structures; Nucleation; Scanning tunneling microscopy; Surface energy; Surface structure, morphology, roughness, and topography

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1. Introduction

The simple model of three basic growth modes in thin film deposition [1] (layer-by-layer, layer + island and 3D island growth) is based on non-intermixing of substrate and film material, unchanged substrate and thermodynamic equilibrium. Even if the latter condition is fulfilled, which is not the case in thin film deposition since film growth is a non-equilibrium kinetic process [2], intermixing and interference of the film material with the substrate seems to be a common phenomenon for miscible [3,4] as well as for immiscible metals [5–8]. Although most interest is focused on systems where epitaxial growth is expected, the deposition of Cu on Pb(111) can give new insights in growth mechanisms. This system exhibits a new growth mode – namely subsurface island growth – instead of the expected 3D island growth which should occur due to the considerably different surface energies of Cu and Pb [9]. The Cu islands, which are covered by a monatomic Pb film, are immersed several layers in the Pb substrate.

In our present study we present a detailed description of different types of Cu islands. Furthermore we found the corrugation of the Pb film covering the islands to increase with decreasing number of Cu layers beneath. A so far unknown superstructure, which most probable is formed by a Cu–Pb reconstruction, will also be presented.

2. Experimental procedure

A detailed description of the STM experiments has been given elsewhere [9]. In short, all experi-

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ments have been performed in UHV with a pressure below 5×10^{-11} mbar and at room temperature (RT). Cu was deposited with an electron beam evaporator at deposition rates of about 1 ML/min on a Pb(111) single crystal (one monolayer (ML) is defined as one Cu atom per Pb(111) surface atom). The accuracy in the amount of deposited Cu was estimated to be better than 5%. Tunneling voltages and currents were between −1 V and −5 mV and 1 and 2 nA, respectively.

3. Results and discussion

3.1. Type "a" and "b" islands

Fig. 1a shows an STM topograph of 1.88 ML Cu deposited on Pb(111) at RT. Three different types of islands are visible, two of which are rather flat and regularly shaped (labelled "a" and "b") whereas the third type is much taller and irregularly shaped (labelled "c"). A detail of Fig. 1a is given in Fig. 1b where two type "a" and one type "b" islands can be seen. From STM images of these two types of islands several results can be deduced:

1. All three types of islands are covered by a monatomic Pb film that has the same appearance as on Cu(111) [6]. This Pb film exhibits a moiré pattern due to the size mismatch of about 37% between Pb and Cu atoms (Figs. 1b and 3). Since Pb grows on Cu(111) in Stranski–Krastanov mode, this infers that the Pb film is indeed of one monolayer thickness (see Ref. [6] and references therein).
2. The Cu islands of type "a" and "b" are (111) orientated with their lattice plane vectors parallel to the substrate.
3. Since the lower part of the type "a" island in Fig. 1b as well as the type "b" island, have almost equal height compared with the adjacent substrate, the Cu islands have to be immersed in the second Pb layer.
4. The height differences between the various levels on the terrace and the Pb substrate next to it can most often not be explained by a monatomic Cu layer. Taking into account the layer thicknesses of Pb and Cu and the monatomic Pb film on Cu(111) the number of Cu layers below the surface can be determined [9] (the numbers on the islands in Fig. 1b represent the number of Cu layers beneath). The Cu islands therefore are immersed up to 11 layers deep into the substrate.

Comparing the type "a" and "b" islands it can be seen that the edges of the former are aligned

Fig. 1. STM images of Pb(111) after deposition of 1.88 ML Cu. (a) 2000 × 2000 Å^2, three different types of Cu islands, labelled "a", "b" and "c", are visible. (b) detail of (a), the numbers denote the numbers of Cu layers beneath. The images are differentiated and illuminated from the left (1000 × 1000 Å^2).

