Probing Electrochemical Interfaces with X-ray Standing Waves

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The utility of the X-ray standing wave technique for the study of electrochemical interfaces is demonstrated. A platinum/carbon LSM (layered synthetic microstructure) with a d spacing of 56 Å and with platinum as the outermost layer was used as a substrate. A layer of iodide was adsorbed, followed by the electrodeposition of a layer of copper. Simultaneously monitoring of the reflectivity as well as the fluorescence intensity arising from the iodide and copper layers showed that the copper layer is deposited on top of the platinum, consistent with previously reported LEED studies of Hubbard and co-workers.

The X-ray standing wave technique[1] represents an extremely sensitive tool for determining the position of impurity atoms within a single crystal[2] or adsorbed onto crystal surfaces.[3-6] This method, based on the dynamical theory of X-ray diffraction,[7] has recently seen a resurgence due to the availability of synchrotron radiation which significantly reduces data acquisition times to the point where many new applications can be explored.

As schematically illustrated in Figure 1 this technique is based on the X-ray standing wave field that arises as a result of the interference between the coherently related incident and Bragg diffracted beams from a perfect crystal. The standing wave develops not only in the diffracting crystal but also extends ca. 1000 Å beyond its surface. The d spacing of the diffracting planes in the crystal determines the distance scale over which the adsorbate can be probed. The nodal and antinodal planes of the standing waves are parallel to the diffracting planes and the nodal wavelength corresponds to the spacing of the diffracting planes d. As the angle of incidence is advanced through the strong Bragg reflection, the standing wave antinodes move inward by one-half of a d spacing. For an atom overlayer which is positioned parallel to the diffraction planes, the nodal or antinodal planes of the standing wave will pass through the atom plane as the angle is varied. Since the photoelectric effect is (by dipole approximation) proportional to the E-field intensity at the center of an atom, the fluorescence emission yield from atoms in the overlayer will be modulated in a characteristic fashion as the substrate is rocked in angle. The phase and amplitude of this modulation (or the so-called coherent position and coherent fraction) are a measure of the mean position $\langle z \rangle$ and width $\langle z^2 \rangle^{1/2}$ of the distribution of heavy atoms in the overlayer. The z scale is modulo the d spacing and points normal to the diffraction planes. As shown in ref 5, standing wave measurements of $\langle z \rangle$ and $\langle z^2 \rangle^{1/2}$ can be accurate to within 1% and 2% of the d spacing, respectively.

Although this is clearly a very powerful technique, its general applicability has been hampered by the need to grow perfect or near prefect crystals. This is especially problematic for relatively soft materials such as copper, gold, silver, and platinum which are not only very difficult to grow in such high quality, but also very difficult to maintain in that state. Thus, with the exception of recent results using copper single crystals,[6] most experiments have been performed on silicon, germanium, or III-V single crystals. This is unfortunate since many reactions of interest take place at the previously mentioned metal surfaces. The advent of so-called LSMs (layered synthetic microstructures)[8,9] has opened up the possibility of using these devices in standing wave experiments with a variety of surfaces. These LSMs are prepared by the sequential deposition of alternate layers of materials (typically a high and a low electron density element) onto a smooth substrate material such as silicon or glass. The d spacings of current LSMs are 10 to 20 times bigger than those of single crystals. Thus, interfaces can be probed on length scales that are much larger

than those that can possibly be obtained with any metal single crystal.

Our interest lies in the use of X-ray standing waves as in-situ probes of electrochemical interfaces. Since high-energy X-rays are used as probes, they allow for the study of surfaces in contact with an electrolyte solution so that electrochemical processes can be investigated in-situ with this technique. Of particular relevance in this respect are the recently developed LSMs based on platinum and carbon (with platinum as the outermost layer), since platinum is one of the most widely used electrode materials in electrochemistry and numerous redox processes have been characterized on both polycrystalline and single-crystal platinum electrodes. These LSMs allow for the investigation of electrochemical processes without the need for growing nearly perfect platinum crystals. We have recently obtained one such platinum–carbon LSM and have been able to follow (although ex-situ) an electrochemical transformation.

