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Superstructures of Pb monolayers electrochemically deposited on Ag(111)

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We report the *in situ* scanning tunneling microscopy observation of incommensurate superstructures at electrochemically deposited lead monolayers on silver (111). The superstructure was always observed at substrate potentials within the range of a full lead monolayer. This superstructure has moiré spot distances between 1.5 and 1.8 nm, and is rotated between 24° and 29° against the lead layer. It is interpreted as a moiré pattern produced by rotation of a compressed Pb adlayer with regard to the topmost silver layer.

INTRODUCTION

Electrolytic scanning tunneling and atomic force microscopy is now an established tool for *in situ* investigations of foreign metal underpotential deposition (UPD) at potential controlled electrodes. The deposition of lead on silver single crystals has been studied by a number of investigators: Vapor deposition in UHV has been studied using standard UHV methods like Auger electron spectroscopy, low-energy electron diffraction, and reflection-high-energy electron diffraction and work-function measurements.[1,2] Electrochemical underpotential deposition has been investigated using cyclic voltammetry and thin-layer methods[3] and using grazing incidence x-ray scattering (GIXS).[4] Recently, atomically resolved UPD metal overlayers on single crystals have been reported, Cu on Au(111) by Magnussen *et al.*[5] and Pb on Ag(111) by Lorenz *et al.*[6] Very recently, Tao *et al.*[7] have claimed the observation of a superstructure of lead on Au(111).

In this paper we report on the observation of moirélike patterns of Pb monolayers on Ag(111) by *in situ* scanning tunneling microscopy (STM).

EXPERIMENT

Ag(111) substrates were first mechanically and then chemically chromate polished by previously described procedures[8] giving surfaces with atomically flat terraces of a few hundred Å width, separated by monoatomic steps. The experiments were carried out in a solution of $0.01M$ $HClO_4$ containing $0.005M$ $Pb(ClO_4)_2$. A platinum wire covered with lead was used as a reference electrode. The counter electrode was a pure platinum wire. All substrate potentials are given as potential differences ΔE versus the equilibrium potential $E_{Pb/Pb^{2+}}$ of the system. The tip potential ranged between 31 and 634 mV versus the equilibrium potential. The electrochemical scanning tunneling microscope is a NanoscopeII with electrochemistry base.[9] The STM tips were commercially available Pt-Ir tips coated with epoxy.[10] The STM parameters (tip potential, tip current, and feedback control values) were always adjusted to yield the best pictures possible. We obtained the same pictures with different STM parameters, and therefore we can be sure that the observed phenomena are independent of the scanning conditions. Before starting the STM experiment, the substrate was checked to yield the typical cyclic voltammogram of Pb adsorption-desorption at Ag(111).[11] This check was repeated several times in the course of the experiment. During acquisition of the STM pictures the substrate potential was held constant. All STM pictures shown in this paper are raw data as delivered by the STM and taken in the height mode.

RESULTS

Figure 1 shows the atomically resolved Pb layer with its hexagonal symmetry and a nearest-neighbor distance of 0.33 ± 0.02 nm, which is in good agreement with the value previously obtained by Lorenz *et al.*[6] The window size is 4.13 nm. The substrate is at $\Delta E = 15$ mV. At this potential the substrate is covered with a full lead monolayer; according to Bort *et al.*[3] a full monolayer coverage is obtained for potentials $\Delta E \leq 125$ mV. A moirélike structure with a characteristic length of approximately 1.7 nm is clearly visible in the picture.

Figure 2(a) shows the Pb layer at a potential of $\Delta E = 36$ mV on a larger scale with a window size of 14.35 nm. The small dots are the atoms whereas the large-scale shading shows the superstructure. The atomic corrugation is 0.03 nm and the superstructure corrugation is also 0.03 nm. Figure 2(b) shows the two-dimensional Fourier transform of 2(a) exhibiting two dominant hexagons, the outer one representing the atomic periodicity of 0.32 ± 0.02 nm, and the inner one the periodcity of the superstructure of 1.65 ± 0.07 nm. The two hexagons are ro-

