

Time-Resolved Surface X-ray Scattering Study of Surface Ordering of Electrodeposited Layers

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The electrodeposition of metals onto solid surfaces is a key aspect of important technological processes. Metal overlayers can be electrodeposited onto dissimilar metal substrates at potentials less negative than the Nernst value (required for bulk deposition). This “underpotential deposition” (UPD) provides a precise means for quantitatively and reproducibly controlling coverage in the submonolayer to monolayer regime.^{1–2} In addition to the surface coverage, the presence of anions and the surface structure of the substrate can profoundly affect the structure of the deposit and the kinetics of deposition.^{1–6}

In-situ probes such as STM,⁷ AFM,⁸ and surface X-ray scattering^{9,10} have been applied to UPD systems offering the possibility of studying the kinetics of deposition and growth.

We report time-resolved surface X-ray scattering measurements of Cu UPD on Pt(111) in the presence of Cl[−], a process that is very sensitive to the presence of anions and which appears to be kinetically controlled. The exact structure of the overlayer at intermediate coverages has been the subject of some controversy. Based on LEED studies, Michaelis et al.¹¹ identified the intermediate overlayer as a 4 × 4 structure. However, based on recent in-situ X-ray diffraction measurements Tidswell et al.¹² proposed a more complicated incommensurate CuCl bilayer.

Time-resolved surface X-ray scattering is a nearly ideal probe for studying the time evolution of UPD processes. The line shape of the scattered X-rays can be interpreted simply in terms of well-known correlation functions. Using signal averaging techniques, transient structures with lifetimes as short as a few microseconds can be studied.¹³

Here, we employed 1 mM Cu²⁺ and 10 mM Cl[−] in a 0.10 M HClO₄ supporting electrolyte. The Pt electrode was oriented and polished so that the surface normal was <0.1° of the (1 1 1)

direction, with a bulk mosaic of about 0.015° (FWHM). The resulting surface figure is better than 0.015° (HWHM). The electrode was flame annealed prior to all measurements. Potentials are referenced to a Ag/AgCl reference.

Experiments were performed at the X20A beamline at the NSLS using an in-situ reflection-geometry X-ray scattering cell similar to that developed by Toney and co-workers.⁹ A thin polypropylene film covered the sample and contained the solution in a thin layer configuration. The incident x rays were monochromatized to 8.80 keV by a double bounce Ge(111) monochromator and focused by a mirror onto the sample. The resolution of the diffracted beam was set by slits such that the 2-θ resolution was 0.05° (HWHM). Chronoamperometric (current/time) measurements were synchronized with the time base of a multichannel scalar, which simultaneously recorded the intensity of the scattered x rays.

A cyclic voltammogram performed in the X-ray cell (see Supporting Information) was essentially the same as that previously reported by a number of research groups^{3–5} and consisted of two sharp and well-defined voltammetric waves centered at potentials of +0.45 (peak 1) and +0.31 (peak 2) volts vs Ag/AgCl. Copper UPD on Pt(111) in the presence of chloride is believed to involve a series of steps which on a negative going sweep can be summarized as follows. At the rest potential (+0.65 V), chloride anions are adsorbed on the platinum surface in a disordered fashion.¹⁴ As the potential is swept negatively, copper is electrodeposited onto the platinum surface at a well-defined potential (peak 1).^{4–6} In between the two aforementioned voltammetric peaks, the electrodeposited copper and chloride anions form an ordered, incommensurate CuCl overlayer on the platinum surface. At more negative potentials there is additional copper deposition (peak 2), yielding a full, commensurate copper monolayer which is, in turn, covered by a disordered layer of chloride.^{3,15} Upon scan reversal (positive-going sweep), the reverse processes take place. These processes are completely reversible and stable for hours so that data acquisition in a “stroboscopic” fashion can be carried out until adequate statistics are obtained. To ensure that the electrode remained clean and well-ordered throughout the X-ray scattering experiments, cyclic voltammograms were taken before and after each X-ray measurement.

We have studied the time evolution of the transition between the incommensurate CuCl overlayer and the commensurate copper monolayer present at different potentials. The CuCl overlayer, present at +0.35 V, has a lattice spacing approximately 30% larger than that between Pt atoms on a (111) surface.¹² Hence, rods of scattering which are sharp in the **a*** and **b*** directions but diffuse in the **c*** (see Supporting Information for indexing) direction should be observable. The full copper monolayer (present at +0.20 V) is commensurate with the Pt(111) surface so that the rod of scattering from the overlayer interferes with the scattering from the crystal truncation rods (CTR) of the Pt(111) surface,¹⁶ making the interpretation intensity changes more complicated.

Figure 1 shows the scattering found at the (0.765 0 1.5) position at +0.35 and +0.20 V clearly demonstrating the presence of the incommensurate CuCl overlayer structure at +0.35 V and its absence at +0.20 V. The background is largely due to scattering from the solution and the polypropylene film.

In order to study the dynamics of these structural transitions, we employed the potential step sequence shown in Figure 2a. The initial potential was +0.20 V, a value at which the copper

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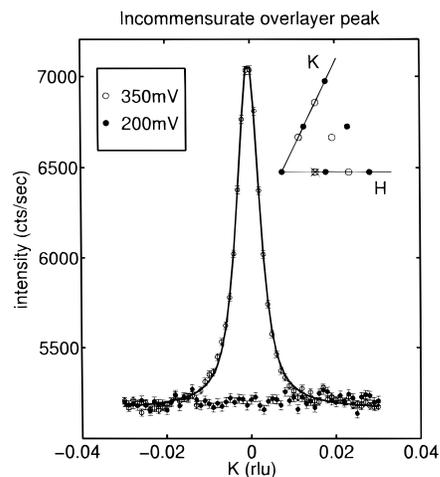


Figure 1. Comparison of the scattered X-ray intensity at (0.765 0 1.5; cross in the inset) corresponding to the incommensurate CuCl overlayer at +0.35 V and +0.20 V. The solid line is a fit to a pseudo-Voigt line shape, to guide the eye.

