Direct Observation of a New Growth Mode: Subsurface Island Growth of Cu on Pb(111)

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Atomically resolved scanning tunneling microscopy on Cu/Pb(111) reveals a new growth mode, contrary to the Volmer-Weber mode expected from the significantly lower surface energy of Pb. (111)-oriented Cu islands with a thickness of 3–11 layers are immersed in the Pb substrate and covered by a single close-packed Pb layer. This subsurface growth mode occurring at room temperature can be explained by simple thermodynamic considerations.

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Intriguing new results and much insight into metal on metal growth phenomena have been obtained by the application of scanning tunneling microscopy (STM) in this field. Recent works showed that the simple model of the three basic growth modes (layer by layer or Frank–van der Merwe, layer plus island or Stranski-Krastanov, and 3D island or Volmer-Weber growth mode) [1] does not hold for many systems in metal on metal growth [2–6]. In immiscible metals, as well as miscible metals, intermixing plays a crucial role and leads to unexpected growth behavior. For example, Rousset *et al.* [2] found a new growth mode for Au/Ag(110), which the authors called the "intermixing Stranski-Krastanov mode." In this system, a monolayer of Au is completely covered by one layer of Ag. On further deposition, 3D islands form on the Au/Ag layer.

In this Letter we report on the deposition of Cu on Pb(111). The surface energies of Pb and Cu, and the fact that these metals are immiscible in bulk, allow us to expect the Volmer-Weber growth mode, i.e., the formation of 3D Cu islands on the Pb surface [7,8]. Nevertheless, the STM images revealed a new growth mode, namely, a subsurface island growth.

STM and Auger electron spectroscopy (AES) experiments were performed in a UHV chamber with a pressure below 5×10^{-11} mbar. All STM images were obtained in constant current mode with the sample negative. The sample was prepared in a separate chamber with a pressure in the 10^{-10} mbar region. The Pb(111) sample was chemically etched and cleaned by 1 keV Ar^+ sputtering. Because of the high surface mobility, no annealing would be necessary after sputtering, nevertheless the sample was annealed to 420 K for further reduction of surface roughness. Cu was deposited with an electron beam evaporator at deposition rates of about 1 monolayer/min, measured by a quartz crystal microbalance. The error in the amount of deposited Cu was estimated to be less than 5%. We define one monolayer (ML) as a complete overlayer with Pb(111) bulk lattice constant = 9.4261×10^{18} m^{-2}. Tunneling voltages and currents were between -1 V and -5 mV, and 1 and 2 nA, respectively. Cu deposition and STM experiments were performed at room temperature.

Monitoring the AES signal of Cu with increasing coverage shows a very weak and almost linear rise, typical for 3D island growth (Volmer-Weber). Figure 1 shows an STM image of Pb(111) after deposition of 0.94 ML Cu, where islands with various heights and shapes are visible. Two flat islands with rather straight edges are aligned along ⟨110⟩ directions (labeled "*a*" in Fig. 1), whereas three other flat ones are more round shaped with a weak correspondence to ⟨112⟩ directions (labeled "*b*"). The remaining two islands (labeled "*c*") differ from type *a* and *b* islands by their heights and shapes. These rectangular *c* islands appear much higher elevated than the triangular *a* islands and round *b* islands.

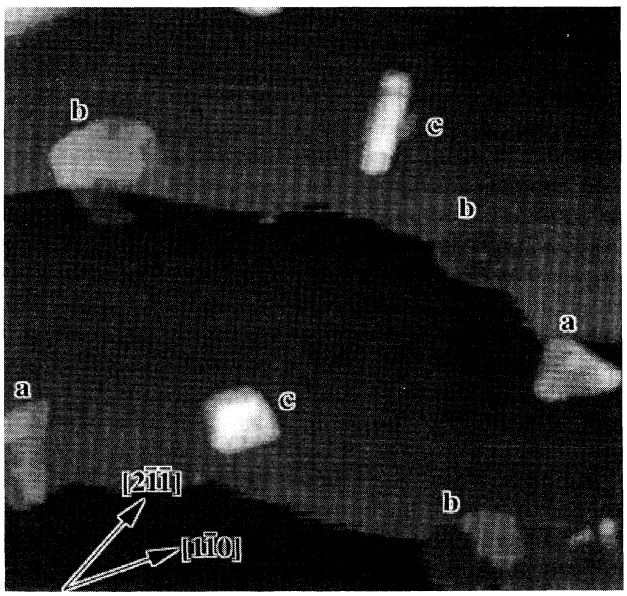

FIG. 1. STM image of Pb(111) after deposition of 0.94 ML Cu. Three different types of Cu islands are visible (100×100 nm^2).