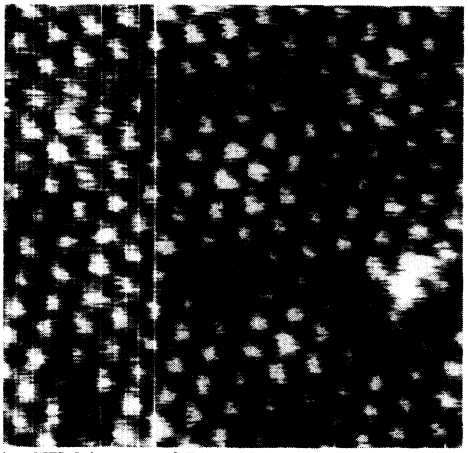

FIG. 1. STM image of Pb monolayer on Ag(111). Scan size 4.13 nm, substrate potential $\Delta E = 15$ mV, bias voltage 16 mV, and tunneling current 20 nA. The gray-scale range from black to white corresponds to 0.08 nm.

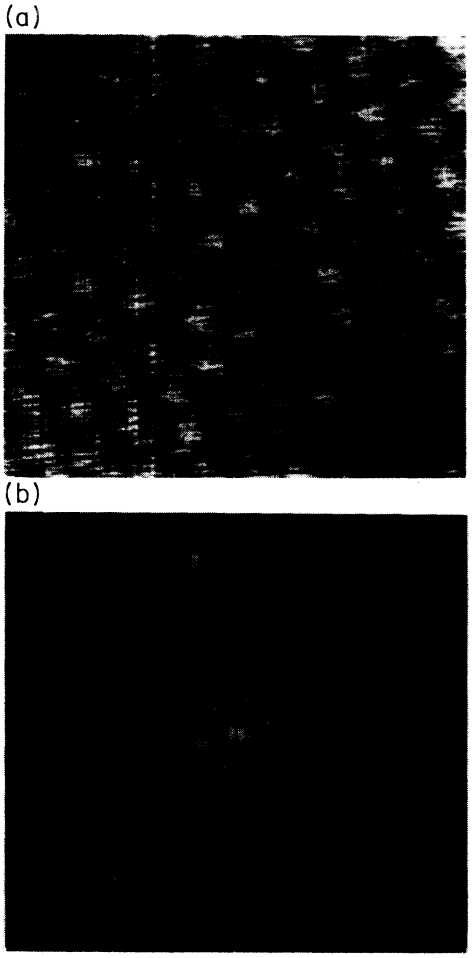

FIG. 2. (a) STM image of Pb monolayer on Ag(111). Scan size 13.52 nm, substrate potential $\Delta E = 36$ mV, bias voltage 81 mV, and tunneling current 20 nA. The gray-scale range from black to white corresponds to 0.06 nm. The atomic periodicity is 0.32 ± 0.02 nm and the superstructure periodicity is 1.65 ± 0.07 nm. (b) Two-dimensional Fourier transform of (a) showing the two hexagons due to the atomic and the superstructure periodicity. The two hexagons are rotated against each other by $27.9° \pm 1.0°$.

tated by $28° \pm 1°$ against each other.

The superstructure was seen in five different experimental runs and always only observed for substrate potentials ranging between 15 and 75 mV in accordance with the stability region of the full lead monolayer. We therefore exclude the possibility that the moiré pattern may be due to multiple-tip effects. The superstructure was found to extend over regions as large as 30 nm, and also close to steps. The distances between the moiré spots range between 1.5 and 1.8 nm and the rotation against the Pb layer varies from 24° to 29°. Both clockwise and counterclockwise rotations were found.

DISCUSSION

GIXS measurements by Samant *et al.*[4] have shown that the Pb adlayer forms an incommensurate overlayer