The system that we have studied involves the adsorption of a layer of iodide onto the platinum surface, followed by the electrodeposition of a layer of copper.

The adsorption of iodide and iodine onto platinum surfaces has been the subject of many electrochemical investigations.[10-13] Both iodine and iodide adsorb strongly to the platinum surface and if the adsorption is carried out from dilute solutions, a monolayer coverage is obtained. This has been documented from radiotracer, LEED, and electrochemical investigations. One of the advantages of adsorbing iodine or iodide on the platinum electrode is that it serves to protect the surface from contamination by organic materials. More importantly, it has been reported by Hubbard and co-workers[14-16] that on such a protected platinum surface,

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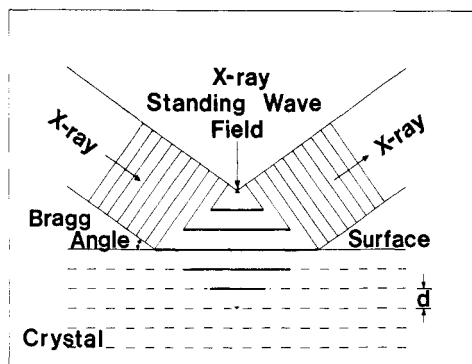§ School of Applied and Engineering Physics.

Figure 1. Illustration of the X-ray standing wave field formed by the interference between the incident and Bragg diffracted beams.
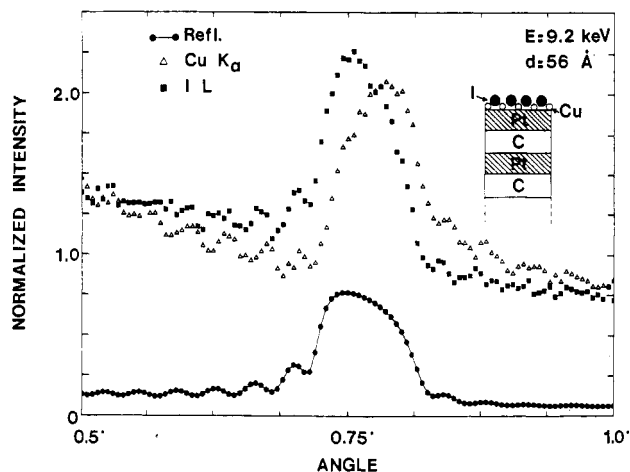

Figure 2. Experimental data vs. Bragg reflection angle for the reflectivity (●–●), iodine L fluorescence (■), and copper Kα fluorescence (○) from a Pt/C LSM covered with an electrodeposited layer of copper and an adsorbed layer of iodide. Incident X-ray energy was 9.2 keV.

Figure 3. Theoretical curves for the angular dependence of the fluorescence yield from an atom on the surface (A) and at 5 (B) and 10 (C) Å above the surface of an LSM with a d spacing of 56 Å.

Figure 4. Cu Kα fluorescence (△) from the Pt/C LSM covered with a layer of copper and a layer of iodide ions and a simulated yield (—) from a randomly distributed copper layer.

metal ions such as copper and silver can be electrodeposited and that the deposition takes place on top of the platinum surface, thus causing a displacement of the adsorbed iodine or iodide layer. We decided to study the copper deposition on an iodide-covered platinum surface with the X-ray standing wave technique since it should be able to show the change in distance of the iodide layer from the surface of the platinum. One of the advantages of using iodide is that it has a very high quantum efficiency for fluorescence and we have previously demonstrated that fluorescence from a monolayer of iodine can be easily detected.

