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OXIDATION-REDUCTION INDUCED ROUGHENING OF PLATINUM (111)
SURFACE*

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Oxidation-Reduction Induced Roughening of Platinum (111) Surface

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Platinum (111) single crystal surface was roughened by repeated cycles of oxidation and reduction to study dynamic evolution of surface roughening. The interface roughens progressively upon repeated cycles. The measured width of the interface was fit to an assumed pow law, $W \sim t^\beta$, with $\beta = 0.38(1)$. The results are compared with a simulation based on a random growth model. The fraction of the singly stepped surface apparently saturates to 0.25 monolayer, which explains the apparent saturation to a steady state roughness observed in previous studies.

I. INTRODUCTION

In recent years the application of x-ray scattering technique to *in-situ* examination of electrochemical interface has become increasingly more popular. A variety of subjects in electrochemistry are under investigation by several groups. Studies of gold surfaces have shown substantial details of electrochemically induced surface reconstruction [1]. Studies of underpotential depositions on epitaxially grown samples [2] have shown that the underpotential deposited films indeed form a two-dimensional lattice that exhibits rich phases. Studies of passive oxide film formation have shown that the well known features in the cyclic voltammogram of copper electrode interfaces are well explained by the evolution of the film thickness and the roughness of the interface [3].

Among the mentioned subjects, the oxidation phenomena at electrochemical interfaces have been a focus of our investigations because of their fundamental importance to microscopic understanding of surface reactions. While the characterization of relatively thick (many atomic layers) oxide films is important both for science and technology, the most fundamental understanding of the oxide film growth requires an examination at the submonolayer level, i.e., at the incipient stages of the process. For these investigations, we have chosen the single crystal platinum (111) surface for two reasons; i) Pt(111) surface is among the most extensively studied due to its importance to corrosion science and electrocatalysis; ii) there is no known reconstruction of the Pt(111) surface in electrochemistry, which simplifies the investigation.

In one series of experiments, it was found that there is a critical oxidation charge transfer amount at which surface roughening begins to occur. For a smaller oxidation charge transfer an oxidation-reduction cycle recovers the original flat surface, while one with a larger oxidation charge transfer leaves the surface roughened. The critical charge transfer amount was approximately $1.6 e^-/\text{Pt}$. It was also found that the structure of the oxidized surface is consistent with the long-suggested place-exchange

mechanism. A detailed report on the observation of the place-exchange mechanism will be given elsewhere [4].

In this article we will discuss oxide-induced roughening of the Pt(111) surface. The Pt(111) surface roughened by an oxidation-reduction cycle has typically no in-plane long range order and the surface roughness involves only the top layer as schematically shown in Fig. 1 for illustration. The motivation for this study is two-fold. Since voltammetry (a standard experimental tool in electrochemistry) involves repeated cycles of oxidation and reduction, it is important to perform structural investigations in a similar manner. On the other hand, the oxidation induced roughening can be considered as an interface growth problem. In the theory of interface growth, the width of the interface should follow the scaling law [5]

$$W(L, t) \sim L^\chi f(t/L^\chi) \quad (1)$$

with a finite-size scaling exponent, χ , and a dynamic scaling exponent, χ/β , for a system of size L at time t . According to this scaling law, the measured interface width should grow with a power of β to time, or in our situation to the number of oxidation-reduction cycles or charge transfer amount. Our x-ray reflectivity measurements involving repeated oxidation-reduction cycles will

FIG. 1. A schematic picture of the Pt(111) surface roughened by an oxidation-reduction cycle.

FIG. 2. (0 0 L) and (1 0 L) scans of an initially clean Pt(111) surface at 0.4 V from hydrogen evolution. An hcp indexing of the reciprocal lattice for an fcc structure is schematically shown as an inset.

be discussed with respect to the dynamic scaling law.

II. EXPERIMENTAL

The sample preparation procedure will be described in detail elsewhere [4], hence, only a brief summary will be given here. Single crystal samples of platinum were pre-cut to expose a rectangular Pt(111) surface with an area of $3 \times 10 \text{ mm}^2$, mechanically polished, and annealed in a high-vacuum furnace to $\sim 1800 \text{ K}$ in advance. The measured mosaic width of the sample used in this study was ~ 0.1 degree and the surface miscut was smaller than 0.05 degree. X-ray reflectivity measurements were carried out in a transmission geometry [3] with $\lambda = 0.9682 \text{ \AA}$ at the X10B bending magnet beamline, National Synchrotron Light Source (NSLS). The longitudinal instrumental resolution was $\sim 3 \times 10^{-3} \text{ \AA}^{-1}$. The x-ray reflectivity measurements were performed in a spill-over geometry and the data were corrected using the x-ray beam spot profile for data analysis. For convenience, we use a hexagonal unit cell [6] to index the reciprocal lattice during experiments and data analysis. An fcc structure in the hcp unit cell is a stack of triangular lattices starting from the top layer along the $(00\bar{1})_{\text{hcp}}$ direction which has an ABCABC... sequence. The indexing of the reciprocal lattice and the direction of the rods are shown in the inset of Fig. 2.

