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Two-dimensional compressibility of electrochemically adsorbed lead on silver (111)

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We report the two-dimensional compressibility of electrochemically deposited lead on silver (111). Measurements were made *in situ* (in contact with solution) using grazing incidence x-ray scattering. Between monolayer formation and bulk deposition, the near-neighbor distance of the lead monolayer decreases linearly with applied potential. Since the lead monolayer is in equilibrium with the lead in solution, the isothermal compressibility of the monolayer can be calculated and is 0.98 Å^2/eV. This is in good agreement with that of a two-dimensional, free-electron gas.

Adsorbed monolayers are of fundamental interest, since they provide physical realizations of two-dimensional (2D) condensed matter. Considerable effort has been devoted to studying monolayers of gases physically adsorbed from the vapor phase onto graphite and metal substrates.[1-8] The isothermal compressibility (κ_{2D}) of rare-gas monolayers has been measured and agrees well with that calculated theoretically using relatively simple molecular interactions.[3-5] However, the compressibility of metallic adlayers has received far less attention due to inherent difficulties in making equilibrium adsorption measurements. Realistic calculations of κ_{2D} for metals are also considerably more difficult, since 2D band-structure calculations that include the effect of the substrate are necessary. In this paper, we report *in situ* grazing incident x-ray scattering (GIXS) investigation of electrochemically adsorbed lead on silver (111) in which the room-temperature compressibility of the monolayer with applied potential has been studied.

Electrochemical deposition of metals onto a foreign metal substrate frequently occurs in distinct stages.[9] The initial steps, corresponding to the formation of different adlayers on the electrode surface, occur at electrode potentials positive of the reversible thermodynamic potential for bulk deposition and hence are termed underpotential deposition (UPD). On single crystals, the different peaks in the current-potential profile profile prior to bulk deposition correspond to the formation of well-defined, presumably ordered, adlayers.[10-13] The current response to a linear sweep of potential for lead on silver (111) and the corresponding adsorption isotherm are shown in Fig. 1. The first peak at approximately -350 mV corresponds to the deposition of a single monolayer of lead. That this is an incommensurate, close-packed triangular monolayer has been shown using a variety of techniques.[10,11,14,15] Between the peak in the current at -350 mV and the onset of bulk deposition (-550 mV), a single monolayer of lead, which coexists with the lead ions in solution, is adsorbed on the silver surface. Although it is difficult to prove that a monolayer is in equilibrium, electrochemically deposited monolayers are frequently treated assuming equilibrium thermodynamics.[9] The adsorbate satisfies the condition that if the electrode is held at the potential where the monolayer is formed and the lead ions removed from solution, the monolayer rapidly desorbs (similar to removing an ideal gas from contact with its adsorbed monolayer). In addition, the monolayer can be removed electrochemically by increasing the potential. In studies specifically directed at probing the equilibrium behavior of electrochemically adsorbed lead on silver (111), nonequilibrium behavior has been observed at coverages less than one monolayer.[16] However, no kinetic effects were observed when polarizing the electrode in the potential range used in this study (i.e., full monolayer coverage).[16] Since the adsorbed-lead monolayer can be described with equilibrium thermodynamics, varying the potential in the region between monolayer formation and bulk deposition changes the chemical potential and is thus analogous to varying the vapor pressure of a gas in equilibrium with its physisorbed monolayer. The presence of the condensed phase (electrolyte) over the electrode, of course, greatly complicates microscopic measurements on UPD monolayers. Most techniques that give direct surface structural information are based on scattering of ions or electrons and are unsuitable for use outside high vacuum. GIXS is, however, ideally suited for *in situ* structural measurements of the solid-liquid interface.

