Dynamics of the Au (001) surface in electrolytes: In situ coherent x-ray scattering

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We studied the dynamics of the Au (001) surface in 0.1 M HClO₄ electrolyte solution using coherent surface x-ray scattering (CSXS). We find that edges of steps and islands on the Au (001) surface are highly dynamic in electrolyte and evolve continuously even at room temperature. The evolving speed increases nearly two orders of magnitude when the quasihexagonal reconstruction is lifted during slow potential sweep and is higher by more than four orders of magnitude than the speed measured previously in vacuum. In addition, we find that surface lattice dynamics appear when the reconstruction is lifted, and they are faster by two orders of magnitudes than the edge dynamics. Complementary scanning tunneling microscopy images are also presented for visual confirmation of the changes measured by the CSXS technique.

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I. INTRODUCTION

Elucidation of the structure and stability of metal surfaces in contact with electrolyte is essential to understanding many fundamental and industrial processes, such as adsorption of ions and molecules, electrocatalysis, corrosion prevention, and electrodeposition/electroplating. Since the early 1990s, new techniques to study interfaces in electrolytes have emerged. *In situ* surface-sensitive tools, most prominently synchrotron surface x-ray scattering (SXS),^{1–3} infrared/Raman spectroscopy,⁴ and electrochemical scanning tunneling microscopy (ECSTM),² have opened new routes leading to deeper understanding of the atomistic processes at the metal-electrolyte interfaces. These techniques have helped to build *in situ* surface electrochemistry into a discipline beyond traditional ultra-high vacuum transfer electrochemical surface science.

More recently, interest into the dynamics of interfaces has increased, and a new time-resolved surface x-ray technique has been developed.⁵ The dynamics of electrochemical interfaces have been studied with surface x-ray scattering on timescales down to 10^{-3} sec. While this incoherent surface x-ray scattering can achieve high time resolution, we took an approach using coherent x rays to study the electrochemical interfaces in order to examine the slow equilibrium dynamics to which incoherent x rays are not sensitive. Coherent x-ray scattering differs from ordinary x-ray diffraction in its high sensitivity to the structural and temporal details. Therefore, coherent surface x-ray scattering (CSXS)⁶ is sensitive to structural and temporal details of surfaces. The coherent fraction of x rays is typically small, and that of diffracted x rays from surfaces is even less. As such, an ensemble sum is necessary to improve counting statistics. In situ scattering further reduces the coherent x-ray intensity due to absorption through the both the electrolyte solution layer and the thin film membrane that encloses the system.⁷ Although all these reducing factors tend to wash out the details, CSXS is sensitive to the time evolution of the surface structure and can provide information on the evolution of surface structures.

Using CSXS, we studied the Au (001) surface in electrolyte while maintaining an applied potential. Au is a natural choice because the low-index surfaces are relatively easily prepared and transferred in a clean manner into an electrochemical cell, while also offering a rich variety of surface phases.⁸ Additionally, Au surfaces exhibit relatively robust stability in the electrolyte within a limited potential range. The principal facets of Au reconstruct themselves9 in a wide variety of conditions. These reconstructed phases that occur in electrochemical environments and their corresponding transformations have been studied by traditional electrochemical techniques such as voltammetry¹⁰ alone or coupled with modern *in situ* techniques such as SXS¹¹ and scanning tunneling microscopy (STM).¹² In particular, the Au (001) surface reconstructs into the hexagonal phase, which is stable over a large potential range. Theoretically, the relative energetics of the static surface structures are understood within the framework of density functional theory,¹³ with the electric field at high potential leading to larger buckling and the eventual lifting of the reconstruction.

However, the dynamics of the transition are less well understood. When the well-annealed denser "hex" phase transforms into the square (1×1) phase, the excess atoms are ejected in the topmost layer and form scattered islands. In the subsequent cycles, the large hex domains do not recover, resulting in morphology of scattered islands on step terraces. Nevertheless, the islands still reconstruct and de-reconstruct depending on the applied potential. Our study here will primarily focus on the motion of islands and step edges. The dynamics of the edges are measured by the comparing CSXS patterns collected at different times. For additional confirmation of the time evolution of the edges, we also present in situ ECSTM images. Our x-ray measurements focus on whether the edges evolve in time, if the changes depend on potential, and subsequently the rate of evolution. As we will show, the edge dynamics are much faster in electrolyte than in vacuum. They are also very sensitive to the surface structures and the applied potentials. Additionally, for the potential range where the hex reconstruction is lifted, we find a second, faster

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time constant. We will show how the faster evolution, while not consistent with the dynamics of step or island edges, is consistent with the dynamics of surface lattices. We will also discuss the activation energies of the edge dynamics in electrolyte and in vacuum and the microscopic origin of the lattice dynamics.