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Figure 2(a) shows an atomically resolved image of a type *a* island. Obviously, the lattice on the island is in line with the substrate lattice. Continuation of close packed substrate rows of atoms onto the island shows that the island has nearly the same lattice constant as the substrate, whereas Cu has a 27% smaller lattice constant. On closer inspection, two more results can be deduced: (1) The island exhibits a moiré pattern and (2) the edges of the islands are well defined in contrast to the frizzy appearance of the Pb substrate step edges [see, e.g., upper part of Fig. 2(a) or Ref. [9]]. A comparison of Fig. 2(a) with the growth of a close packed Pb film on Cu(111) [10] shows an equal appearance of the moiré patterns, i.e., what is seen in Fig. 2(a) is a Pb monolayer [7] on at least one Cu layer with (111) orientation.

However, a section through the island [Fig. 2(b)] shows height differences of the various levels that do not correspond in a simple manner with a Cu step (0.208 nm) or a Pb step (0.286 nm), even accounting for the reduced apparent height of a close packed Pb film on Cu(111) of 0.22 nm [8]. Figure 2(c) shows a model that best fits the observed height differences. In this model the Cu island reaches up to 11 Cu and 9 Pb layers deep into the Pb substrate, respectively [11]. Even if the interatomic distances were different at the Cu-Pb interface, which might alter the number of layers given in Fig. 2(c), such an effect would not change the relative height differences on the island. This way, the difference in the number of Cu layers below can be determined precisely. For example, the height difference of the terrace on the upper right in Fig. 2(a) and the terrace in the middle of the island is about 0.11 nm. To obtain this height difference with a reasonable accuracy, the island has to have five more Cu layers in the center than in the right part; i.e., the middle of the island reaches at least six Cu layers deep into the Pb substrate. Another proof of the above model is given by comparing the average number and size of the islands from several large scan STM images with the total amount of deposited Cu, which results in a thickness of 5–10 layers. (This analysis includes the type *c* islands, which protrude from the surface by 10–15 Å, i.e., 3–5 layers. Since they amount to about one-fifth of all islands, their volume is insufficient to influence this calculation significantly.) Furthermore, the sagging in the middle and left part of the island in Fig. 2(a) requires a certain thickness of the Cu island, since otherwise a single-layered Cu would form a well-localized step at the surface.