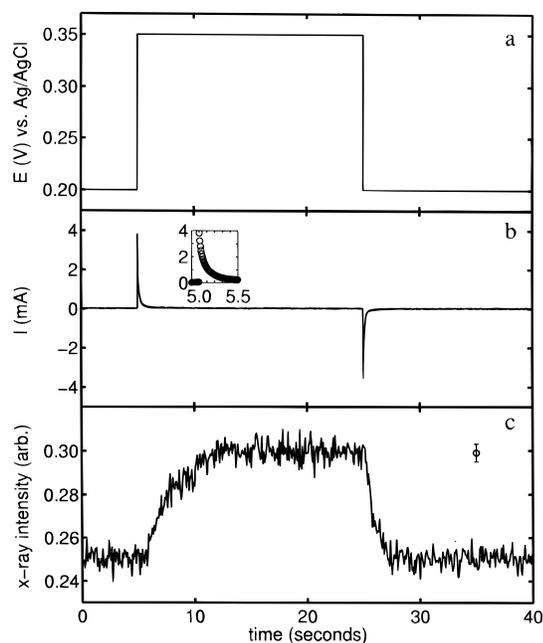


Figure 2. (a) Applied potential step sequence, (b) current/time response (inset: transient at $t = 5$ s on an expanded time scale), (c) time dependence of the scattered X-ray intensity at (0.765 0 1.5).

monolayer, commensurate with the Pt(111) electrode surface, is present. At $t = 5$ s, the potential was stepped to +0.35 V leading to the formation of the incommensurate CuCl overlayer structure. At $t = 25$ s, the potential was stepped back to +0.20 V. This cycle was repeated in order to obtain appropriate statistics.

Figure 2b shows the transient currents observed when this potential step sequence is performed. These currents are generated by the stripping of Cu^{2+} and/or the adsorption of Cl^- on the positive-going step and the reverse for the negative-going step. The charge associated with these transients (area under each current transient after background subtraction) was consistent ($\pm 10\%$) with the processes described above as well as with previous electrochemical studies. The time for the current to fall to $1/e$ of its original value is about 0.08 s for the positive-going step and 0.12 s for the negative-going step.

Time-resolved X-ray data, acquired simultaneously with chronoamperometric measurements, are presented in Figure 2c which shows the intensity of the (0.765 0 1.5) overlayer peak as a function of time. The solid line is a fit to an exponential

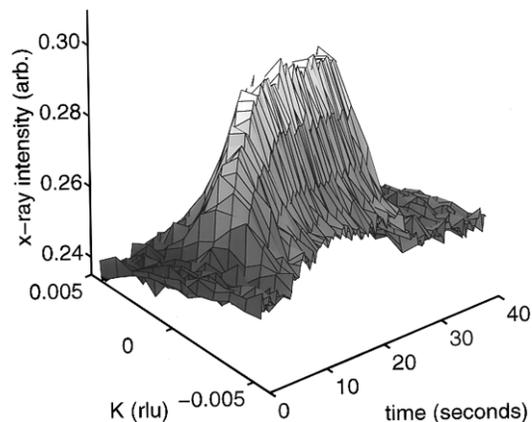


Figure 3. Scattered intensity as a function of time t , and scattering vector, $\mathbf{q} = (0.765 \text{ K } 1.5)$.

line shape for the purpose of estimating time constants. The intensity rise at $t = 5$ s, due to the formation of the CuCl overlayer, has a time constant of 2.3 s. In contrast, the intensity fall at $t = 25$ s has a characteristic time constant of 0.75 s suggesting that the formation of the CuCl overlayer is much slower than its destruction, which from a physical standpoint is an intuitively satisfying result.

What is most surprising, however, is the dramatic difference in time scales between the current transients (panel b) and the X-ray scattered intensity (panel c). Clearly, the development of long-range periodic order in the CuCl overlayer requires significantly more time than that required for electrodeposition. Thus, the latter is not the rate-limiting process. We have also confirmed that ohmic drops are not responsible for these effects (see Supporting Information).

An alternative possibility is that the diffraction peak could be moving in H or K as a function of applied potential. At the (0.765 0 L) position, this would correspond to the overlayer expanding/contracting or rotating with respect to the underlying platinum lattice. Hence, it was necessary to take time-resolved \mathbf{q} -scans, rather than simply monitor the intensity at a single point in reciprocal space. A representative \mathbf{q} - t scan is shown in Figure 3. From these and similar scans, it is clear that only the peak intensity varies, while its periodicity remains constant in reciprocal space.

In summary, by combining chronoamperometric measurements with time-resolved surface X-ray scattering, we have demonstrated that the electrochemical deposition/stripping processes are far more rapid than the time required to form an ordered CuCl overlayer. Thus, electrochemical measurements alone are insufficient to fully characterize the microscopic structural and kinetic details of UPD systems. This example illustrates the power of time-resolved X-ray scattering as an in-situ probe of the kinetics of UPD processes in particular and of interfacial growth in general.

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Supporting Information Available: Indexing of surface peaks, cyclic voltammetric profile in X-ray cell under thin-layer configuration, current time transients in thin-layer and extended configurations, comparison of specular and nonspecular CTR with beam on and off center (5 pages). See any current masthead page for ordering and Internet access instructions.