



Experiment title: The structure of Pb films electrochemically deposited onto Si(III):H studied in-situ with x-ray diffraction
(Experiment changed in agreement with User Office)

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Report:

In this experiment we investigated the crystallographic properties of Pb films deposited electrochemically onto hydrogen terminated silicon (111) surfaces [Si(III):H] from perchloric acid solution *in situ* by surface x-ray diffraction. Si(111):H electrodes exhibit a well defined surface morphology and show a remarkable stability towards aqueous acidic electrolytes. There were two major motivations for this experiment, namely the desire to understand the difference between UHV- and electrodeposition of metals onto Si(III):H, and to clarify how the presence of the monohydride layer at the interface influences the electrochemical metal deposition process [1].

The measurements were performed at the six-circle diffractometer of BL11/ID32, employing an electrochemical cell specially designed to monitor electrode processes with large mass transfer continuously *in situ* with x-rays [2]. The experiments were done under potentiostatic control in a three-electrode setup, using a miniaturized Ag/AgCl reference and a platinum counter electrode. To penetrate the electrolyte layer of ≈ 1 cm thickness with sufficient transmission, the x-ray energy was set to 23keV. Samples of 2x2 mm size were cut from phosphorous doped Si(111) wafers ($n_D \approx 10^{15} \text{cm}^{-3}$) of 0.5 mm thickness. Prior to etching, they were refluxed for 2 hours in isopropyl alcohol. Etching of the samples was done by a multi-step procedure to obtain clean and well defined monohydride terminated surfaces: 1) 15 min boiling in a mixture of $\text{NH}_3:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:5 by volume) at $\approx 80^\circ\text{C}$; 2) 1 min etching in 50% HF solution; 3) 15 min boiling in a mixture of $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:5 by volume) at $\approx 80^\circ\text{C}$; 4) 1 min etching in 50% HF solution. This treatment results in a surface terminated by monohydride and dihydride groups. Then, the samples were mounted onto sample holders with epoxy resin, so that only the front face of the crystal was exposed to the electrolyte. Ohmic contact to the back of the sample was made by an In/Ga eutectic alloy. Prior to use, the mounted samples were etched for 3 min. in 40 % NH_4F solution to obtain a uniform termination by Si-monohydride.

Lead was deposited onto the Si(III):H electrode from 0.1M $\text{HClO}_4 + 0.1\text{mMPb}^{2+}$, by stepping the potential from -0.49 V_{SCE} , where no lead deposition occurs, to -0.71 V_{SCE} , i.e. into the bulk deposition region. Diffraction studies were performed for Pb layers of several ten ML thickness. Specular $\theta/2\theta$ scans showed pronounced reflection maxima at $Q_{\perp} = 2.198 \text{ \AA}^{-1}$ and $Q_{\perp} = 4.397 \text{ \AA}^{-1}$, corresponding to the Pb(111) and Pb(222) lattice spacing of 2.858 and 1.429 \AA , respectively, indicating that the Pb grows unstrained with its bulk lattice constant and with the (111) lattice planes oriented parallel to the substrate surface. From the halfwidth of θ -scans a mosaic spread of $0.26\text{-}0.30^\circ$ was deduced. Radial in-plane scans showed reflection maxima corresponding to the Pb (200) and (220) reflections. However, w-scans at these reflections did not show any pronounced angular dependence but revealed a circular isotropic intensity distribution, with sharp spikes that varied from scan to scan in position as well as in intensity (Fig. 1). Thus, we conclude that Pb grows epitaxially onto Si(III):H in the direction normal to the surface, with Pb [111] parallel to Si [111], without any preferential in-plane orientation. This is a surprising result and we intend to compare this with UHV deposited Pb on Si(III):H. In contrast, UHV deposited Pb on bare Si(III)-(1x1) exhibits at higher coverage incommensurate overlayers with defined in-plane orientations [3]. The reasons for the temporal behaviour of the spikes is unclear at present.

With further experiments, we monitored the growth and dissolution behaviour of lead time-dependently. The analysis of these results is still in progress. Figure 2 shows the development of the Pb(111) reflection during deposition. The half width of the peak decreases only in the beginning of the process and then approaches a constant value ($\Delta q/q \approx 10^{-3}$), whereas the integrated intensity rises constantly. From this we conclude that the lead crystallites grow rapidly in height during the beginning of the deposition process, but then continue to grow laterally only. The growth of Pb is purely Vollmer-Weber like and we did not find any indication of a Stranski-Krastanov starting layer, as is reported for Pb on Si(III):H deposited in UHV.

[1] D.M. Kolb, R.J. Randler, R.I. Wielgosz, and J.C. Ziegler, *Mat. Res. Proc. Symp. Soc.* 451 (1997) 17.

[2] G. Scherb, A. Kazimirov, and J. Zegenhagen, *Rev. Sci. Instrum.* 69 (1998) 512.

[3] see, e.g. H.H. Weitering, D.R. Heslinga, and T. Hibma, *Phys. Rev. B* 45 (1992) 5991.

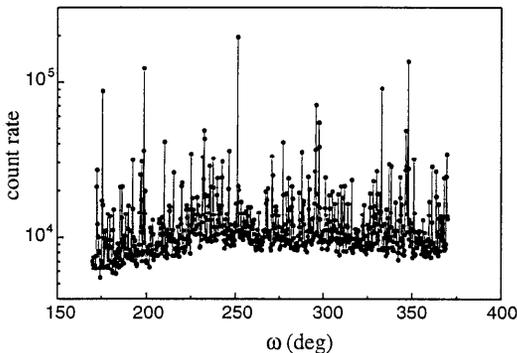


Figure 1: Azimuthal scan of the Pb(220) peak showing an almost uniform circular intensity distribution.

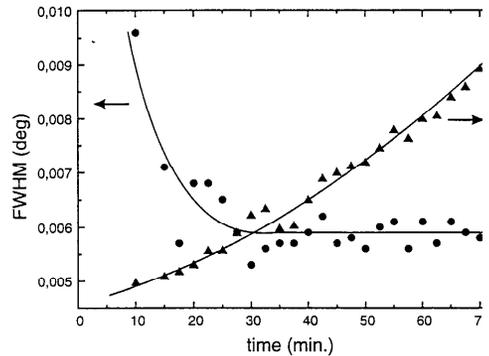


Figure 2: Time dependence of FWHM (deg) and integrated intensity (triangles) of Pb(111) reflection during deposition. Solid lines serve as a guide to the eye only.