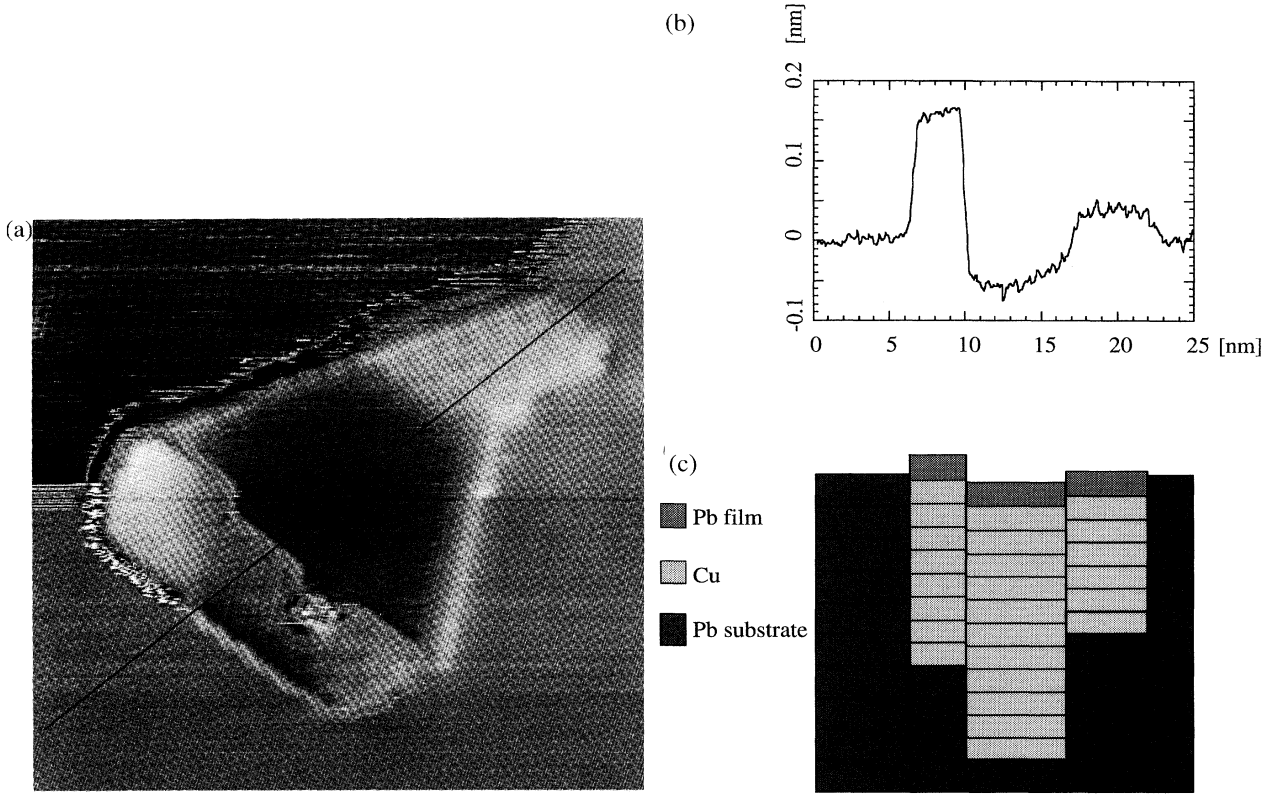

FIG. 2. (a) Atomically resolved STM image of a type *a* Cu island. The island is covered by a Pb overlayer showing the moiré pattern of Pb on Cu(111) [10]. Both the Pb overlayer and the Cu island [as indicated by comparison of the moiré pattern with Pb/Cu(111)] are aligned with the crystallographic directions of the substrate. For better contrast, this image has been slightly differentiated. Furthermore, the height difference between the various levels has been reduced artificially (20×20 nm^2). (b) Section through (a) taken along the line. (c) Model for Cu islands in (a) and for the section through this island in (b), respectively. Each rectangle represents a monatomic layer of either Pb substrate, Cu island, or Pb overlayer.

Figure 3(a) shows an atomically resolved STM image of a type *b* Cu subsurface island with a round shaped border. Evidently, there is a 30° rotation of the Pb-film lattice, the moiré pattern, and therefore the underlying Cu lattice, with respect to the Pb substrate. From several large scan STM images, the overall distribution of nonrotated and 30° rotated islands displays a 3:2 ratio. This indicates that only a small energetic difference exists between the two possible orientations of the nuclei at the beginning of growth. The 30° rotation can be easily deduced by the superposition of a Pb and a Cu lattice, where in both cases, visibly, and equal number of Cu atoms take bridge, hollow, or on-top absorption sites.

Figures 3(b) and 3(c) display a section through the island and the corresponding model. Here the best fit model is achieved when the island extends up to 5 layers deep into the Pb substrate. As mentioned above, the nonrotated *a* and the 30° rotated islands *b* exhibit different Cu to Pb bulk interfaces at their edges. The nonrotated islands show hexagonal shapes, whereas the 30° rotated islands are more round shaped. This difference can be explained by a lower interface energy of aligned (111) planes of Pb and Cu, comparing to the high-index orientations necessary between Pb and the rotated Cu islands.

The Pb film on the nonrotated and the 30° rotated Cu islands is compressed by 2%–5% with respect to the Pb bulk lattice. This compression agrees with the lattice constant of a Pb monolayer on Cu(111) [12]. Deposition of larger amounts of Cu leads to an increased size and number of the islands. In other words, there is no deeper immersion than approximately ten layers given the deposition conditions.