II. EXPERIMENTAL METHODS

To obtain well-prepared, consistent facet surfaces for the experiments, 6 mm gold crystals from Matek GmbH were mounted in a goniometer, oriented to the desired direction by x-ray diffraction, and cast in epoxy resin. The crystals were then mechanically polished using sandpaper ranging from 600 to 4000 grit, followed by polishing with 1 μ m, 0.3 μ m, and 0.05 μ m alumina suspensions. Single crystal surfaces prepared in this way have a miscut typically less than 0.2° . The crystals were then bulk annealed using a radio frequency (RF) induction heater set up at $\sim 900 \,^{\circ}$ C for 24 hours in a quartz tube under flow of argon/hydrogen (3% hydrogen, high purity) and typically showed $\sim 0.10^{\circ}$ to 0.15° mosaic spread at the (002) reflection when checked with an x-ray diffractometer. Subsequent surface annealing was performed in the same RF heating assembly for 15 minutes at 900 °C in argon/hydrogen flow. After the crystal had cooled, a droplet of Millipore filtered ultrapure water (18 M Ω cm⁻¹) was then placed on the gold surface while still in the argon/hydrogen flow to protect the surface from ambient contamination during transfer.

The crystal was mounted in an x-ray cell⁷ or ECSTM cell for subsequent experiments. Platinum counter electrodes were used in both cells. All electrolyte solutions were prepared from J. T. Baker Ultrex II reagents and 18 M Ω cm⁻¹ water purified by a Milli-Q reagent water system. STM images were acquired using a DI ECSTM system controlled by a Nanoscope IIIa station interfaced with a computer. ECSTM measurements were performed in a homemade Kel- $F^{\mathbb{R}}$ cell with a Kalrez^{\mathbb{R}} O-ring pressed against the working electrode surface to seal the cell. Pt-Ir STM tips were insulated with nail varnish and left to dry overnight prior to use.¹⁴ A homemade Ag/AgCl reference electrode was used for the ECSTM experiments. For x-ray measurements, a low-leakage Ag/AgCl (KCl sat.) reference electrode from Bioanalytical Systems Inc. was used. Synchrotron SXS experiments were performed in a standard reflection cell⁷ made from Kel-F[®] in 0.1 M perchloric acid. All potentials in the text are stated with respect to this reference electrode. The gold crystal was mounted in the x-ray cell with a taut thin polypropylene film following established procedures,¹⁵ which ensured the crystal surface remained free of contaminants. This included placing the entire assembled cell in an enclosure purged with ultrahigh-purity nitrogen gas to remove traces of oxygen from the thin-layer electrolyte cell and to protect the system from contamination during the experimental run.

The coherent x-ray surface scattering experiments were performed at the Advanced Photon Source at beamline 8ID on three consecutive occasions. A single bounce Si (111) monochromator was used to set the photon energy to 7.36 keV. Precision slits were placed in front of the sample and narrowed to $10 \times 10 \ \mu m^2$ to achieve the desired transverse coherence. With the slits narrowed, incident flux on the sample was

 $\sim 10^9$ photons/sec. This is a small fraction, $\sim 10^{-5}-10^{-6}$, of the incident monochromatic beam typically used for ordinary SXS measurements. The observed potential shift by radiolysis effect¹⁶ was negligible. The experiments were performed in reflection geometry, and the detector counts were $\sim 10^2$ photons/sec at the anti-Bragg condition ($\theta \approx 12^\circ$), the point of the weakest intensity but most surface-sensitive position. The electrolyte-polypropylene interface presents almost no change in electron density, and hence no x-ray reflectivity signal. The polypropylene-air interface, with an RMS roughness of ~ 20 nm,¹⁷ will contribute negligibly to the scattering signal at L = 0.17 when compared against the relatively smooth and high-Z Au surface.

