ELECTROCHEMICALLY ADSORBED Pb ON Ag (111) STUDIED WITH

GRAZING INCIDENCE X-RAY SCATTERING

J.B. Kortright*, P.N. Ross*, O.R. Melroy**, M.F. Toney**, G.L. Borges** and M.G. Samant**

Lawrence Berkeley Laboratory
*Center for X-ray Optics
Accelerator and Fusion Research Division
*Materials and Chemical Sciences Division
University of California
Berkeley, CA 94720

**IBM Almaden Research Center
650 Harry Road
San Jose, CA 95120

DISCLAIMER

MASTER

ELECTROCHEMICALLY ADSORBED Pb ON Ag (111) STUDIED WITH GRAZING-INCIDENCE X-RAY SCATTERING

J.B. KORTRIGHT, P.N. ROSS, O.R. MELROY[*], M.F. TONEY[*], G.L. BORGES[*] and M.G. SAMANT[*]

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA
[*]IBM Almaden Research Center, 650 Harry Road, San Jose, California, 95120, USA

Résumé - Nous présentons les études, par la dispersion de rayons-X d'incidence rasée, de l'évolution de couches de plomb sur argent (111) déposées électrochimiquement en fonction du potentiel électrochimique. Les mesures ont était faites avec des couches adsorbées en contact avec la solution dans une cellule échantillon spécialement preparée. Les structures de plomb observées sont en fonction du potentiel et domaine appliqué d'une couche monomoléculaire disproportionné resultant d'un dépôt sous-potentiel à un ensemble polycristallin de plomb orienté au hasard résultant des potentiels de dépôt plus bas. Ces premières experimentations démontrent l'abilité des mesures de la diffractions des rayons-X *in situ* de determiner les structures résultant du dépôt électrochimique.

Abstract - Grazing-incidence x-ray scattering studies of the evolution of electrochemically deposited layers of lead on silver (111) as a function of applied electrochemical potential are presented. Measurements were made with the adsorbed layers in contact with solution in a specially designed sample cell. The observed lead structures are a function of the applied potential and range from an incommensurate monolayer, resulting from underpotential deposition, to randomly oriented polycrystalline bulk lead, resulting from lower deposition potentials. These early experiments demonstrate the ability of *in situ* x-ray diffraction measurements to determine structures associated with electrochemical deposition.

1 - INTRODUCTION

The electrochemical deposition of Pb on Ag (111) (and related systems like Tl and Bi on Ag) occurs in two distinct stages, as illustrated in Fig. 1. Lead ions from the electrolyte adsorb on a Ag electrode at potentials positive of the Nernst potential at which Pb^{2+} ions are reduced to form bulk Pb /1/. The terms underpotential deposition (UPD) and bulk deposition refer to these two stages of Pb deposition, respectively. A variety of *ex situ* and *in situ* techniques have been used to draw inferences about the nature of structures resulting from UPD of Pb on Ag (111) (see ref. /2/). From these studies it was thought that UPD resulted in formation of a close-packed hexagonal monolayer of Pb on the Ag electrode. Until recently, however, no direct structural measurements had been made of long range order in the overlayer, or its orientation with respect to the substrate. Grazing-incidence x-ray scattering (GIS) techniques allow these measurements to be made. This paper summarizes results of an initial series of GIS experiments following the electrochemical deposition of Pb on Ag (111) as a function of applied potential /2-5/. The collective results of these experiments reveal how the initial stages of electrochemical growth of this system proceed. Details of background, experimental procedures, and discussion not presented here can be found in refs. /2-5/.

2 - EXPERIMENTAL METHODS

Flat, single crystal Ag substrate electrodes were formed by evaporation onto mica. The electrolyte used for the experiments described here was 0.5 M sodium acetate, 0.1 M acetic acid and 5.0×10^{-3} M lead acetate. Electrochemical potentials are referenced to a Ag/AgCl electrode.

