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

U. Müller

Swiss Federal Laboratories for Materials Testing and Research, EMPA Abt. 124, Überlandstrasse 129,
CH-8600 Dübendorf, Switzerland

D. Carnal, H. Siegenthaler, and E. Schmidt

Institute of Inorganic, Analytical and Physical Chemistry, University of Bern, CH-3000 Bern 9, Switzerland

W. J. Lorenz, W. Obretenov, and U. Schmidt

Institute of Physical Chemistry and Electrochemistry, University of Karlsruhe, D-7500 Karlsruhe, Germany

G. Staikov and E. Budevski

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, BG-1040 Sofia, Bulgaria

(Received 28 June 1993; revised manuscript received 26 October 1993)

In our original article [Phys. Rev. B **46**, 12 899 (1992)] we observed a superstructure in lead underpotential deposits on Ag(111). In their paper, Toney *et al.* point out that one should see a potential dependent variation in period and angle of the long-wavelength pattern. Using the dimensionless ratio κ of the long-wavelength periodicity of the moiré pattern and the atomic spacing of the lead atoms we compare the calculated dependence of κ based on the data by earlier grazing incidence x-ray-scattering experiments with data from scanning-tunneling-microscopy investigations. We find a potential dependence of the lead nearest-neighbor distance close to the expected one. Horizontal displacements proposed by Toney *et al.* as an explanation of the superstructure could not be detected by scanning tunneling microscopy.

In their paper, Toney *et al.* suggest that the superstructure observed with *in situ* scanning tunneling microscopy (STM) at lead monolayers electrochemically deposited on silver (111) (Ref. 1) should be explained in terms of a static distortion wave (SDW) model, according to McTague and Novaco.² Furthermore, they ask whether the observed data scatter may be caused by a potential dependent interatomic spacing of the lead layer.

It should be said that in our paper,¹ the model of a rigid adsorbate was used only to simulate an STM image for comparison with the measurement, and we explicitly excluded any implication on the physical origin. This is because the STM cannot a priori discriminate between corrugations due to changes in the density of states and corrugations due to vertical displacements. Horizontal displacements as inherent to the SDW model were not observed. However, with our STM instrumentation in plane variations less than 0.02 nm cannot be detected. The authors of the preceding paper reported a "lack of agreement" between grazing incidence x-ray-scattering (GIXS) results and the McTague-Novaco model³ regarding the rotational epitaxy angle. Furthermore, Eq. (1) in the preceding paper by Toney *et al.* strictly applies to the rigid layer model if a is assumed to be constant for a given potential.

As suggested by Toney *et al.* in their paper, we were also interested in whether we could see a potential variation in period and angle of the long-wavelength patterns. Recently, we therefore carried out experiments in the same way as described in Ref. 1 except that we used a

solution of 0.5 M NaClO₄ containing 10⁻³ M Pb(ClO₄)₂ with pH ≈ 2 as electrolyte. In order to avoid systematic errors in evaluating the STM data due to miscalibration, creep of the piezo, and thermal drift it is necessary to extract a dimensionless quantity from the images. For this purpose we use the lead lattice as intrinsic calibration for each image by calculating the ratio κ ,

$$\kappa = \frac{\Lambda}{a} = \frac{b}{\sqrt{a^2 + b^2 - 2ab \cos \Omega}} \quad (1)$$

using the atomic periodicity a of the adsorbed lead layer and the superstructure periodicity Λ as given by Toney *et al.* in the preceding paper. b is the nearest-neighbor distance of the silver substrate and Ω the rotational angle of the overlayer with respect to the substrate (4.5°, not depending on the potential, as measured by GIXS experiments by Melroy *et al.*⁴). These periodicities are measured simultaneously in each STM image using the two-dimensional fast Fourier transform provided by the NanoScope II⁵ software. Only STM images which provide clear spots in the Fourier space in all directions for the superstructure as well as for the atoms are used. The periodicities are first averaged over all three directions and then the ratio κ is calculated.