The LSM samples were generously supplied by T. W. Barbee (Lawrence Livermore Laboratory) and each consisted of 15 platinum–carbon layer pairs. The thickness of the platinum and carbon layers were 26 and 30 Å, respectively ($d = 56$ Å). These were grown on a flat silicon 111 single-crystal substrate. 9.2-keV radiation from the Cornell High Energy Synchrotron Source (CHESS) was used to excite L-level and K-level fluorescence from the iodide and copper, respectively. Fluorescence intensities were monitored with a solid-state lithium-drifted silicon detector (Si(Li)). The incident and reflected intensities used to obtain reflectivity curves were measured with gas-filled ion chambers. Higher-order harmonics from the sagitally focused Si(111) monochromator were eliminated by placing a platinum mirror between the monochromator and the LSM.

Initially, the LSM was contacted with an aqueous 35 mM solution of sodium iodide for 15 min. It was rinsed with water and studied by the X-ray standing wave technique. A well-defined I_L fluorescence could be detected and its angular dependence was indicative of the fact that the layer was on top of the platinum
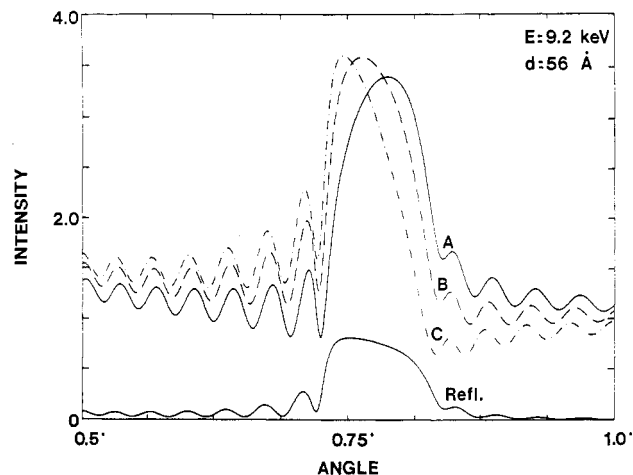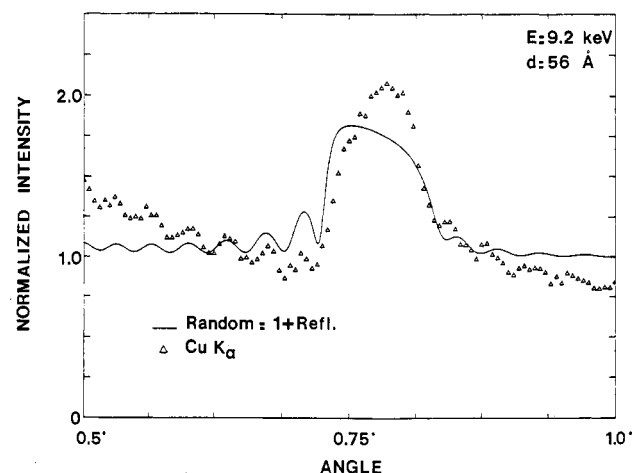
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surface layer. Well-developed reflectivity curves were also obtained. Following this, the LSM was placed in an electrochemical cell and half a monolayer of copper was electrodeposited.

The LSM (now with half a monolayer of copper and a monolayer of iodide; each layer containing ca. 6×10^{14} atoms/cm^2) was again analyzed via the X-ray standing wave technique. Since the incident X-ray energy (9.2 keV) was capable of exciting fluorescence from both the iodide and the copper, the fluorescence intensity of both elements (as well as the reflectivity curve) were obtained simultaneously. The results, presented in Figure 2, show the reflectivity curve and the modulation of the iodine and copper fluorescence intensities. The most important feature of this figure is the noticeable phase difference between the iodine and copper modulations, i.e. the location of the iodine and copper fluorescence maxima relative to the peak of the Bragg reflectivity curve, with the copper maximum being to the right and the iodine maximum being to the left of the peak, respectively. Since the antinode moves inward as the angle increases, the order in which these maxima occur can be unambiguously interpreted as meaning that the copper layer is closer than the iodide layer to the surface of the platinum. Since the iodide had been previously deposited on the platinum, this represents unequivocal evidence of the displacement of the iodide by the electrodeposited copper. Figure 3 represents a theoretical calculation of the fluorescence modulation from an adsorbate at positions 0, 5, and 10 Å above the surface of an LSM of similar dimensions to the one used in our experiments and the same trend is observed. Figure 4 shows a comparison of the experimental Cu Kα fluorescence intensity with a simulation for the expected fluorescence intensity if the layer had been randomly distributed. The large discrepancies are indicative of a relatively

well ordered and coherent copper layer.