III. RESULTS AND DISCUSSION

A. Scanning tunneling microscopy results

Unlike an Au (001) surface in vacuum, even when we begin with a well-annealed surface, the hex reconstruction in electrochemical solution tends to remain in patches and islands after several potential cycles due to the lack of thermal annealing that can restore the long-range reconstruction. Examples of such topographic (not atomic) images are shown in Fig. 1 at three different potentials obtained after several cycles to ~ 1 V. The islands appear much more coarsened when the reconstruction is lifted at 400 mV, while they appear as smaller patches at 0 mV. The coarsening is consistent with the island expansion associated with the hex-to-(1 × 1) transition. Since the density decreases, the occupied area of the islands will have to expand to accommodate the transition.

For applied potentials of 300 mV and below, the shapes of the islands on the surface have no well-defined edges or orientations. The corresponding Fourier transformation, Fig. 1(c), of the image shows round contours (slightly elliptic due to the distortion of STM images), which is consistent with a large fraction of 120° angles with no preferred in-plane orientation. However, at 400 mV, the Fourier transformation of the image, Fig. 1(d), shows significantly rectangular contours.



FIG. 1. (Color online) *In situ* STM images over $0.4 \times 0.4 \mu m^2$. The contour plots of the Fourier transformation of the corresponding images are also shown in the lower panels. The symmetry of the contours evolves from circles or ellipses to rhombi between 0 and 400 mV. The islands expanded significantly when the potential is held at 600 mV.

The change to square topography, where the edges run along the crystal symmetry directions, indicates that the internal symmetries of the islands may have changed. The change seen in the Fourier transformation further indicates that the transition took place. The rectangular features when the potential is held at 600 mV become clearer in both the real image, Fig. 1(c), and its Fourier transformation, Fig. 1(e). This coarsening and shrinking behavior repeats with further cycling of the potential. Subsequent voltammetry (not shown) does not improve the overall morphology, indicating the surface structures have reached a steady state. The voltammetry also does not show evidence of any impurities or contaminants present on the surface.

B. Coherent surface x-ray scattering results

The CSXS measurements are performed, similar to incoherent SXS, along the specular (00L) rod. However, instead of the usual point detector, a low-noise charge-coupled device (CCD) area detector is used to collect the speckle patterns. Our CSXS measurements contain two kinds of information about changes occurring on the surface. Just as in ordinary SXS, we are capable of measuring potential-dependent changes to the overall scattering intensity, albeit much reduced, which provide information regarding the structure and kinetics of the structural change of the surface. In CSXS, however, the microstate of the surface, with a complex arrangement of surface features over a large area, manifests as a reciprocal space image of the microstate, better known as speckle patterns, which are composed of fine features within the average scattering envelope. Therefore, even when the system is in macroscopic equilibrium, the CSXS speckle pattern changes if the surface changes locally, representing the dynamic evolution of the microstate.

For the potential-dependent data, we typically applied a given potential and then collected data for \sim 5000 sec before proceeding to the next potential. We obtained the data only in positive potential sweeps due to experimental time constraints (the measurements in negative sweeps are assumed to be reversible because of the extremely slow effective scan rate). Each exposure of the CCD lasted typically 1–5 sec. The surface sensitivity of our measurements would have been highest at L = 1 anti-Bragg position for the same intensity. However, the speckle intensity is weakest at L = 1 and increases rapidly as L decreases. The empirical sensitivity of the x-ray speckle measurements is $\sim L \cdot I(L)$ for 0 < L < 1, and the overall best sensitivity to surface dynamics is typically obtained at intermediate positions between (0 0 0.1) and (0 0 0.5). In this study, the optimum sensitivity was found at L \sim 0.17, and we obtained most of our data using this position.

Before we discuss the speckle patterns, let us examine the integrated intensity at (0 0 0.17) as a function of applied potential, as shown in Fig. 2. Even though L = 0.17 is chosen for the highest sensitivity to speckles, the integrated intensities at other L values behave similarly. The x-ray intensity points to two different possible starting configurations for the sample surface. In the case of newly polished and vacuum- or inert-atmosphere annealed samples, the surface consisted of large terraces, fully reconstructed, with no islands.²¹ In the case of subsequent reannealing of electrochemically cycled crystals, the surface quality does not fully recover the fresh polished



FIG. 2. (Color online) Scattering intensity vs applied potential at $(0\ 0\ 0.17)$, where the intensity has an optimum sensitivity for surface dynamics. The intensity drop after lifting of hex from metastable equilibrium is shown as an arrow, and its time dependence is shown in the inset. Solid lines are the guides to eye.