GIXS is becoming an established technique and has been applied to the structural determination of surface reconstruction on metals[17] and semiconductors,[18] the melting of adsorbed monolayers,[19] and the characterization of solid-solid interfaces.[20] One of the key obstacles to overcome before applying GIXS to electrochemical systems is the development of a suitable cell. The requirements for x-ray scattering and good thin layer electrochemistry are difficult to meet simultaneously. The x-ray

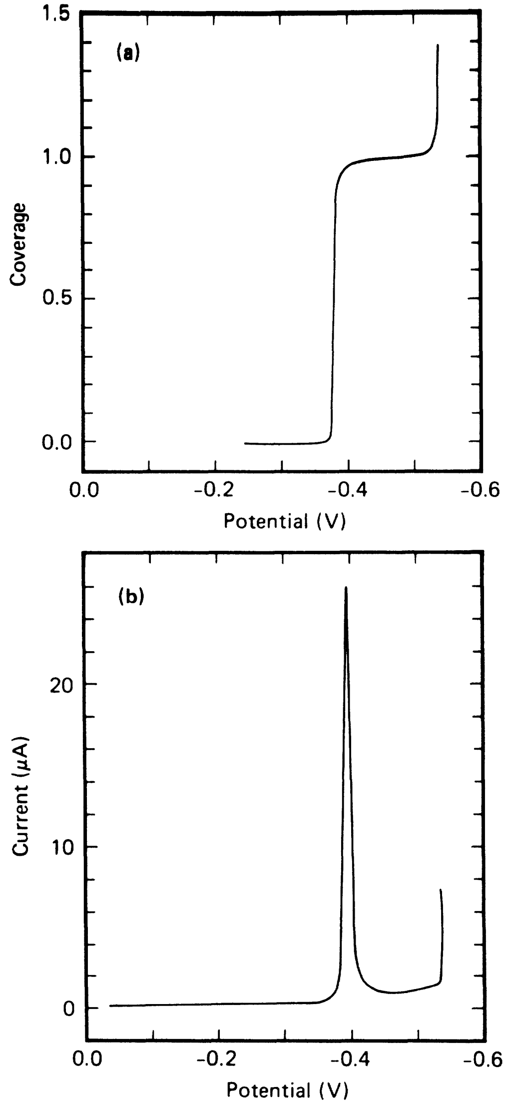

FIG. 1. Voltammogram for the deposition of lead on silver (111) and corresponding adsorption isotherm. Potentials are measured relative to Ag/AgCl. Scan rate 20 mV/s, $5\times10^{-3}M$ lead acetate, $0.1M$ sodium acetate, $0.1M$ acetic acid. Voltammogram was recoded in the cell used for the GIXS with a thick layer of electrolyte covering the electrode.

scattering must be measured with only a thin layer of electrolyte covering the electrode to minimize the diffuse background scattering. Eliminating the large ir drop in the thin layer is also problematic. This ir drop distorts the voltammetry making it difficult to compare with that reported in the literature. To use GIXS to study UPD monolayers, an electrochemical cell was developed that allows deposition with a relatively thick layer of electrolyte covering the electrode.[15] Electrolyte was then withdrawn so that only a thin layer of electrolyte covered the electrode.

The electrode preparation and electrochemical cell have previously been described in detail and will not be discussed here.[15] Lead was electrochemically deposited at room temperature on the silver (111) electrode at −400 mV (vs Ag/AgCl) from a $0.1M$ sodium acetate, $0.1M$ acetic acid and $5\times10^{-3}M$ lead acetate solution. The cell was then changed into the thin layer configuration and experiments conducted by varying the potential after the reconfiguration. The x-ray-diffraction data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated beam conditions on a focused 54-pole wiggler beam line (VI-2) equipped with a four-circle diffractometer (Huber) on which the electrochemical cell was mounted. The sample was held in the vertical plane and the scattered radiation collected at an exit angle equal to the (grazing) incidence angle. The incident x-ray-beam energy was chosen to be 12350 eV (1.003 Å) using a silicon (220) double-crystal monochromator and calibrated with the diffraction from a silicon (111) crystal. The in-plane resolution was approximately 0.005 $Å^{-1}$.