From Figs. 2(a) and 2(b), it is obvious that the Cu(111) planes are parallel to the substrate planes. In contrast, atomically resolved type *c* islands, similar to those in Fig. 1 (not shown here), suggest that the (111) planes of this type are not parallel to the substrate; e.g., some islands also show vicinal planes. Because of the misorientation between this type of island and the substrate, the depth of immersion of these islands cannot be determined. They are, however, likewise covered by a monatomic Pb film.

Because of the high mobility of Pb and Cu at room temperature, the structures observed are close to thermodynamic equilibrium and therefore are determined mainly by surface and interface energies. In general, it is assumed that the Volmer-Weber growth mode occurs if the surface energy of the film γ_f plus the interface energy γ_i is larger than the surface energy of the substrate γ_s : $\gamma_f + \gamma_i > \gamma_x$. This is the case for Cu on Pb(111), where the surface energy of Cu(111) (1.96 J/m^2) [13] is four times higher than the surface energy of Pb(111) (0.5 J/m^2) [14]. Using effective medium theory [15] simulations, we have estimated the interface energy for (111) surfaces of Pb and Cu to be less than 0.3 J/m^2, i.e., significantly smaller than both the surface energies of Pb and Cu, and their differences.

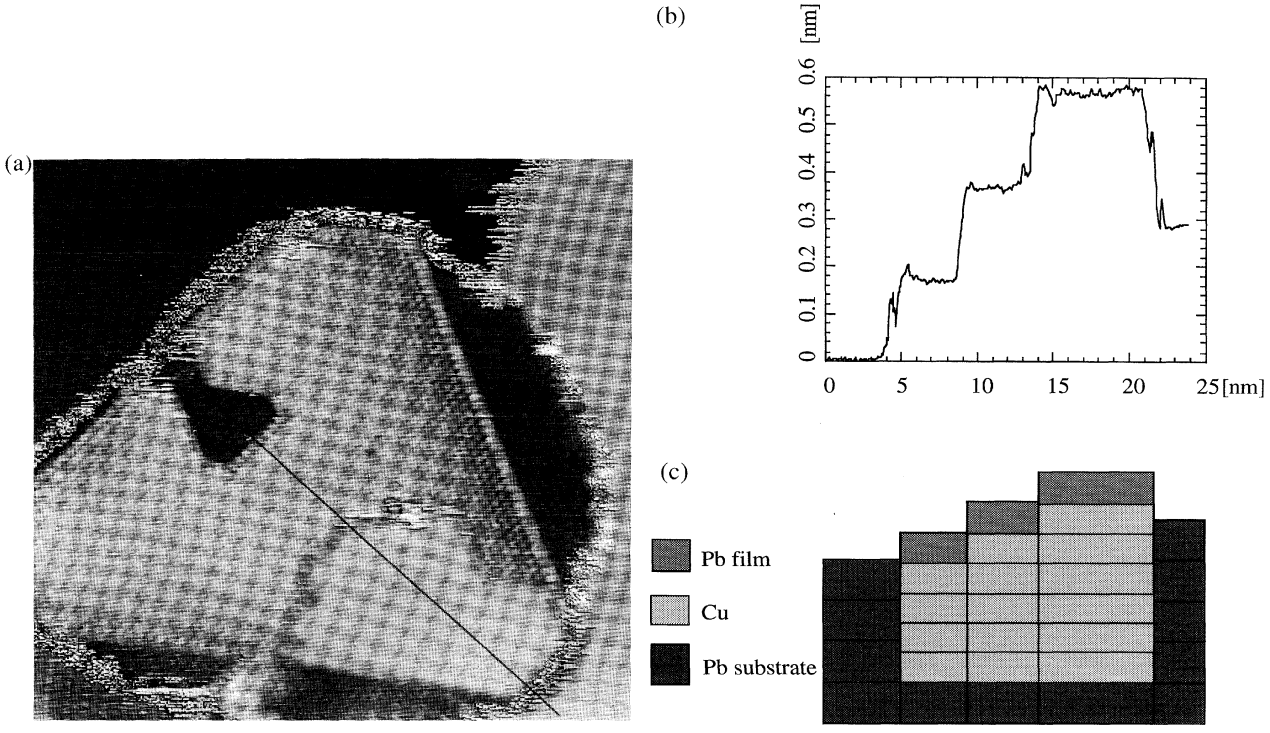

FIG. 3. (a) STM image of a type *b* Cu island. The lattice of the Pb overlayer as well as the Cu island lattice is rotated by 30° with respect to the Pb substrate. The Pb overlayer exhibits the moiré pattern of Pb on Cu(111). As Fig. 2(a), this image has been slightly differentiated, and the height difference between various terraces has been reduced (20 × 20 nm^2). (b) Section through (a) marked by the line. (c) Model for the Cu island that best fits the section in (b). Each rectangle represents a single layer.

In our case, where the film island is covered by substrate material, the energy per island area is $\gamma_i + \gamma_i' + \gamma_s'$ (the prime denotes the energies for a single monolayer of substrate on film material, which may be somewhat different from the respective energies of thick layers or bulk material). Comparing this with normal Volmer-Weber growth, we get the condition

$$\gamma_i' + \gamma_s' < \gamma_f \quad (1)$$

for growth covered by a substrate monolayer as observed for Cu/Pb(111). Because of the large difference between γ_{Cu} and γ_{Pb}, and since the interface energy γ_i' should be comparable to γ_i, Eq. (1) is clearly fulfilled.

Since covered *island* growth (in contrast to layer growth covered by substrate material) is observed and therefore energetically favorable, we must also have

$$\gamma_i + \gamma_i' + \gamma_s' > \gamma_s . \quad (2)$$