Just prior to an experiment, the samples were reannealed to $\sim 1200 \text{ K}$ in a hydrogen flame, immediately exposed to I_2 vapor [7], and then placed in a specially designed electrochemical cell for transmission measurements [8]. The measurements were performed in an acidic solution (0.1 M HClO_4) with Ag/AgCl (3 M KCl) as the reference electrode. (The chemisorbed iodine was first removed in a NaOH solution to obtain a clean surface.) Potentials measured against the reference electrode will

be reported here with respect to that of the hydrogen evolution (HE) potential.

III. BACKGROUND

A. X-ray reflectivity

In this section a brief review of x-ray reflectivity from a single crystal will be given. From the well known Fresnel equation for scattering of an electromagnetic plane wave at an interface of two media, one can find a simple form of the reflection amplitude that applies to the x-ray regime [9],

$$R(Q) \approx \left(\frac{Q_c}{2Q_\perp} \right)^2 \quad (2)$$

for $Q_\perp \gg Q_c$, where Q_c is the critical momentum transfer. The critical momentum transfer can be found using Snell's law as $Q_c = 0.029 \sqrt{\rho Z/A}$. Then the reflectivity from a general form of interface can be written with a step function $\Theta[g(\vec{r})]$, where $g(\vec{r}) = 0$ defines the surface.

$$R(Q) = \frac{i0.029^2 \rho Z/A}{4Q_\perp} \int e^{i\vec{Q} \cdot \vec{r}} \Theta[g(\vec{r})] d\vec{r} \quad (3)$$

This expression is mathematically equivalent to the surface integral of Sinha et al. [10].

For a single crystal case the same equation should be applied for each Fourier component of the Bloch wave expansion [9] and summed over all the reciprocal lattice points.

$$R(\vec{Q}) = \frac{i0.029^2 \rho/A}{4Q_\perp} \sum_{\vec{G}} S_{\vec{G}} \int e^{i(\vec{Q}-\vec{G}) \cdot \vec{r}} \Theta_{\vec{G}}[g(\vec{r})] d\vec{r} \quad (4)$$

where $\Theta_{\vec{G}}$ is a step-like function for each Fourier component which may not necessarily be an abrupt step function for a non-ideal surface. When the surface is parallel to a crystallographic plane, reflections from the aligned reciprocal lattice points interfere and signify quite directly the interfacial structure of the sample as previously pointed out [11,12]. In this case, the reflectivity can be written as a simple one dimensional sum of the scattering from each plane.

$$R(\vec{Q}) = \frac{i0.029^2 \rho/A}{4Q_\perp} \sum_{\vec{G}_\parallel} \delta(\vec{Q}_\parallel - \vec{G}_\parallel) \times \sum_{n=0} V_n(Q) e^{i(Q_\perp + \vec{Q}_\parallel \cdot \vec{r}_\perp + \vec{Q}_\parallel \cdot \vec{r}_\parallel)} \quad (5)$$

where $V_n(Q)$ is the scattering factor of the n^{th} layer, including the Debye-Waller effect, and $\vec{Q}_\perp$, $\vec{Q}_\parallel$, $\vec{r}_\perp$, $\vec{r}_\parallel$ are perpendicular and parallel components of $\vec{Q}$ and $\vec{r}$, respectively. Finally, the integrated intensity over the

open detector slits that we measure can be obtained by a surface integral over a small surface area defined by the detector slits, $\Delta\vec{Q}_{\parallel}$ as

$$I(\vec{Q}) = A(\vec{Q}) \int_{S=\Delta\vec{Q}_{\parallel}} d\vec{Q} \left| R(\vec{Q}) \right|^2 \quad (6)$$

where $A(\vec{Q})$ is a geometric factor dependent on polarization and the cross section of the beam profile and the sample.