At potentials where lead is adsorbed (negative of −375 mV), diffraction from the lead monolayer is observed. Radial and azimuthal scans of the (10) reflection of the lead monolayer with the electrode held at −550 mV are shown in Fig. 2. The diffuse background scattering is largely due to the thin layer of solution covering the electrode. The peak in the radial scan appears at $Q=2.13$

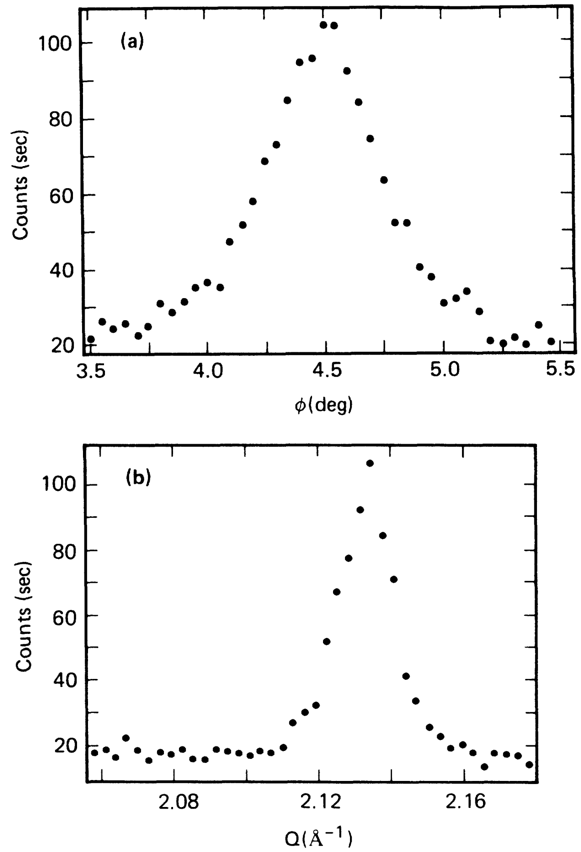

FIG. 2. The (10) reflection of the lead monolayer on silver (111) at −550 mV. The silver $(\bar{2}11)$ is defined as $\phi=0$. (a) Rocking scan at $Q=2.13$ $Å^{-1}$. The 0.02 $Å^{-1}$ width of the peak indicates a domain size of about 290 Å. This domain size is about twice that observed in Ref. 15, which we attribute to a better silver substrates. (b) Radial scan at $\phi=4.5°$.

Å^{-1} corresponding to a lead-lead near-neighbor distance at 3.40 Å for the incommensurate close-packed monolayer. The lead monolayer is not aligned along a silver symmetry direction, but is rotated 4.5° from the silver $(\bar{2}11)$ direction.[15] Neither the line shape, peak position, or intensity changed with time, consistent with the monolayer having achieved equilibrium.

As the potential of the electrode decreases from -375 to -550 mV, the scattering vector of the lead (10) reflection increases. (The near-neighbor decreases.) A plot of the lead-lead near-neighbor distance vs electrode potential is shown in Fig. 3. The near-neighbor distance decreases linearly with potential until the onset of bulk deposition. At this potential, the near-neighbor distance is 3.40 Å, a 2.8% contraction from bulk lead. No additional change in the spacing was observed for potentials cathodic of the potential for bulk lead deposition since the chemical potential is pinned at that for bulk. The thin layer of electrolyte covering the electrode only contains a few (ca. 3) monolayer equivalents of lead. Measurements on thicker layers of bulk lead (ca. 100 equivalent monolayers) indicate that bulk lead is deposited as (111) fiber textured islands which are somewhat randomly oriented in the plane of the substrate. Thus, diffraction from the bulk lead deposited from the thin layer at potentials negative of -550 mV could not be observed.[21]

The 2D isothermal compressibility $\kappa_{2\text{D}}$ is[2]

$$\kappa_{2\text{D}} = -\left(\frac{1}{a}\right)\left(\frac{\partial a}{\partial \phi}\right)_T = -\left(\frac{\partial a}{\partial \mu}\right)_T , \tag{1}$$

where ϕ is the 2D spreading pressure, a is the atomic area, and μ is the chemical potential. For a physisorbed monolayer in equilibrium with its (ideal gas) vapor,[2] $d\mu = k_B T (d\ln P)_T$. This equilibrium relationship has been used in previous experimental measurements of $\kappa_{2\text{D}}$ for rare-gas monolayers.[3-5] Similar experiments on metallic adlayers have not been possible because the very low vapor pressure of the metals necessitates the use of nonequilibrium conditions. However, changing the applied potential in electrochemical adsorption experiments is analogous to changing the vapor pressure in the vapor-solid experiments, since the chemical potential is related to the applied potential (V) as[22]

$$d\mu = -zedV , \tag{2}$$

where z is the number of electrons transferred per atom deposited and e is the electron charge. Thus $\kappa_{2\text{D}}$ can be determined from equilibrium measurements of either pressure or applied potential. However, in electrochemical experiments the potential can be accurately controlled over a wide range without the experimental difficulties of controlling and measuring pressure over a large range (e.g., $d\mu \propto d\ln P$).