surface, and the SXS intensity drops by a factor consistent with significant numbers of islands still being present on the terraces. However, while not visible in Fig. 1 at 0 mV, the x-ray scattering measurements after similar preparation indicate the surfaces with islands are reconstructed. As the potential is increased, there is at first no change in the scattering intensity until 300 mV, where the intensity drops sharply. This observation is largely consistent with the lifting of the hex reconstruction in the earlier SXS measurements.¹¹

We observed one additional feature due to our long dwell times at constant applied potentials. We typically took a step of ~ 100 mV and then held that potential for significant periods of time for data collection. This was done to ensure the surface was given enough time to equilibrate (and for subsequent data collection once equilibrium was reached). As such, the surface spent significantly longer at a given applied potential than is typical in cyclic voltammetry measurements. The hex reconstruction lifts mostly at 300 mV, which is consistent with previous studies. We were then surprised to find that, occasionally, the hex phase would begin to lift at 200 mV, or even at 100 mV, albeit rarely. In these cases, after significant periods of time (30–45 minutes) with no changes, the surface began spontaneously lifting the reconstruction within a few minutes. An example of such spontaneous lifting is shown as the red square with the arrow in Fig. 2, and the rate of intensity drop is shown in the inset. The apparent potential shifts may be a result of the x-ray radiolysis inducing local potential shift over the x-ray illumination area. We speculate that the local potential shift can build up with an *ir* drop, even though the potential shift averaged over the whole crystal surface (6 mm) is not observable, when the circulation of electrolyte is insufficient. This shift, therefore, represents the uncertainty of our experimental potentials. To minimize this effect, our reported correlation times are drawn from multiple data sets of different dwelling times. The intensity drops further above 600 mV, probably due to surface oxidation.^{8,18} We believe the STM image held at 600 mV of Fig. 1 already shows the sign of the initial oxidation of islands that appear enlarged. Although the Au density does not change by the oxidation, the surface intensity should drop because of the buckling due to the oxidation.

C. X-ray photon correlation analysis

By correlating evolving CSXS patterns over time, known as x-ray photon correlation spectroscopy (XPCS) analysis,^{19,20} we can apply the XPCS technique to atomic-scale dynamics on surfaces. In recent years, the coherent fraction, or brilliance, has increased dramatically due to the third-generation synchrotrons. The improved brilliance enabled the successful demonstration of CSXS at atomic length scales,^{21,22} which was not possible with the previous generation synchrotron sources. More importantly, the brilliance will further substantially increase as modern x-ray light sources²³ advance.

The CCD pattern is obtained from the illuminated surface area, typically limited to $\sim 10 \ \mu m$ across the beam and $\sim 100 \ \mu m$ along the beam, proportional to 1/L by the incident x rays defined to $10 \ \times \ 10 \ \mu m^2$ by a pair of precision slits before the sample. The limited illumination is necessary to select a coherent portion of the beam and results in significantly lower overall intensity than ordinary SXS.

Examples of the speckled scattering patterns collected along the specular rod are shown in Fig. 3. The scattering at the (001) anti-Bragg condition, while the most sensitive to atomic layer height surface changes, is generally weakest and was not sufficient to perform the experiments directly, whereas it has been sufficient in vacuum studies.²¹ However, any changes in response to electrochemical solution or applied potential will be restricted to the surface region of the scattering volume. Because the bulk is effectively static, we can collect speckle dynamics along the specular rod at positions where the total intensity is greater, and yet retain the surface sensitivity, provided the static background signal is effectively smoothed and subtracted during the analysis.



FIG. 3. (Color online) Example speckle patterns collected for various (00L) at an applied potential of +100 mV. The scattering is long for small L. The scattering angle (2q) increases along the horizontal axis.

As can be seen in the bottom-right panel of Fig. 3, significant structure is present in the scattering near the (002) Bragg peak. It means that the mosaic of the Au (001) is small compared to the illuminated area, and there is a mosaic distribution within it. However, the (002) speckles do not directly represent the mosaic distribution, as in the ordinary incoherent diffraction. Rather, they are the interference pattern of the mosaic distribution.

The CCD images of the speckles are elongated along the direction of the 2θ scattering angle because the angle of the CCD surface crosses the Ewald's sphere with an angle of θ . Therefore, assuming that the width of the rod in momentum space is uniform along the rod, the CCD images are longer at smaller angles, and the length is proportional to $\frac{\sqrt{4c^2-(\lambda L)^2}}{L}$, where c, λ , and L are the lattice constant, wavelength of x rays, and the reciprocal lattice unit, respectively.