The energy difference between covered island and covered layer growth for Cu/Pb(111) must be small, however, since the Stranski-Krastanov growth of Pb on Cu(111) [16] implies that $-\gamma_i + \gamma_i' + \gamma_s' < \gamma_s$ (subscript s stands for Pb). Together with kinetic limitations, this may explain the large lateral extent of the Cu islands compared to their thickness.

We have shown that island types a and b are immersed several layers in the substrate. Such an arrangement is energetically favorable if

$$\gamma_i < \gamma_i' + \gamma_s' , \quad (3)$$

where the left-hand side represents the energy per border area in the case of immersed islands, and the right-hand side is the same quantity for protruding islands covered by substrate material. Because of the small values of interface energies, condition (3) is usually true for metals. Therefore, we expect subsurface (immersed) growth to be thermodynamically stable in most cases where islands are covered with substrate material.

With regard to kinetics of the subsurface island growth, there are at least two mechanisms conceivable for the immersion of Cu islands in the Pb substrate:

(i) The Cu island grows upward but sinks into the Pb substrate. This mechanism requires only diffusion of Pb atoms along the Cu-Pb interface. The driving force is the minimization of the surface energy at the edge of the Cu island [see condition (3)]. The diffusivity of Pb along the Cu-Pb interface should be between the Pb bulk diffusivity at room temperature (10^{-19} cm^2/s) and the surface diffusivity, on the order of 10^{-7}–10^{-6} cm^2/s for fcc metals. The value given for bulk diffusivity might be even somewhat higher due to a larger vibrational amplitude at, and in the vicinity of, the surface. The given diffusivities result in a reasonable time constant for this mechanism.

(ii) The Cu island grows into the Pb. This mechanism requires diffusion of Cu atoms along the Cu-Pb interface beneath the Cu island, followed by an exchange of Cu and Pb. The released Pb atoms must diffuse towards the surface along the Cu-Pb interface. We consider this mechanism to be highly unlikely since it requires diffusion of Pb *and* Cu atoms along the Cu-Pb interface.

To conclude, we have shown that Cu deposited on Pb(111) grows in subsurface islands which are several monolayers thick and covered by a single Pb layer. Cu islands may be aligned with the Pb substrate or rotated by 30° with respect to the substrate. Simple considerations [see Eq. (1)] have shown, for all systems in which the deposited metal has significantly higher surface energy than the substrate, growth of covered islands is thermodynamically stable and energetically favorable to the classical Volmer-Weber growth. For Cu/Pb(111), the high mobility of Pb allows this state to be reached even at room temperature.