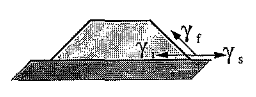
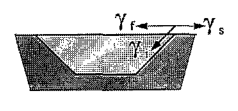
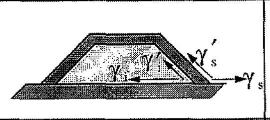
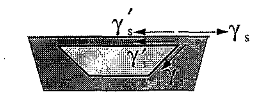
	$\gamma_f+\gamma_i>\gamma_s$ $\gamma_i>\gamma_f$	**a)**
	$\gamma_f+\gamma_i>\gamma_s$ $\gamma_i<\gamma_f$	**b)**
	$\gamma_i'+\gamma_i+\gamma_s'>\gamma_s$ $\gamma_i'+\gamma_s'<\gamma_i$	**c)**
	$\gamma_i'+\gamma_i+\gamma_s'>\gamma_s$ $\gamma_i'+\gamma_s'>\gamma_i$	**d)**

Fig. 2. Thermodynamic equilibrium inequations of surface and interface energies for various types of 3D island growth where the index "i" stands for interface, "f" for film and "s" for substrate. The prime denotes the interface and surface energies of the thin film covering the island. These energies might be different from the substrate surface. The first inequation of each panel determines either non-covered ((a) and (b)) or covered ((c) and (d)) 3D island growth, the second condition determines whether the islands protrude from the surface or immerse into the substrate. In the case of Cu/Pb(111) the inequations of panel "d" are fulfilled.

along ⟨110⟩ directions whereas the edges of the latter are aligned along ⟨112⟩ directions. The orientation of the moiré pattern as well as atomically resolved images show where this difference comes from: the type "b" islands are rotated by 30° with respect to the Pb substrate whereas the type "a" islands are aligned with the substrate lattice vectors.

3.2. Thermodynamics

Simple thermodynamic considerations (Fig. 2) give the reason for this unexpected subsurface growth mode: since in our case the surface energy of Cu(111) (1.96 J/m^2) [10] is considerable larger than that of Pb(111) (0.5 J/m^2) [11], Pb tends to cover the Cu islands. The low melting point of Pb causes a high surface mobility that enables this process to take place at RT. The interface energy has been estimated by effective medium theory (EMT) [12] simulations; it results in an upper limit of about 0.3 J/m^2, i.e. significantly smaller than the surface energy of Cu as well as that of Pb. A comparison of the inequations for covered islands growing *on* the substrate and covered islands that immerse *into* the substrate show that the latter should be favourable for all systems with highly diverging surface energies [9].

3.3. Corrugation enhancement

Fig. 1b shows another interesting feature. The moiré pattern of the monatomic Pb film covering the Cu island labelled "a" exhibits different heights of corrugation on several regions. A section through the lower part of the large type "a" island shows a corrugation of about 0.15 Å whereas the upper part of this island or the whole "b" island exhibits only 0.05 Å corrugation. A comparison with the estimated numbers of Cu layers beneath indicates that the higher corrugation occurs when just two Cu layers are situated beneath the Pb film. This higher corrugation can also be seen on two small regions of the "a" island in the upper part of Fig. 1b. Even more pronounced is this phenomenon on the small part of the lower "a" island that is formed by just one Cu layer. There we found a corrugation of 0.3 Å. This corrugation enhancement can be explained by the

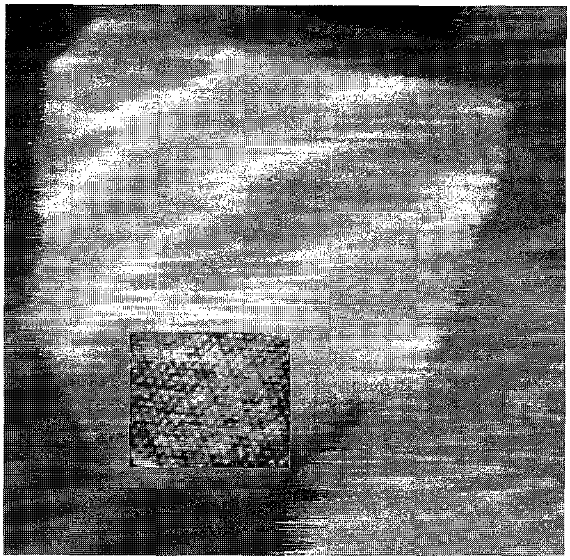


Fig. 3. STM image of a type "c" Cu island. The rectangular region has been contrast enhanced to show the atomic corrugation and the moiré pattern typical for Pb/Cu(111). The island protrudes 6 Å from the lower terrace (200×200 $Å^2$).