Due to the highly coherent x rays, detailed information about the microstate of the system is recorded in the speckled diffraction patterns. As the microstate changes, the positions and intensities of the speckles will change in response. By sampling along the specular rod, we are primarily sensitive to vertical changes to the electron density configuration, with lower resolution in the planar directions of the sample surface. First, however, it is useful to determine where there are observable dynamics of the surface, as well as to demonstrate the overall stability of the experimental apparatus. Figure. 4 shows example speckle patterns collected at three different conditions. The first row shows patterns generated by the bulk mosaic over the course of 10 hours. The first (a) and the last (c) images separated over 10 hours are essentially identical. The time of evolution of a one-dimensional (1D) slice of the image (marked by a white line) is shown in (b) just to further



FIG. 4. (Color online) Time evolution of speckle patterns: The first column is the initial images, the third column is the last images, and the second column shows the time evolution of the lines of intensity marked by the white lines in the first column. The first row, (a)–(c), shows the speckles of (0 0 1.95), essentially a bulk reflection, the second row, (d)–(f), shows speckles of (0 0 0.17) at -350 mV, and the third row, (g)–(i), at +350 mV. Lengths of the horizontal streaks in (b), (e), and (h) indicate durations of correlation. Note that the duration of the streaks in (b) is longer than 10 hours, indicating that the image is static, that of (e) is \sim 30 min, and that of (h) is less 10 min, indicating that the image is highly dynamic.

demonstrate that no intensity fluctuation is seen over 10 hours. The second row of speckle patterns in (d) and (f) was collected at L = 0.17 with an applied potential of -350 mV, ~ 50 minutes apart. The images, while highly correlated as shown in (e), do indicate slow evolution of the surface. Lastly, the patterns in (g) and (i) show the system at L = 0.17 and 20 minutes apart, but with the potential set to +350 mV. Here it is evident that the initial and final speckle patterns shown do not resemble each other. The 1D slice of speckle patterns vs time shown in (h) indicates that the speckle pattern decorrelates in ≤ 10 min, which is a considerably shorter time than the previous two other cases. The horizontal streaks indicate approximately the correlation time of the speckle.

To obtain quantitative measurements of the evolution rates, we calculated an autocorrelation from a given data set. Prior to correlation, backgrounds were subtracted from the images to eliminate dark-current and camera artifacts. The normalized autocorrelation was then calculated on a pixel-by-pixel basis from

$$g_2(\Delta t) = \frac{\langle I(t_0)I(t)\rangle}{\langle I(t_0)\rangle \langle I(t)\rangle},$$

where $\Delta t = t_0 - t$, using a symmetric normalization scheme.²⁴ Autocorrelations from single pixels were then averaged together with the neighboring pixels. Only pixels with sufficient intensity were used in the average, typically at least 3 photons/pixel, and the dynamic range of the pixel was limited to 10^2 because of the saturation level of a CCD pixel. A lower-level discrimination was applied for any individual pixel with less than 50 CCD counts (1 photon = 780 CCD counts) being set to 0 to prevent anomalous dark currents from artificially increasing the correlation.

For the surface speckles, the correlation time is a measure of how long it takes for the illuminated area to reconfigure, in this case, by locally transforming between the triangular and square symmetries, or growing islands. For low potentials, we found typically that a single compressed exponential of the form $g_2(\Delta t) = \beta e^{-(\Delta t/\tau)^{\gamma}} + 1$ was capable of describing the autocorrelation calculations. For potentials of 300 mV or greater, the secondary timescale (τ_2), as well as the primary time scale (τ or τ_1), was required with two additional fit parameters: $g_2(\Delta t) = \beta_1 e^{-(\Delta t/\tau_1)^{\gamma}} + \beta_2 e^{-(\Delta t/\tau_2)^{\gamma}} + 1.^{24}$ An independent compression exponent did not significantly increase the statistical quality of the fits. Examples of twotimescale fits are shown in Fig. 5.