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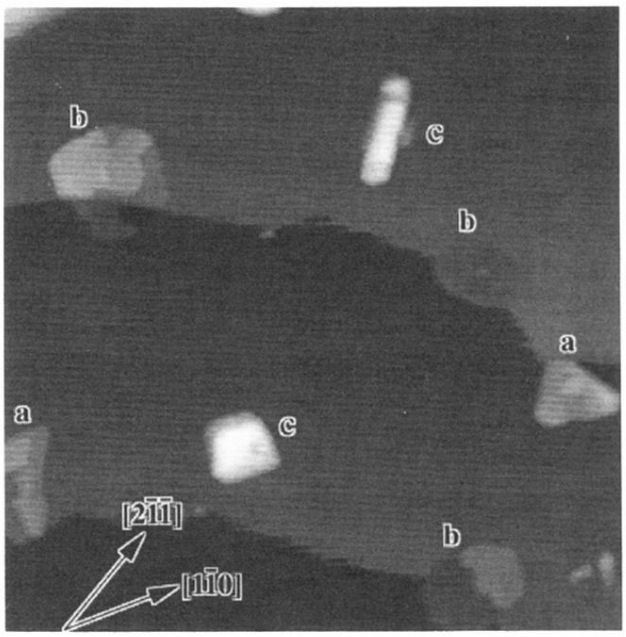

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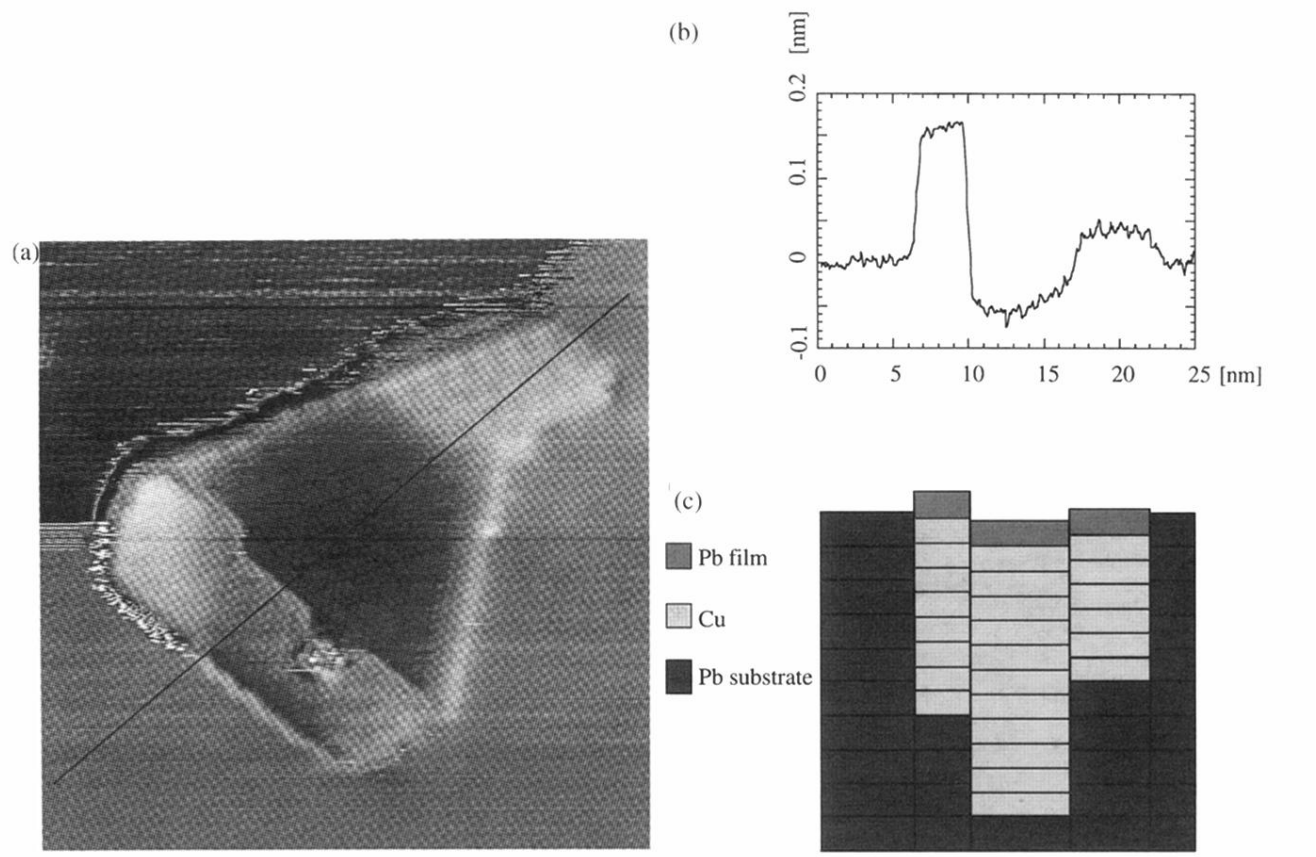