A sample cell was designed to allow electrochemical depositions to be made with the sample installed and aligned on the diffractometer, and x-ray measurements to be made with the deposited layers in contact with the electrolyte. The cell is shown in Fig. 2. The body of the cell is made of Kel-F®, which, together with a 13 µ polypropylene window, encloses the electrolytic solution. Various electrode and solution ports are made in the body of the cell.
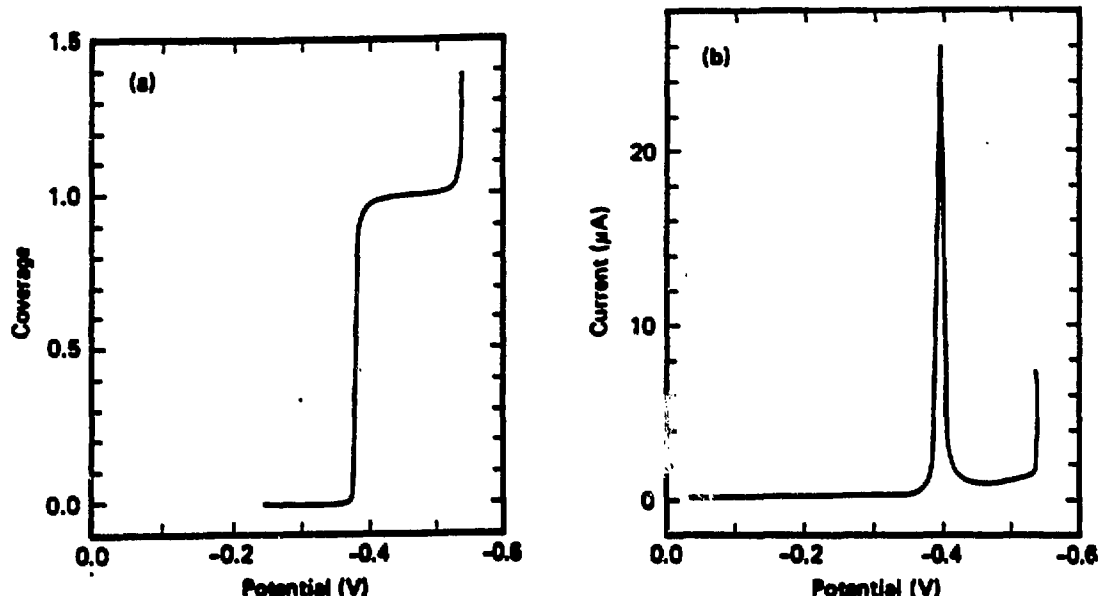
Figure 1. Voltammogram (b) and adsorption isotherm (a) for the electrochemical deposition of Pb on Ag (111) show two distinct stages of deposition. An UPD monolayer of Pb results from deposition at roughly -0.4 V potential, while bulk Pb deposition proceeds for potentials less than roughly -0.55 V.

The Ag substrate electrode is positioned above the body of the cell to allow grazing-incidence x-ray measurements of the Ag-electrolyte interface. Changes in the electrochemical potential (to deposit or remove Pb) were made with the electrolyte under enough hydrostatic pressure to stretch the polypropylene window and allow a relatively large bath of electrolyte to surround the electrode. Then, withdrawal of much electrolyte from the cell caused the window to conform to the electrode surface, thus minimizing absorption losses and measurement of unwanted scattering from the electrolyte. In this configuration capillary action provides a thin (1-10 μ) layer of electrolyte between the electrode and window so that the freshly deposited Pb remains in contact with solution during diffraction measurements.

X-ray measurements were made on several different occasions at the Stanford Synchrotron Radiation Laboratory using a conventional Huber 4-circle diffractometer at two different beamlines, each with a Si (111) double crystal monochromator. Radiation from the 8-pole wiggler beamline 7-2 was monochromatized to provide 8.048 keV radiation, while that from the 54-pole wiggler beamline 6-2 was monochromatized to provide 10.000 keV radiation. After aligning the Ag substrate normal parallel to the ϕ axis of the diffractometer and determination of the substrate orientation, three types of scans were performed to collect data; rod scans, radial scans, and rocking scans.