The correlation times were obtained from the measurements conducted while the surface was in equilibrium and the integrated surface scattering intensity was constant. The primary correlation time ranges from 10^4 and 10^3 sec for slow dynamics to 10^2 sec for fast dynamics. The primary correlation time is the measure of the step and island edge dynamics. It is important to note that the correlation times of reconstructed surfaces at low potential are similar to those measured at ~1000 K from the reconstructed surfaces in vacuum.^{7,21} This means that at room temperature, the surface atoms are considerably more mobile in solution than in vacuum. The high mobility of surface atoms in solution has been recognized for a long time, but our measurements in solution place it quantitatively in comparison to that in vacuum.^{7,21} Since the correlation time is proportional to the surface diffusion or hopping rate, the



FIG. 5. (Color online) Autocorrelation from the Au (001) surface at three different potentials collected at L = 0.17. For potentials at +200 mV and below, the decay is slow and governed by a single exponential decay. For higher applied potentials, the autocorrelation decays much faster, and we see two distinct timescales develop in the autocorrelation functions.

correlation at a given temperature is given by $\frac{1}{\tau} \propto v_1 e^{-E_b/k_B T}$, where E_b is an energy barrier for an atom to detach from a step edge, and v is the so-called attempt frequency. The attempt frequency is a thermally driven vibration frequency of an atom and indicates how many times an atom attempts to overcome the energy barrier per unit time (see Chapter 10 of Ref. 25 for more accurate definition). Using this simple approximation and an assumption that the attempt frequency of Au atoms depends only on *T*, we can estimate the reduction of the energy barrier from vacuum to electrolyte environments. In Fig. 6, we show the obtained correlation time vs potential.



FIG. 6. (Color online) Time constants for Au (001) plotted as a function of applied potential as measured at L = 0.17. For +300 mV and higher, there are two distinct correlation-time constants that are required to fit the data. The solid lines are guides to help make the distinction between medium and fast timescales. The insets are three atomic configurations (see the text for discussion).

At low potentials (below 0 mV), the correlation time of the hex-reconstructed phase is 2×10^4 sec, which is smaller by a factor of ~100 than that in vacuum.²¹ The reduction in E_b (ΔE_b) then can be estimated to be $\ln(10^2)k_BT$ or ~0.14 eV. At the Au (001) and water interface, the water-water bonds at the interface are broken and replaced by Au-H₂O bonds. This means that Au atoms, with which nothing interacts in vacuum, will be constantly interacting weakly with water molecules. In this case, ΔE_b can be the Au-water bond energy (0.15 eV) estimated by a density functional theory (DFT) study.²⁶ It is also reasonable to assume that it will be difficult for two water molecules to bond simultaneously to one Au atom, even though there are twice as many water molecules as Au atoms at the interface.

The primary correlation time also changes dramatically in response to the applied potential, as shown in Fig. 6. Focusing only on the squares, we see that the correlation time decreases by a factor 50 over a 300 mV change in potential. Remarkably, the change coincides well with the hex-to- (1×1) transition. The edge dynamics are higher by a factor of ~ 20 in the (1×1) phase than in the hex phase. This compares well with an increase of the island decay rates in sulfuric acid,²⁷ although the increase is less than an order of magnitude and occurs at higher potential. The difference between the STM work and our results comes probably because sulfuric acid is more likely to adsorb to the surface and affect the dynamics. Another possibility can be considered if the effect of the sulfuric acid is assumed not to be strong. Comparing the decay rate of Ref. 27 to Fig. 6, the STM work shows the data only for the potential range of 300 mV or higher. This is the potential range, after the reference electrode difference is corrected, where the hex is already lifted. Therefore, we expect that the decay rate should have been much slower if it were measured for the low-potential region. Since the range of the decay rate measurement is estimated to be a factor of $\sim 10^{27}$ the slower dynamics are probably below their detection limit. On a close examination of the STM data, we also note that only two data points significantly deviate from the horizontal line at 600 mV. This is the potential where we see that the x-ray intensity drops again (see Fig. 2) and the STM images (see Fig. 1) change significantly, indicating the incipient-stage island oxidation.

According to previous studies,^{11,15} the lifting transition is fairly rapid under voltammetric conditions, while the reverse transition from (1×1) to "hex" exhibits a slow kinetics, requiring ~10 min after jumping well into the hex reconstruction potential. The lifting transition from hex to (1×1) occurs rapidly because the edges of the islands and steps move faster to transform to the (1×1) structure, and the transition process is not limited by ad-atom diffusion. The reverse is also true, and the hex structure can form only slowly. The hex nucleates at the step edges and then moves inwards, along the terraces.²⁸ This requires significantly longer times because the two possible orientations for the "hex" domains can inhibit each other during growth, and mass transport due to the higher density of the hex domains compared to the (1×1) structure must occur.