B. Surface scattering in an occupational disorder limit

In this section we will consider surface x-ray scattering factor in a limit where the positions of atoms in the lattice do not change but occupancy of a lattice site is either 1 or 0. This limit is obviously a very simple picture of surface roughness. However, the surface scattering factor can be isolated as is done for the form factor and the data analysis becomes remarkably simple. The data analysis will require fitting only the surface scattering factor. Equation (4) can be rewritten so that the surface integral term can be taken out of the summation over $\vec{G}_{\perp}$. The position, vector $\vec{r}$ on the surface, is commensurable with the bulk lattice spacing in this limit and $e^{i\vec{G}_{\perp} \cdot \vec{r}}$ is always 1. Now the reflection amplitude becomes [9]

$$\begin{aligned} R(\vec{Q}) &= \frac{0.029^2 \rho / A}{4Q_{\perp}} \sum_{\vec{G}} \frac{S_{\vec{G}}}{\vec{Q}_{\perp} - \vec{G}_{\perp}} \int_S e^{i(\vec{Q} - \vec{G}) \cdot \vec{r}} d\vec{S}_{\perp} \\ &= \sum_{\vec{G}_{\perp}} R_S(\vec{Q}) \left[\frac{0.029^2 \rho / A}{4Q_{\perp}} \sum_{\vec{G}_{\perp}} \frac{S_{\vec{G}}}{\vec{Q}_{\perp} - \vec{G}_{\perp}} \right] \end{aligned} \quad (7)$$

where $R_S(\vec{Q}) = \int_S e^{i\vec{Q} \cdot \vec{r}} d\vec{S}_{\perp}$. The term in the square bracket is the rod amplitude for an ideally terminated surface. Then the surface scattering term can be rewritten as a sum of the coverage at each height with the corresponding phase factor over all allowed heights as follows:

$$I'(\vec{Q}_{\perp}) \Big|_{\vec{Q}_{\parallel} = \vec{G}_{\parallel}} = |R_S|^2 \left| \sum_{i=-N}^N \theta_i e^{i(Q_{\perp} c + \vec{Q}_{\parallel} \cdot \vec{r}_{i-\mathbf{1}})} \right|^2 \quad (8)$$

where c is the interlayer spacing, N is the number of allowed step heights measured from the original surface height, $2N+1$ is the total number of layers involved, θ_i is the coverage at the i^{th} step height, and $\sum_{i=-N}^N \theta_i = 1$, by definition. For an ideally terminated surface, $I'(\vec{Q}_{\perp}) = 1$ along the delta function as expected. Now the measured reflectivity data can be analyzed with Eq. (8) after it is divided by the theoretical reflectivity for an ideally terminated surface.

Since there is no a prior knowledge of the distribution function for θ_i , we will assume a Gaussian distribution function, $\theta_i = e^{-\frac{(i-z_0)^2}{2\sigma^2}} / C$ with $C = \sum_k e^{-\frac{(k-z_0)^2}{2\sigma^2}}$. Here z_0 and σ are the center of the distribution and width of the distribution, respectively, measured in the unit of interlayer spacing. We will further assume that the distribution is symmetric about the height zero, i.e., $z_0 = 0$ for simplicity. Then the surface scattering intensity becomes

$$I'_{\text{Gauss}}(\vec{Q}_{\perp}) \Big|_{\vec{Q}_{\parallel} = \vec{G}_{\parallel}} = \left| \frac{1}{C} \sum_n e^{-\frac{n^2}{2\sigma^2} + i(nQ_{\perp} c + \vec{Q}_{\parallel} \cdot \vec{r}_{n-\mathbf{1}})} \right|^2 \quad (9)$$

Since the width of the distribution may have an intrinsic roughness due to the sample preparation, the width σ has two components; the intrinsic roughness σ_0 and the cycle-dependent roughness $W(t)$.

The scaling law given by Eq. (1) can be rewritten as $W^2(t) \sim t^{2\beta}$ for a limit where $t^{\beta} \ll r^{\kappa}$. This limit can be satisfied when the power-law fraction of the height-height distribution function is small compared to the x-ray coherence area [13]. Since the width of the surface after roughening by several cycles is still much smaller than the x-ray coherence length, this limit should be satisfied for our experimental conditions.

Then the width σ should be written for an interface growing with a rate of a as,

$$\sigma^2 = \sigma_0^2 + at^{2\beta} \quad (10)$$

Equations (9) and (10) can be used to fit the measured normalized x-ray reflectivity.