It is clear that the X-ray standing wave technique is ideally suited for following the course of electrochemical processes involving the deposition of metallic layers and we are currently involved in the in-situ study of the deposition of layers of copper, silver, and lead. By measuring the phase and amplitude of the modulation of the iodine fluorescence intensity we will be able to characterize the thickness and uniformity of the underlying deposit.

In addition, by combining surface EXAFS with the X-ray standing wave information, we hope to further elucidate (in-situ) the three-dimensional structure of electrodeposited layers.

Photochemical Hole Burning and Strong Electron–Phonon Coupling: Primary Donor States of Reaction Centers of Photosynthetic Bacteria

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A theory for photochemical hole burning valid for arbitrarily strong linear electron–phonon coupling is developed and applied to the P-870 and P-960 states of *Rh. sphaeroides* and *viridis*. The mechanism responsible for the unusually large hole widths of these states is established.

Very recently, transient photochemical hole burning (PHB) has been reported for the P-870[1,2] and P-960[3] absorption bands of the primary electron donor states of isolated reaction centers of *Rhodopseudomonas sphaeroides* and *viridis*, respectively. These states correspond to the lowest excited singlet state (Q_y) of the special bacteriochlorophyll (Bchl) pair. Time domain studies had previously shown that electron transfer from the special pair to a bacteriopheophytin occurs in about 2 and 5 ps for *Rh. sphaeroides* and *Rh. viridis*, respectively, at cryogenic temperatures.[4,5] These decays correspond to homogeneous line broadenings of 2.5 and 1 cm^{-1}.

By contrast, the PHB experiments yielded hole widths at $T \sim$ 1.5 K equal to $\sim$400 cm^{-1}, a significant fraction of the absorption line widths for P-870 and P-960. Given the current interest in the rate of the initial charge separation process of photosynthesis[4,6–10] and the electronic structures of P-870 and P-960,[11] the

question of whether or not the hole widths represent homogeneous broadening is very important. Meech et al.[2] interpreted the hole width of P-870 in terms of an ultrafast (25 fs) *dynamical* charge separation process within the special pair prior to electron transfer to the bacteriopheophytin. The same interpretation was offered by Boxer et al.[1,3] who also mentioned the possibility that the hole is inhomogeneously broadened due to strong electron–phonon coupling. However, the question of which interpretation is correct was left open and no quantitative theoretical discussion was presented.

The purpose of this Letter is twofold: to present the key results of a new theory for PHB valid for arbitrarily strong linear electron–phonon coupling; and to demonstrate with this theory that the aforementioned holes are essentially what one would expect on the basis of the absorption and fluorescence spectra of the primary donor states. That is, the holes are *inhomogeneously broadened*. The relationship between these spectra and the hole profiles was not considered in ref 1–3. An important point is that for both P-870 and P-960 the Stokes shift (between absorption and fluorescence maxima) is large, $\sim$500 cm^{-1}.[12,13] For *Rh. viridis* the T dependence of the absorption and fluorescence line widths and Stokes shift have been studied between 2 and 300 K.[12] The Stokes shift is weakly dependent on temperature while the absorption and fluorescence maxima undergo comparable red shifts with decreasing T. Although less complete, the data for P-870 show similar behavior.[13] A method of moments analysis (based on strong linear electron–phonon coupling) of the P-960 line widths, which exhibit a $T^{1/2}$ dependence, revealed that the Huang–Rhys factor (S) is very large, $\sim$8.[12] Furthermore, the average phonon frequency associated with this factor is $\sim$30 cm^{-1}. In this Letter we use these facts as a guide to interpret the hole burning data for *Rh. sphaeroides* since the S/N for these data is higher than for *Rh. viridis*. The reaction center pigment

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