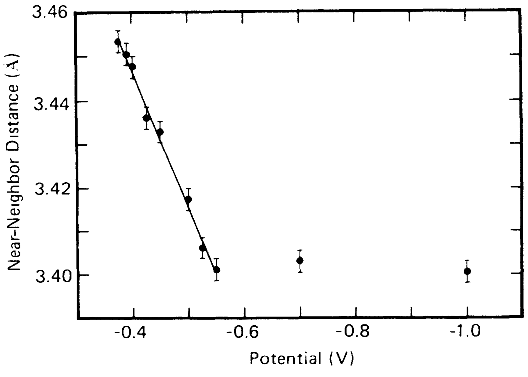

FIG. 3. Lead-lead near-neighbor distance vs electrode potential.

For a close-packed triangular layer, $a = (\sqrt{3}/2)r^2$ and thus

$$\kappa_{2\text{D}} = \frac{\sqrt{3}r}{ze}\left(\frac{\partial r}{\partial V}\right)_T . \tag{3}$$

Evaluating the slope from Fig. 3 and substituting above, the value obtained for $\kappa_{2\text{D}}$ is 0.98 $\text{Å}^2/\text{eV}$. Since for most bulk metals, the compressibility is dominated by the electron compressibility, a similar domination is expected for metal monolayers.[23] Using a 2D noninteracting free-electron-gas model,[23] the isothermal compressibility estimated for a lead monolayer is 0.3 $\text{Å}^2/\text{eV}$. This is in good agreement with the measured value, which is probably a result of the free-electron nature of lead. While this agreement is gratifying, a more realistic calculation is desirable. This would involve a 2D band-structure calculation that included effects of the silver substrate and is outside the scope of this Rapid Communication. Since the slope in Fig. 3 is constant, $\kappa_{2\text{D}}$ is independent of near-neighbor spacing, to within 3%. This is unexpected, since in bulk lead the compressibility drops by 7% when the near-neighbor distance decreases from 3.45 to 3.40 Å.[24]

As shown in Fig. 2, the angle between the lead (10) reflection and the silver $(\bar{2}11)$ direction (rotational epitaxy angle) is 4.5°. No change in this angle was observed with the compression of the adlayer. This was unexpected, since the application of the models of rotational epitaxy developed either by Novaco and McTague[6] (weakly modulated overlayer) or Shiba[7] (large modulations in adatom-substrate energy) predict 0.5° or more changes in the rotation epitaxy angle for a compression of about 1.5%. Also, we were unable to detect any satellite diffraction that would result from a strong periodic modulation of the adlayer by the substrate as would be expected from a strongly modulated incommensurate overlayer. However, the presence of diffuse scattering from the electrolyte prevents the observation of a satellite with less than 3% of the intensity of the (10) peak. This lack of change in the rotational epitaxy may indicate that the surface of the silver substrate is affected by the lead overlayer.

At the potential for bulk deposition, the adlayer is highly strained. Recent theories on wetting[25-27] have suggested that, in addition to the ratio between substrate-adsorbate and adsorbate-adsorbate interactions, another important factor affecting the wetting behavior is compressive strain in the adsorbed layers, resulting from a strong adsorbate-substrate interaction. Although these theories were developed for physisorption, the compressive strain appears to be an important factor in electrochemical deposition as well. These results will be discussed in detail in a later paper.[21]

In summary, the variation in the lead near-neighbor distance with applied potential was measured and the 2D isothermal compressibility determined for electrochemically adsorbed lead monolayers on silver (111). This equilibrium measurement is possible for metals because the chemical potential can easily be varied and the in-plane near-neighbor distance measured *in situ* using GIXS. *In situ* structural studies of the solid-liquid interface using techniques such as GIXS will lead to a greater understanding of this interface. The ability to make equilibrium measurements at this interface should also enhance our understanding of 2D layers.

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