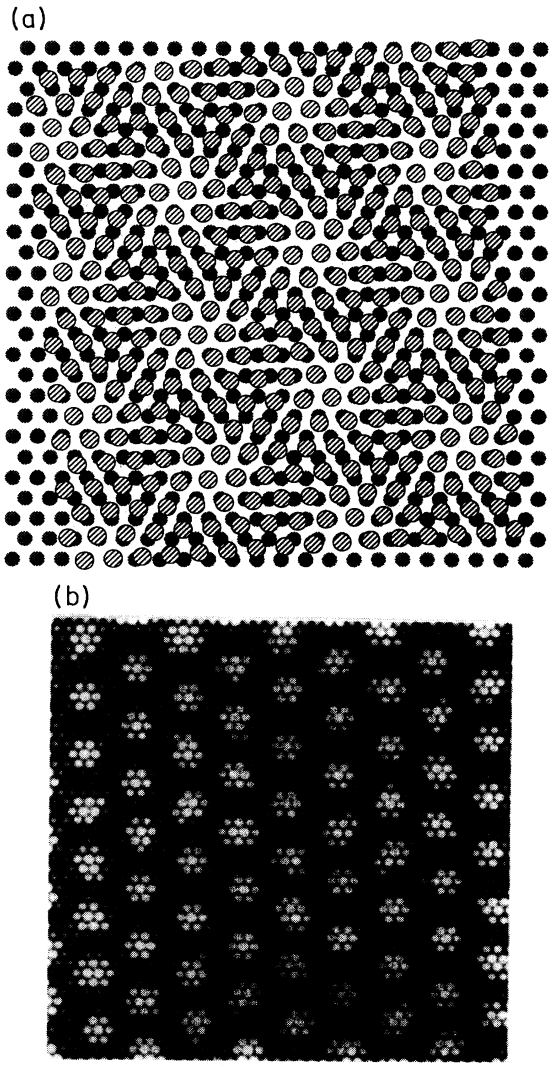

FIG. 3. (a) Model of the position of the Pb (dashed closed circles) hcp adlayer on the Ag (open dotted circles) layer according to Samant *et al.* (Ref. 4). (b) Simulated STM picture based on the model in (a). The closer a Pb atom is located over an Ag atom, the brighter it appears. This gives a superstructure with 1.74 nm periodicity and an apparent rotation against the Pb layer of 27°.

on top of the silver surface rotated by 4.4°. Melroy *et al.*[12] measured a lattice contraction of the lead adlayer of 0.341–0.346 nm in the underpotential range $0 \leq \Delta E \leq 140$ mV. Figure 3(a) shows a schematic model of a perfectly flat hcp lead atom layer having a nearest-neighbor distance of 0.341 nm, superimposed to a perfectly flat hcp silver layer with a nearest-neighbor distance of 0.289 nm, and rotated by 4.4°. The lead nearest-neighbor distance used corresponds to the substrate potential of $\Delta E = 36$ mV at which Fig. 2(a) was taken. Using this model, an STM picture was simulated [Fig. 3(b)] assuming that a lead atom appears brighter the closer its center coincides with the center of an underlying Ag atom. A moiré pattern results with an apparent rotation of 27° and an average distance of 1.74 nm. This is close to the observed superstructure in Fig. 2(a). No implication is made whether the brightness in the simulated picture reflects variations of the electron density of states and/or vertical displacements in the lead overlayer.

In Fig. 3(a), the Pb layer is incommensurate with the silver substrate. We cannot exclude the possiblity that the combination of the Pb adlayer and the silver sublayer corresponds to a pinned commensurate structure with slightly altered interatomic distances. There are two commensurate structures with parameters close to those of the experimental structure. One is $(\sqrt{28} \times \sqrt{28})R40.9°$ yielding a moiré structure with 1.53 nm periodicity and a rotation of 23.4° against the lead layer. These values are both at the lower limit of our experimental values. The other one is $(\sqrt{37} \times \sqrt{37})R34.7°$ yielding a periodicity of 1.76 nm and a rotation of 30°. These values are at the upper limit of our experimental values. We conclude that within the accuracy of our experiment we cannot distinguish between the incommensurate and the two pinned commensurate structures. On the contrary, we expect that there exists a continuous sequence of incommensurate structures with moiré spot distances between 1.53 and 1.76 nm and rotation angles between 4.3° and 4.7° with respect to the Ag substrate, depending on the lead atom distance as determined by the underpotential.

CONCLUSION

This work on Pb monolayers deposited on Ag(111) shows that with *in situ* STM in electrolytic environment in addition to atomic resolution in the topmost layer, long-range moiré patterns can be observed. In the present system the experimentally observed pattern is compatible with an incommensurate Pb layer. These moiré patterns reflect electronic interactions and/or geometric relations between the adlayer and the underlying electrode substrate and may prove to be a sensitive tool for studying the structure of adlayers in UPD deposits.