3 - RESULTS AND DISCUSSION

Diffraction from three distinct structures was observed in these experiments. These different intensity features are discussed in turn, starting from the substrate.

Diffracted intensity from the Ag (111) substrate in the wet electrochemical cell reveals expected Ag peaks in expected positions. Observed substrate diffraction features are shown as open circles in Fig. 3, and consist of the bulk in-plane ($\bar{2}02$) and symmetry-related reflections. Also seen from the Ag substrate is the crystal truncation rod labeled 1/3($\bar{4}22$) and symmetry-related features. Each of these sets of features exhibits 6-fold symmetry, and their positions are in agreement with the accepted value of the Ag lattice constant.

Lead overlayer structures deposited in the UPD range exhibit sharp in-plane diffraction peaks consisting of two equivalent sets of 6-fold features symmetrically disposed about the Ag features as indicated in Fig. 3. This pattern is interpreted as resulting from a monolayer coverage of hexagonal close-packed Pb atoms which are incommensurate with the Ag (111) substrate. This 2-dimensional Pb overlayer consists of 2 sets of equivalent domains, each
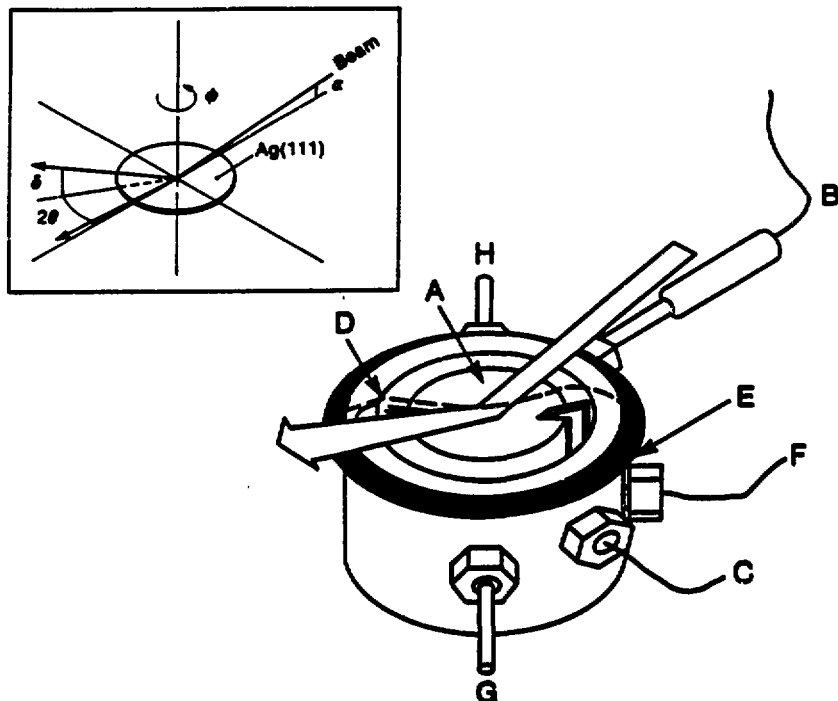
2

Figure 2. **Electrochemical cell:** (A) Ag (111) electrode, (B) Ag/AgCl reference electrode, (C) Pt counter electrode, (D) polypropylene window, (E) O-ring holding polypropylene to cell, (F) external electrical connection to the working electrode, (G) electrolyte inlet, (H) electrolyte outlet. The inset defines the angles used in the grazing-incidence scattering experiments: α and δ are grazing incident and take-off angles with respect to the sample surface, 2θ the scattering angle, and ϕ the sample azimuthal angle.

rotated 4.5° about the 6-fold axis of the Ag substrate. Figure 4 shows an α scan along a (10) rod of the Pb monolayer as well as ϕ and $\theta-2\theta$ scans through this feature. Using 2-dimensional indexing, both Pb (10) and (11) features were observed. $\theta-2\theta$ scans of these Pb spots provides a lower limit on the domain size of these Pb domains of 150 Å. The significant background intensity results from Compton and diffuse elastic scattering from the polypropylene window and electrolyte.