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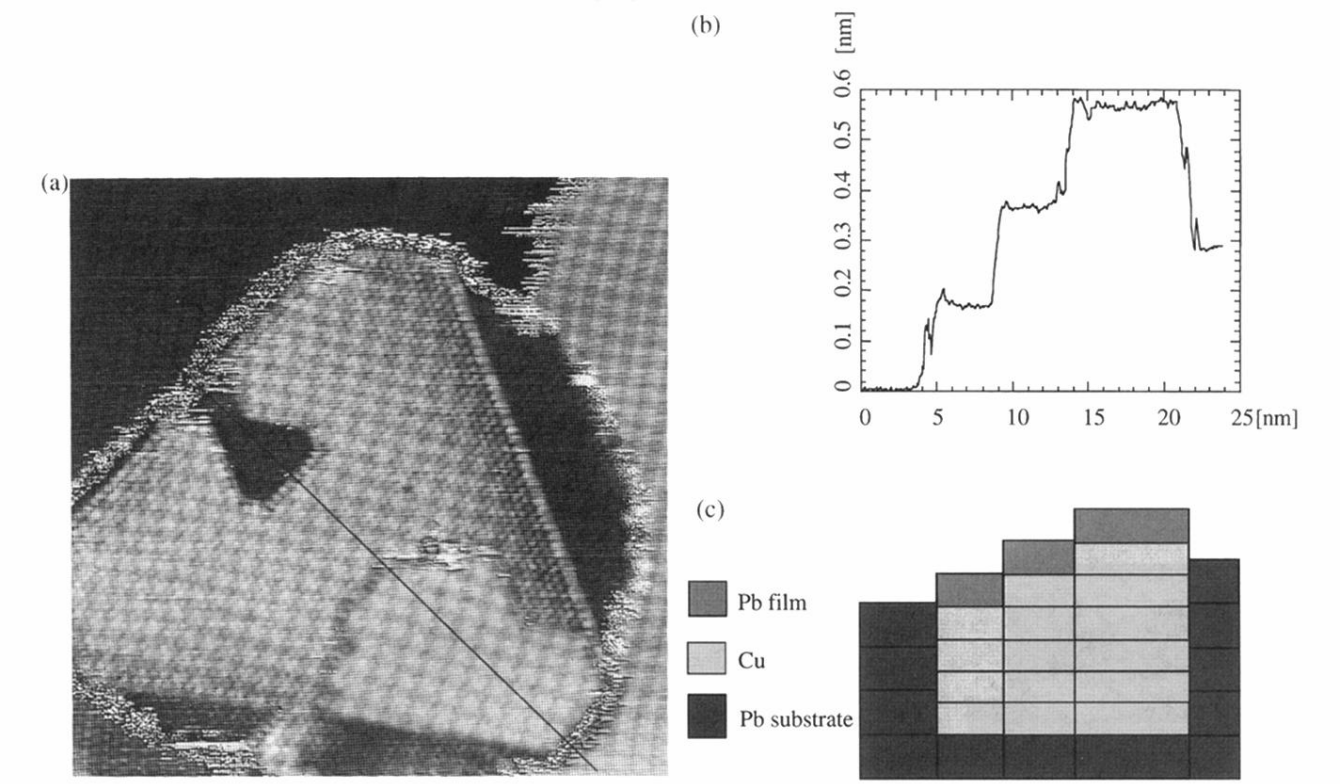

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