IV. RESULTS AND DISCUSSIONS

A. Clean initial surface

Once the cell was filled with the 0.1 M HClO_4 solution, the potential was held at 0.4 V, a reducing potential where no surface reaction is expected. At this potential, (0 0 L) and (1 0 L) rod intensities, shown in Fig. 2, were measured. The solid lines are the fit to the data using Eq. (5) and allowing the top layer density and the spacing to vary. Remarkably the (0 0 L) rod, sensitive only to the electron density perpendicular to the surface, is nearly that of an ideally terminated surface, indicating that an average step spacing is $\gtrsim 1000\text{\AA}$. Nevertheless, the best fit was obtained for a top layer density of 1.04(4) and a spacing of 1.05(3). However, the (1 0 L) rod, which is sensitive to the ABC stacking sequence, is significantly different from that of an ideally terminated surface (dashed line). The best fit (solid line) to the (1 0 L) rod is obtained for a top layer A stacking density of 0.85(5), C stacking density of 0.05(5), and spacing of 1.03(5). This means that the initial surface is nearly ideally terminated in the surface normal direction but

about 15 % of the top layer is displaced from the A site, violating the ABC stacking sequence. We attribute the origin of the in-plane disorder to our HV annealing procedure, in which the reconstructed surface [6] might have been kinetically locked, and/or to our iodine procedure, in which adsorption and desorption of iodine might have partially disordered the surface. This initial clean surface is reproducible within counting statistics almost without exception using our sample preparation procedure.

B. Rough surfaces and dynamic scaling

We will begin by making a comparison between our cyclic measurements of interface roughness and the interface growth problem. In the case of interface growth, a continuous stream of incoming particles arrives at the interface and the height of the interface increases linearly in time. Meanwhile, the shape of the interface continuously evolves and the effective width of the interface should grow in time. In this situation we can apply a Galilean transformation in which the interface is examined under a moving frame of reference with the velocity of interface growth. Since the underlying physics is invariant under this transformation, it is commonly used in most theoretical and computational studies where only the interface itself is of interest. In this moving frame of reference, the interface is initially flat with one step at height zero; becomes rough within two step heights during submonolayer deposition with some sites down and some sites up from the height zero; becomes rough within three steps with some sites down and some sites up from height zero during, near, or after a monolayer deposition; and so on. This situation is very similar to our cyclic oxidation-reduction roughening. The only difference is that the number of step heights involved in the interface roughness goes 1, 2, 3, ... in the interface growth case, while it takes only odd numbers (i.e. 1, 3, 5, ...) because the oxidation-reduction roughening of the surface is a mass-conserving process. The mass conservation results from the fact that the solubility of platinum in our solution is extremely small, therefore, the platinum atoms lifted from one place in the surface tend to remain elsewhere on the surface. We speculate that this difference may affect the rate of roughening (the coefficient of the power-law behavior) but will not likely change the nature of the interface growth and the exponent β . While we have no solid theoretical justification for this speculation, we will assume a power-law evolution of the interface width in our cyclic roughening measurements and show indeed that the data is consistent with this assumption.

Another difference is that the interface growth is a continuous process while our cyclic measurement is a discrete process. Nevertheless, in the slow deposition limit, where the time required to deposit a monolayer is sufficiently larger than the time required to complete the diffusion of particles on the surface, the deposition rate itself be-

comes unimportant. In this condition the only relevant parameter is the total amount of deposition, as long as the condition is maintained at all times. Therefore, a type of measurement that requires a long measurement time can be meaningfully applied to the growth dynamics problem by halting or significantly slowing down the deposition during the measurements [13]. Our cyclic measurements are done in a manner that the deposition halts and allows us to reduce the surface and take x-ray reflectivity measurements.

The cyclic x-ray reflectivity measurements were performed in the following manner. First the measurements of the reflectivity were made at a reducing potential of 0.4 V (vs HE) for a clean, ordered, as-prepared surface. Then the potential was raised to 1.4 V, kept at this potential for 15 minutes to allow a charge transfer of approximately $3 e^-/\text{Pt}$, reduced down to 0.0 V, and raised back to 0.4 V for another set of x-ray reflectivity scans. The potential scan rate was 10 mV/sec. This process was repeated several times. The measured (0 0 L) and (1 0 L) rod intensities were normalized against that of an ideally terminated surface to isolate the surface scattering contribution. Then the normalized reflectivity data were fit with Eq. (9) using the Gaussian model. It was assumed that the height with largest coverage (θ_{max}) is at the center of the distribution so that the distribution is symmetric about the height zero. The only variable in the fit was the width of the distribution, σ . The normalized reflectivity and the fits to the data for the (0 0 L) and (1 0 L) rods are shown in Fig. 3 (a) and (b), respectively. The top most data set in Fig. 3 (a) and (b) is from the clean initial surface, the data set second from the top is obtained after two cycles, the next down after three cycles, and so forth. (The data set after the first cycle is not available due to an experimental error.) (0 0 L) rod data are available up to the ninth cycle and (1 0 L) rod data are available up to the eighth cycle. The solid lines are the fit to the data using the Gaussian interface model given by Eq. (9). As seen in Fig. 3 (a) and (b), the top most normalized reflectivity for (0 0 L) is a straight line showing that the surface is nearly ideally flat but the deviation of the (1 0 L) normalized reflectivity from a straight line indicates imperfect registry of the top most layer with respect to the stacking sequence.