It is significant that we observe dynamics not only during the transition, but also at all higher potentials once the reconstruction has lifted. The surface remains in a state of



FIG. 7. (Color online) STM images for 200 mV (a) and 500 mV (b). Each image shows a region of 0.4 \times 0.4 μ m². Panels (c) and (d) show the same regions 10–15 minutes later. (a) and (c) are similar, while (b) and (d) are quite different.

dynamic equilibrium even though the surface phase transition from hex to (1×1) has already occurred. Since the logarithm of the inverse correlation time is proportional to the surface activation energy of desorption from the step or island edges, the correlation time is fit to a change in activation energy. If we assume that the attempt frequency is not very sensitive to the surface symmetry, a factor of 50 corresponds to an additional decrease in the activation energy of ~0.1 eV. Therefore, compared to the hex phase in vacuum, the atoms in the (1×1) phase in electrolyte desorb/adsorb 5000 times more frequently at room temperature.

The change in dynamics caused by the potential is also confirmed in the STM images shown in Fig. 7. Two pairs of images are selected, one at 200 mV and one at 500 mV. The first image of each pair [Figs. 7(a) and 7(b)] was taken shortly after the potential was changed. The second image of each pair [Figs. 7(c) and 7(d)] was taken ~ 10 min later. We can see that the two images taken at 200 mV are largely the same, indicating very slow evolution of the step/island morphology. The two images taken at 500 mV are quite different, which indicates significant dynamics during the same time period. From these observations, it is evident that the structure is changing more quickly at 500 mV, but quantifying how much it is changing becomes more difficult due to STM drift, tip-surface interaction, and the significant decrease in sampled area when compared to the area probed by the x rays. Nonetheless, we can barely recognize the step/island morphology of (b) from (d). It is likely that after more time, the surface at 500 mV becomes unrecognizable from the initial state. The approximate timescale that can be determined from STM measurement agrees well with the correlation time of \sim 400 sec measured from the x-ray speckles.

There exists a second correlation time at high potentials as discussed with Fig. 5. This correlation time, shown as open red circles in Fig. 6, is even faster, approaching the experimental time-resolution limit. In fact, this is $\sim 3 \times 10^5$ times faster than the correlation time in vacuum.^{7,21} Since it is much faster than the step motion, we believe it is from the local fluctuations of microstates within the terraces and islands, not from their edges. We speculate that one possibility is fluctuations of the local surface atomic symmetry. Examples of local symmetries are shown as the insets in Fig. 6. The cubic symmetry can easily change to hexagonal symmetry and vice versa. The fluctuations of such local symmetries should exist down to the atomic scales. However, our CCD size limits the smallest domain size that we can measure to the length scales of ~ 10 nm and the corresponding correlation timescales. Note that the average maintains the cubic symmetry, even though the symmetries may locally fluctuate. These fluctuations are most likely driven by water and ions in double layers since such fast fluctuation is not seen in vacuum at room temperature. On the other hand, the hexagonal symmetry at low potentials does not have room for fluctuation due to the close-packed structure, which explains why we do not see the fast correlation times in the low-potential range. Ultimately further measurement and analyses are necessary before a complete understanding of the observed dynamics can be obtained. XPCS analysis of data obtained at significantly different q-values could perhaps be used in the future to deduce something akin to a diffusion rate, as done in other studies.

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IV. SUMMARY AND CONCLUSIONS

We have demonstrated that XPCS analysis of CSXS images yields unique equilibrium dynamics information of the Au (001) surface in perchloric acid electrolyte. We found that edge dynamics dramatically increase as the hex reconstruction is lifted. The edge dynamics are orders of magnitudes larger than that in vacuum. We give an estimation of energy barrier reduction in electrolytes. We also find previously unknown surface lattice dynamics, which are much faster than the edge dynamics. We believe that this is a novel, powerful technique for studying dynamics of electrochemical interfaces over several orders of magnitudes.⁷ We anticipate that future experiments can be performed with different facets of gold, electrochemical potential ranges, and electrochemical solutions with strongly or weakly adsorbing anions. Another application that could prove favorable would be to extend in situ studies of electrodeposition. Step-flow sublimation studies of Pt at high temperature in vacuum have already been successful,²⁹ and it seems likely that the technique will be extended to growth at the solid-liquid interface.³⁰

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