ACKNOWLEDGMENTS

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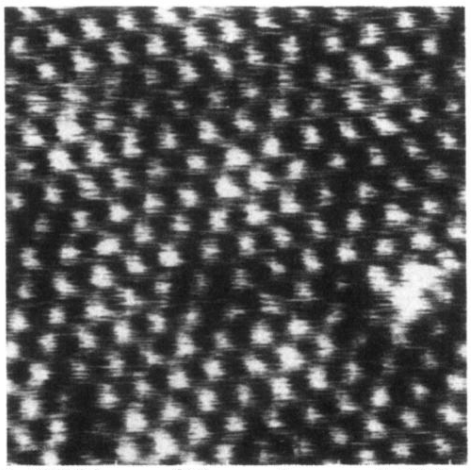

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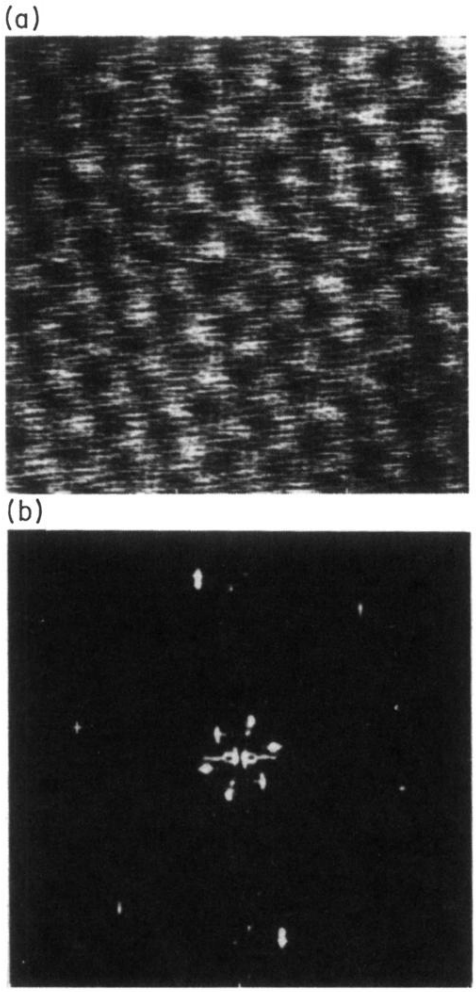

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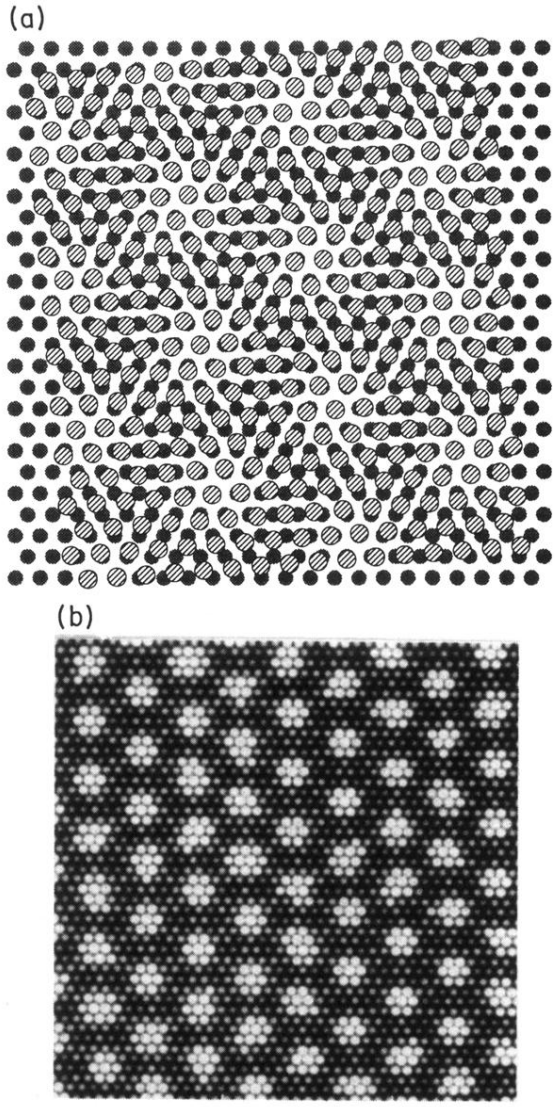

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