From a microscopic point of view, an oxidation-reduction cycle simply lifts some fraction of the surface atoms exposed to the solution and puts them on top of the nearby surface atoms. In reality this process involves surface diffusion of atoms, which results in formation of clusters or islands or preferential growth at the step edges. While theoretical studies for this type of experimental situations are needed, we will consider the simplest possible situation where the lifted atoms can be relocated anywhere on the surface in a random manner and no surface diffusion is allowed afterwards. This situation can easily be simulated with a random number generator in a computer and the result for θ_n is shown in Fig. 4. All the sites are at a step height of zero in the beginning,

FIG. 3. A series of normalized reflectivity scans along (0 0 L) and (1 0 L) measured for repeated oxidation-reduction cycles. The solid lines are fit to the data.

FIG. 4. The evolution of height distribution by the number of simulated cycles. A 200×200 lattice was used in the computation.

approximately 10% of the sites are at height +1 or -1 step levels after one cycle, some sites are at height +2 and -2 after two cycles, and so forth. The width continues to broaden as shown in the Fig. 4. Only selected cycles are shown in the figure for clarity. From this simulation we calculated the width of the distribution and found that the width increased as $W \sim t^\beta$ with $\beta = 0.50(1)$. This is not surprising because the situation is identical to the shot noise case except that a pair of events occur simultaneously (one increases the surface height and the other decreases). Since the shot noise follows Poisson statis-

tics and the width is naturally proportional to $\sqrt{M}$ for M number of events, $\beta = 0.5$ for the random deposition model used our simulation.

The widths, $W(t)$'s, of the interface obtained for each cycle from the fit are shown on a log-log scale in Fig. 5. The widths for (1 0 L) were obtained by subtracting σ_0 using Eq. (10). The width from the simulation of the random model ($\square$), the fit value from the (0 0 L) rod ($\circ$), and the fit value from the (1 0 L) rod ($\bullet$) are shown with the power-law fits (solid lines). The values of β are 0.38(1) and 0.39(2) for (0 0 L) and (1 0 L), respectively. Although a direct relation to the computer simulations in 2+1 dimensions is not clear, a predicted value of 0.25 based on a 2+1 dimensional growth model such as the restricted solid-on-solid model [14], is also shown as a dashed line for comparison.

A final remark needs to be made about our experiments and simulation: the coverage at the single-step height ($i = +1$ and -1) apparently shows a maximum value of 0.25 after a number of cycles corresponding to approximately a full monolayer growth. Also, the smaller the β value, the broader the maximum. Therefore, it appears that the coverage for the single-stepped height grows initially but saturates to 0.25 after many cycles. Furthermore, the coverage of the double-stepped heights is very small (a few percent) and grows slowly over many cycles. These facts explain the satisfactory fit of our data by a three-step model [15] even for the normalized reflectivity obtained after several repeated oxidation-reduction cycles. It also explains scanning tunnelling microscopy observations of saturation, i.e., that the steady state after many oxidation-reduction cycles involves only three

FIG. 5. The width of the roughened interface vs. number of oxidation and reduction cycles on log-log scales.

step heights in the STM images. [16].

V. CONCLUSION

We suggest that the dynamic scaling behavior proposed for interface growth models is applicable to cyclic oxidation-reduction roughening of a platinum (111) single crystal surface. The exponent β found in our study is 0.38(1) which is smaller than a random growth model but larger than the results from most computational studies based on a 2+1 dimensional growth model. A theoretical model that more closely resembles the experimental situation is needed to explain the observed exponent. A more detailed study of cyclic roughening is in progress. Since a typical experimental study in interfacial electrochemistry involves cyclic voltammetry, *in situ* structural studies such as this study and theoretical studies performed in parallel with electrochemical measurements are essential to the development of a deeper understanding of electrochemical interfaces.

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