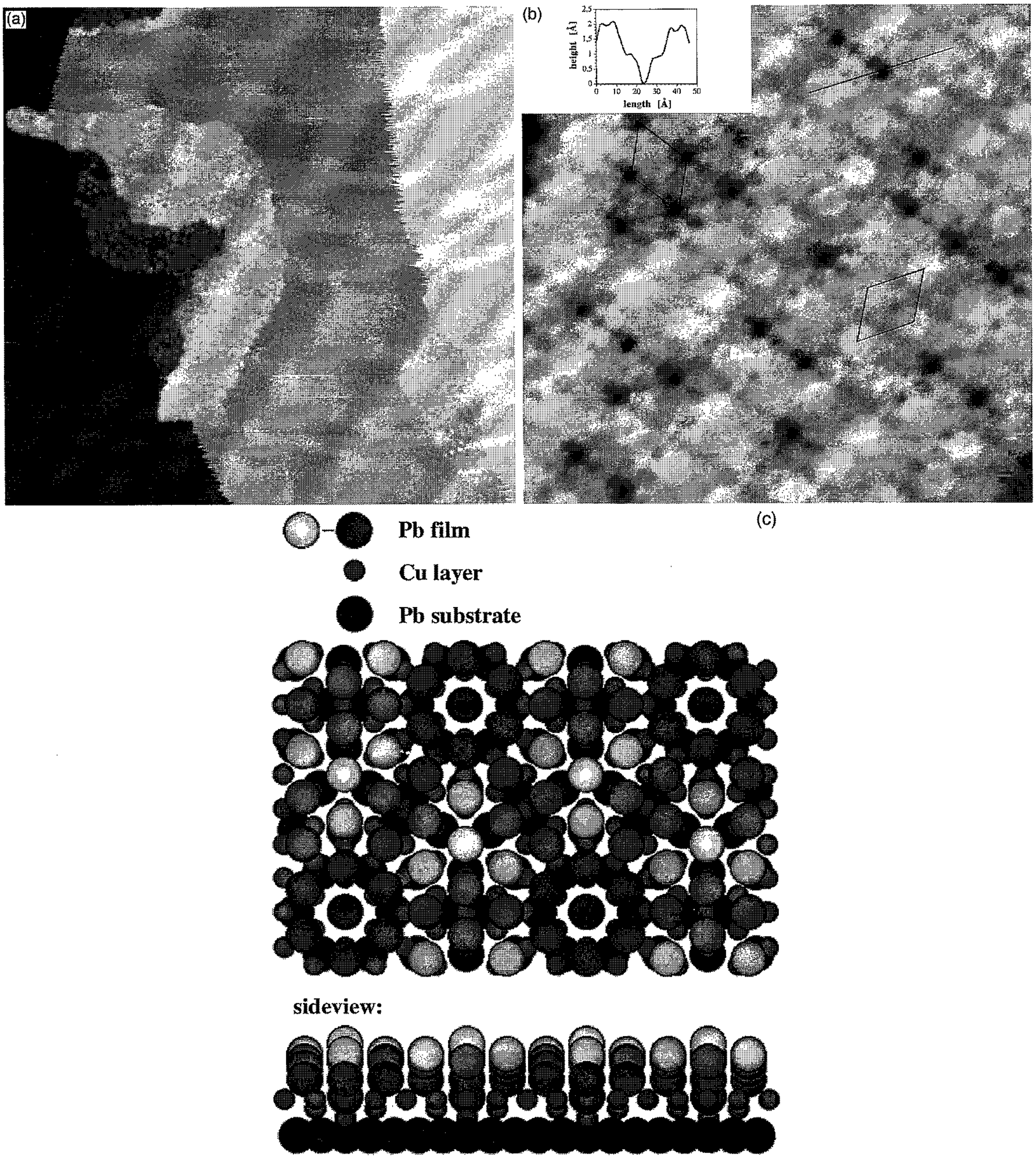


Fig. 4. (a) STM image of a (5 × 5) superstructure islands found after Cu deposition on Pb(111) (1000 × 1000 Å^2). (b) Detail of (a). The (5 × 5) unit cells of both modifications are marked. The linescan is taken along the line (200 × 200 Å^2). (c) Model for the superstructure modification with the dark indentations. The Pb substrate atom at the dark indentation is removed. Note that the Pb film as well as the Cu layer are rotated by 30° with respect to the substrate. The greyscale of the Pb film atoms represents their height as it appears in the STM image.

superposition of moiré patterns in agreement with EMT simulations. In other words, this phenomenon, which is found rather rarely, again proofs that most of the islands are thicker than two layers. A detailed description of the corrugation enhancement will be given elsewhere [13].