Figure 1 shows the measured κ values versus the substrate potential. The full line is a linear least-mean-square fit to the data with the parameters

$$\kappa_{\text{exp}}(\Delta E_{\text{sub}}) \approx 5.325 - 0.00515 \Delta E_{\text{sub}} / \text{mV}, \quad (2)$$

FIG. 1. Potential dependence of the ratio κ of the superstructure and atomic periodicities. Open circles (○) denote measured values, the full line (—) is a least-mean-square fit to the data, and the dotted (· · ·) line is the calculated dependence, according to Eq. (1), using the data by Toney *et al.* in the preceding paper [see Eq. (6)]. The single κ values have an error bar of 10%. The potential is given with respect to the equilibrium potential Pb/Pb^{2+} of the system.

where ΔE_{sub} is the substrate potential given as potential difference versus the equilibrium potential $E_{\text{Pb}/\text{Pb}^{2+}}$ of the system. The correlation coefficient R^2 is 65%, which is not very good but the tendency is clearly visible.

Assuming a linear potential dependence of a in accordance with Melroy *et al.*⁴ and with adlayer strain considerations by Obretenov *et al.*⁶

$$a(\Delta E_{\text{sub}}) = a_0 + a_1 \Delta E_{\text{sub}}. \quad (3)$$

Equation (1) may be linearized to give

$$\kappa(\Delta E_{\text{sub}}) \approx \frac{b}{\sqrt{a_0^2 + b^2 - 2a_0b \cos \Omega}} \times \left[1 + \frac{(b \cos \Omega - a_0)a_1}{a_0^2 + b^2 - 2a_0b \cos \Omega} \Delta E_{\text{sub}} \right]. \quad (4)$$

Using this linearization and fit (2) we calculate the potential dependence of the lead atomic distance

$$a_{\text{exp}}(\Delta E_{\text{sub}}) = 0.337 \text{ nm} + 5.78 \times 10^{-5} \Delta E_{\text{sub}} \frac{\text{nm}}{\text{mV}}. \quad (5)$$

The dependence of the lead nearest-neighbor distance on the potential measured by Toney *et al.* in the preceding paper is

$$a_{\text{Toney}}(\Delta E_{\text{sub}}) = 0.339 \text{ nm} + 4.24 \times 10^{-5} \Delta E_{\text{sub}} \frac{\text{nm}}{\text{mV}}. \quad (6)$$

Comparing Eqs. (5) and (6) we note that the difference at zero potential is less than 1%, which is well within our experimental error. The difference in the linear increase, which is 35% higher than that from the preceding paper seems to be larger than the experimental error. In perchlorate medium it is well known that the monolayer coverage is in the undervoltage range between 0 and 125 mV positive of the equilibrium potential.⁷ Toney *et al.*, however, measured the lead nearest-neighbor distance over a potential range of 150 mV. This makes the direct comparison of the results by Toney with ours not completely conclusive. Nevertheless, the agreement is remarkably good.

¹U. Müller, D. Carnal, H. Siegenthaler, E. Schmidt, W. J. Lorenz, W. Obretenov, U. Schmidt, G. Staikov, and E. Budevski, *Phys. Rev. B* **46**, 12 899 (1992).

²J. P. McTague and A. D. Novaco, *Phys. Rev. B* **19**, 5299 (1979).

³M. G. Samant, M. F. Toney, G. L. Borges, L. Blum, and O. R. Melroy, *J. Phys. Chem.* **92**, 220 (1988).

⁴O. R. Melroy, M. F. Toney, G. L. Borges, M. G. Samant, J. B.

Kortright, P. N. Ross, and L. Blum, *Phys. Rev. B* **38**, 10 962 (1988).

⁵Digital Instruments Inc., Santa Barbara, CA 93117.

⁶W. Obretenov, U. Schmidt, W. J. Lorenz, G. Staikov, E. Budevski, D. Carnal, U. Müller, H. Siegenthaler, and E. Schmidt, *J. Electrochem. Soc.* **140**, 692 (1993).

⁷H. Bort, K. Jüttner, W. J. Lorenz, and E. Schmidt, *J. Electroanal. Chem.* **90**, 413 (1978).