In the UPD monolayer, the Pb-Pb nearest-neighbor distance is smaller than in bulk Pb, and this distance depends sensitively on the applied electrochemical potential at which the UPD is held after deposition. All UPD depositions were made at -0.4 V, and the potential was then decreased. Potentials between roughly -0.4 V and -0.55 V result in a linearly decreasing nearest-neighbor distance with potential. This behavior corresponds to increasing compression of the Pb monolayer with potential, with values of compression ranging from 1.4 % to 2.8 % compared to the nearest-neighbor distance in bulk Pb. Because the Pb adatoms are in equilibrium with Pb in solution, the isothermal 2-dimensional compressibility of the monolayer can be calculated and is 0.9 Å^2/eV /4/. For potentials more negative than about -0.55 V, deposition of additional Pb onto the UPD monolayer occurs. The ordered UPD monolayer remains unchanged during the initial stages of bulk Pb deposition since the chemical potential is pinned at the bulk value. The rotated domain structure of the UPD monolayer, including the rotation angle, are independent of the potential.

To study the growth of subsequently deposited Pb, bulk Pb was deposited at constant potential following the initial deposition of the UPD monolayer /5/. The amount of Pb deposited was determined from the integral of the electrochemical current and is given in equivalent monolayers, i.e. the amount which would exist in one uniform close-packed monolayer. Subsequent growth does not occur epitaxially onto the UPD layer because of the large compression. After deposition of about 5 equivalent monolayers, the initial UPD monolayer features disappear as enough bulk Pb is present to induce reconstruction of the UPD layer.
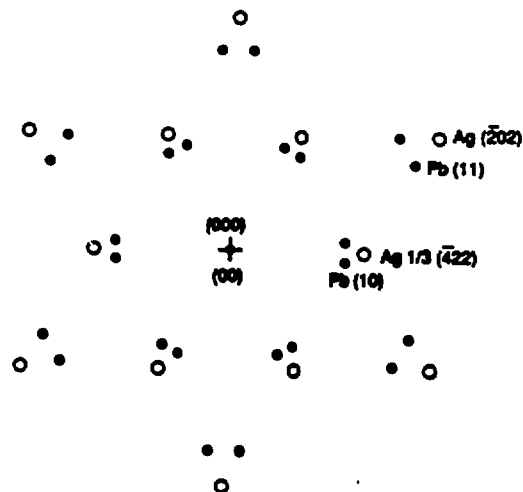
3