3.4. Type "c" islands

In Fig. 3 a close up of a type "c" island – the one that appears much higher elevated and irregularly shaped – is shown. In contrast to the type "a" and "b" islands where the (111) planes of the Cu island are parallel to the substrate, the (111) planes of this type of island are tilted with respect to the substrate. This can be seen in Fig. 3 where a rectangular region has been contrast enhanced. Obviously this plane, which is not parallel to the substrate, is (111) orientated as it can be seen by the moiré pattern. The topmost face exhibits many steps, i.e. it is a vicinal face. The misorientation between this type of islands and the Pb substrate as well as the most often irregular shape prevents a detailed analysis of the depth of immersion.

3.5. 5 × 5 Cu–Pb superstructure

Figs. 4a and 4b show STM images of a superstructure that can be found rarely after Cu deposition. Comparison with the Pb lattice constant results in a (5 × 5) periodicity within the experimental error. Several experimental observations lead us to the assumption that this (5 × 5) superstructure is formed by a single Cu layer that induces a reconstruction of the topmost Pb substrate layer:

(i) A chemisorbed impurity island like Cu–O [14] should be rather stable whereas the observed superstructure islands alter their shape during several hours, smaller ones even disappear. Moreover, there is no similarity between the (5 × 5) superstructure and the Cu–O superstructures observed by Besenbacher et al. [14]. In addition, we did not find any of these islands after Cu deposition on Al(111) and Cu(111).

(ii) On a 30° rotated island, we never observed a single layer of Cu buried in the Pb substrate that resembles several layer thick regions, whereas single Cu layers can occur on the non rotated type "a" island (Fig. 1b). It is therefore interesting to find out whether the structure in Fig. 4b can be related to a single 30° rotated layer of subsurface Cu. A possible model might be the following (Fig. 4c): to avoid an adsorption site where the Pb film atom is on top of a Cu atom which is on top of a Pb substrate atom, the Pb atom beneath the on top Cu atom is removed, resulting in the dark indentation seen in Fig. 4b. This indentation might act as a nucleation site for the second Cu layer visible as the small hexagons. Indeed the height difference between an indentation and a hexagon corresponds to the Cu(111) interlayer spacing of about 2.1 Å (see linescan in Fig. 4b). The height difference between the (5 × 5) superstructure and the pure Pb substrate beside it indicates that the Cu layer slips between the topmost Pb layer and the layer beneath. In other words, the Pb film layer is formed by the topmost substrate layer.

(iii) Furthermore the strongly enhanced corrugation of the one layer region in Fig. 1b indicates a tendency towards reconstruction. This is supported by EMT simulations of a single Cu layer on Pb(111), covered by a Pb film, where the Pb film and the topmost Pb substrate layer become unstable when both a Pb film atom and a Cu atom are on top of a Pb substrate atom. Recently, Jacobsen et al. [15] revealed a new type of reconstruction for Au deposited on Ni(111). To avoid on top adsorption sites small triangular regions in the topmost substrate layer move from fcc to hcp sites. This model, however, does not fit to Fig. 4b since it cannot reproduce the sixfold symmetry.

4. Conclusion

Several types of islands in a new growth mode could be revealed: 3D-Cu islands are immersed several layers deep into the Pb substrate and covered by a monatomic film. The islands appear in three different modifications dependent on the orientation of their lattice vectors with respect to the substrate. A fourth modification, which shows a (5 × 5) superstructure is most probably formed by a reconstructed Pb substrate layer, covered by a Cu and a Pb film layer. The monatomic Pb film, which covers the three types of islands, shows a corrugation strongly dependent on the numbers of Cu layers beneath.

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