Comments

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Comment on "Superstructures of Pb monolayers electrochemically deposited on Ag(111)"

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Using scanning tunneling microscopy, a long-wavelength pattern was observed by Müller *et al.* [Phys. Rev. B **46**, 12 899 (1992)] in Pb monolayers on Ag(111) formed by underpotential electrochemical deposition. We point out that the monolayer is incommensurate and so it should be described as having substrate-induced spatial modulations, and we also demonstrate that one can accurately calculate the long-wavelength spacing and rotation angle, which are shown to depend on electrode potential.

Recently, Müller *et al.*[1] conducted an elegant scanning-tunneling-microscopy (STM) study of Pb monolayers on Ag(111) formed by electrochemical underpotential deposition (UPD) in a perchlorate electrolyte. In addition to confirming the rotated hexagonal structure of the monolayer as found by x-ray scattering,[2,3] Müller *et al.*[1] observed a long-wavelength pattern in the monolayer. This pattern consisted of "Moire" spots that are spaced 15–18 Å apart and rotated 24°–29° with respect to the Pb rows and was ascribed to a "superstructure" in the Pb layer. In this paper, we discuss two added refinements to the picture proposed by Müller *et al.*[1] First, we demonstrate that the monolayer is incommensurate and suggest that it is appropriate to describe the monolayer as having substrate-induced spatial modulations. Second, one can calculate the superstructure spacing and rotation angle, using our x-ray-scattering data for the near-neighbor spacing and rotation angle of UPD Pb/Ag(111). This calculation is consistent with the STM results and also predicts that the superstructure spacing and rotation angle depend on electrode potential. We note that the results on this system nicely illustrate the complementarily of *in situ* STM and x-ray scattering.

The STM measurements were not able to determine whether the monolayer forms an incommensurate or a high-order commensurate structure; however, our surface x-ray-scattering data show that the layer is, in fact, incommensurate with the substrate. The near-neighbor spacing changes continuously with electrode potential to within our experimental error (5 mV in potential and 0.002 Å in near-neighbor spacing) and also does not exhibit any potential-dependent hysteresis [i.e., the near-neighbor spacing is independent of whether the electrode potential is reached in an anodic (positive) or cathodic (negative) scan].[2,3] In such an incommensurate layer, the periodic potential of the substrate creates small amplitude, static displacements in the adatom positions,[4,5] which are referred to as a static distortion wave (SDW). These displacements are relative to the positions that the

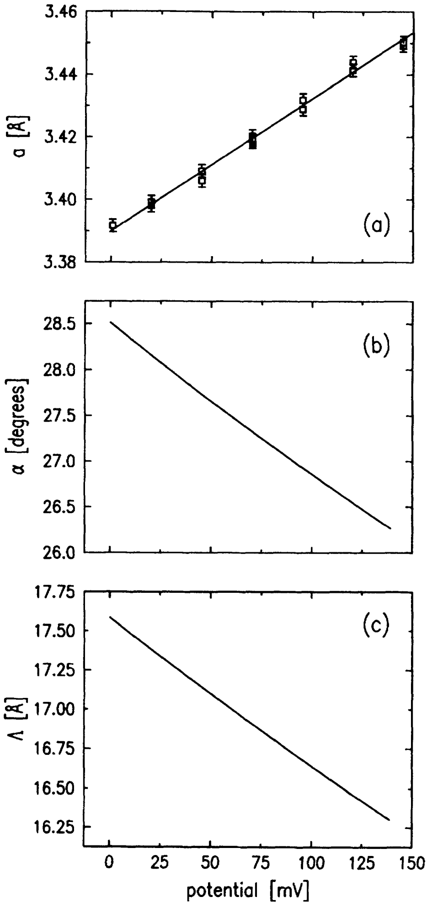

FIG. 1. (a) Potential dependence of the overlayer near-neighbor spacing a for Pb/Ag(111) in 0.1-M Na_2ClO_4 containing 5-mM Pb $(ClO_4)_2$ and 10-mM $HClO_4$. The solid line is a linear least-squares fit through the data ($a = 3.390 + 0.424 \times 10^{-3}$ V, where V is the potential in mV). Potential dependence of (b) the wavelength Λ and (c) rotation angle α as calculated with Eq. (1). The potential is with respect to the equilibrium potential for bulk Pb deposition.

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adatoms would have in a (hypothetical) rigid lattice, and they occur both parallel and perpendicular to the substrate surface. SDW's in adsorbed monolayers were originally suggested by McTague and Novaco[6] and have been observed experimentally for rare gases adsorbed on graphite[7] and UPD Tl/Ag(111) (Ref. 8). Thus, we believe the SDW description of the incommensurate Pb monolayer is an appropriate picture for the monolayer structure, and the superstructure observed by Müller *et al.*[1] is due to the SDW in the incommensurate layer. We agree with Müller *et al.*,[1] that the STM contrast is most likely due to perpendicular displacements of the adatoms

For the purpose of calculation, it is simpler to consider the wave vector of the superstructure (or SDW) rather than to construct a real-space model, as was done in Ref. 1. The superstructure wave vector is the difference between the first-order reciprocal-lattice vectors of the monolayer and the substrate surface. Since the latter is known, and the former can be accurately measured (as we have done), the wavelength Λ and rotation angle α of the superstructure can be easily calculated. Let a and b be the near-neighbor spacings of the overlayer and substrate, respectively, and Ω the rotational epitaxy angle of the monolayer (with respect to the Ag[01$\bar{1}$] direction), then

$$\begin{aligned} \Lambda &= \frac{ab}{\sqrt{a^2+b^2-2ab\cos\Omega}}\ , \\ \alpha &= \Omega + \arcsin[(\Lambda/a)\sin\Omega]\ , \end{aligned} \tag{1}$$

where α is measured from the Pb(10) direction (as defined by Müller *et al.*[1]). Figure 1(a) shows data for a as a function of electrode potential, where the potential is with respect to the equilibrium Pb/Pb^{2+} potential. These data were obtained in 0.1-M Na_2ClO_4 containing 5-mM $Pb(ClO_4)_2$ and 10-mM $HClO_4$,[3] but are almost the same as in an acetate electrolyte.[2,3] The solid line is a linear least-squares fit through the data. Using this and from $\Omega = 4.5°$,[2,3] Figs. 1(b) and 1(c) show Λ and α calculated from Eq. (1). The calculated Λ varies from 16.3–17.6 Å and α from 26.2–28.5° and these are in excellent agreement with the STM observations: $\Lambda = 15-18$ Å and $\alpha = 24-29°$ (where the STM measurement uncertainties are ±0.7 Å and ±1°).[1] It is interesting to note that Fig. 1 predicts that Λ and α systematically depend on electrode potential. While Müller *et al.*[1] report a variation in period and angle of the long-wavelength pattern, it is unclear whether this was a potential dependent variation. It would be interesting to see if this were the case.

Finally, Grey and Bohr have developed a symmetry principle that is argued to underlie the phenomenon of rotational epitaxy.[9,10] They suggest that an overlayer will adopt a rotational epitaxy angle such that the superstructure wave vector is along a high-symmetry direction of either the overlayer or the substrate. In the present case, this suggestion would give $\alpha = 30°$ or $\alpha = 30° - 4.5° = 25.5°$. Unfortunately, these are outside the measured (and calculated) values. Thus, while the symmetry principle suggested by Grey and Bohr qualitatively gives the rotational epitaxy for Pb/Ag(111), it does not quantitatively predict this.

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