Figure 3. Observed Ag (open circles) and Pb (closed circles) intensity projected onto a plane through the origin of reciprocal space parallel to the Ag (111) substrate surface.
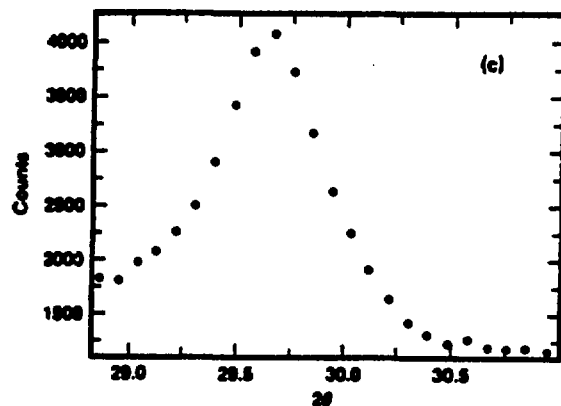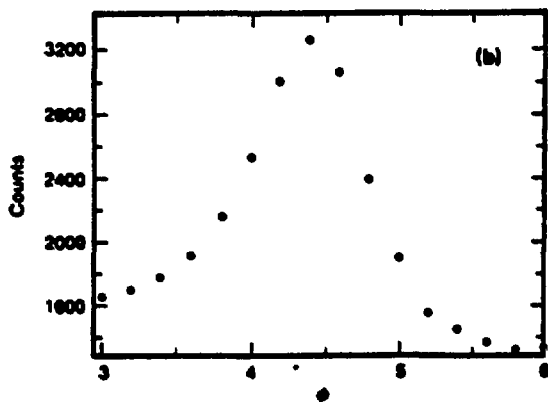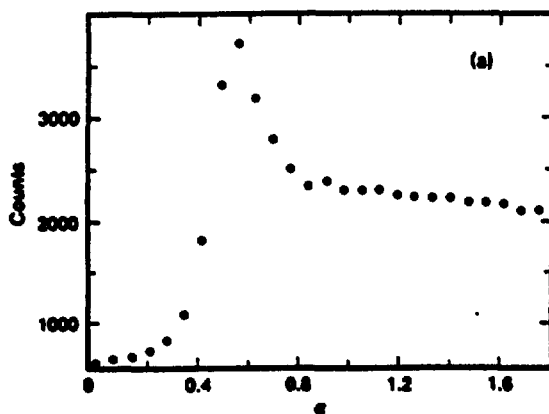

Figure 4. Intensity from a Pb monolayer deposited in the underpotential deposition regime. (a) shows a rod scan along the Pb (10), while (b) and (c) show rocking and radial scans through this feature.

4

No discernable signal from bulk Pb was observed until roughly 100 equivalent monolayers were deposited, at which time the (220) reflection of Pb was observed at the expected position for unstrained Pb. ϕ scans revealed no preferred orientation of this bulk Pb with respect to direction in the Ag substrate plane.

4 - SUMMARY

These results show that grazing-incidence x-ray scattering techniques can follow *in situ* growth of electrochemically deposited overlayers on single crystal substrates. For the case of Pb on Ag (111) reported here, the first monolayer of lead shows well-ordered, incommensurate domains of close-packed Pb atoms with a specific rotation angle with respect to the substrate and a potential-dependent compression. These phenomena are not specific to the Pb on Ag electrochemical system reported on here; experiments are underway which show that they are exhibited by other systems, e.g. Pb on Au (111) and Tl on Ag (111) /6/. The study of well-ordered overlayers on well-ordered substrates is facilitated by easily observed Bragg features. Electrochemical growth which proceeds via less well-ordered structures will be more difficult to study with this technique because of the significant background scattering from the electrochemical cell.

ACKNOWLEDGEMENTS

REFERENCES

/1/ Kolb, D., in: Advances in Electrochemistry, Vol. 2, Eds. H. Gerischer and C. Tobias (Wiley, New York, 1978) p. 125.

/2/ Samant, M.G., Toney, M.F., Borges, G.L., Blum, L. and Melroy, O.R., J. Phys. Chem. 92 (1988) 220.

/3/ Samant, M.G., Toney, M.F., Borges, G.L., Blum, L. and Melroy, O.R., Surf. Sci. 193 (1988) L29.

/4/ Melroy, O.R., Toney, M.F., Borges, G.L., Samant, M.G., Kortright, J.B., Ross, P.N. and Blum, L., Phys. Rev. B 38 (1988) 10962.

/5/ Melroy, O.R., Toney, M.F., Borges, G.L., Samant, M.G., Kortright, J.B., Ross, P.N. and Blum, L., J. Electroanal. Chem. 258 (1989) 403.

/6/ Toney, M.F., Gordon, J.G., Borges, G.,L., Samant, M.G., Kau, L.S., Melroy, O.R., Sorensen, L. and Yee, D, to be published.