Monitoring the Transitions of the Charge-Induced Reconstruction of Au(110) by Reflectance Anisotropy Spectroscopy

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(Received 30 July 2001; published 26 March 2002)

Missing-row reconstructions on Au(110) immersed in electrolytes have been studied by *in situ* reflectance anisotropy spectroscopy. Transitions between the 1 × 3, 1 × 2, and 1 × 1 surface structures were monitored as a function of the applied potential. A kinetic model allowed us to reproduce the data satisfactorily. These results confirm the theoretical predictions showing that the surface charge determines the surface reconstruction. The transition potentials and the activation barriers were determined.

DOI: 10.1103/PhysRevLett.88.147403 PACS numbers: 78.68.+m, 68.08.–p, 68.35.Bs, 78.40.Kc

Low-index surfaces of metal single crystals immersed in an aqueous electrolyte can display various reconstructions, determined by parameters such as the potential-induced surface charge or the adsorption of anions [1]. In ultrahigh vacuum (UHV), the (110) surface of Au displays a (1 × 2)-missing-row (MR) reconstruction at room temperature [2]. On the contrary, in an electrochemical environment, a 1 × 2 single-MR reconstruction, a 1 × 3 double-MR reconstruction, and a well-ordered 1 × 1 unreconstructed surface can be obtained on Au(110). Although these surface structures have been demonstrated by different techniques, in particular by scanning tunneling microscopy (STM) [3–6], there is still no clear statement about which transitions occur between them: Some authors observe a 1 × 2 ↔ 1 × 1 transition in acidic electrolytes, others a 1 × 3 ↔ 1 × 1 transition in salt electrolytes, and also others observe coexistence of small domains of different reconstructions. Local-density-functional calculations have shown that the reconstructions are related to the surface charge induced by the applied electrochemical potential, and have predicted a transition from the 1 × 3 to the 1 × 2 reconstruction, to finally the 1 × 1 unreconstructed surface, when going from a negatively charged surface to a positively charged one [1,7], but this has not been shown by experiments thus far. The discrepancy between this prediction and the former experiments is likely due to the fact that, in the theory, the effects of the adsorption of anions or cations are not taken into account. In order to isolate the effect of the surface charge on the reconstruction, we have used an acidic electrolyte, H_2SO_4, and a neutral one, Na_2SO_4 (whose cations and anions are not specifically adsorbed on gold) [1].

Few techniques can investigate the liquid-metal interface. Usual electrochemical techniques such as cyclic voltammetry are not successful for monitoring the surface transitions of Au(110) [1]. Besides STM, the main usable *in situ* techniques are optical ones, either in the x-ray range [8] or in the visible and ultraviolet one, such as electroreflectance spectroscopy (ERS) or second-harmonic generation (SHG). However, ERS, efficient for investigating other electrolyte-metal interfaces, does not give information in the case of Au(110) [1]. SHG, on the other hand, allowed monitoring the transition between a smooth Au(110) surface and a "microfaceted" one, without distinguishing the 1 × 2 and 1 × 3 reconstructions [9]. Another optical technique, reflectance anisotropy spectroscopy (RAS), which has been used for a long time for semiconductor surfaces, has recently proven to be powerful in the case of metal surfaces, and studies of (110) surfaces of Ag, Au, and Cu crystals, either in air or in UHV, have been performed [10,11]. We have shown in a preliminary paper [6], by *in situ* STM and RAS, that RAS can be indeed used successfully for studying the reconstructions of Au(110) surfaces in a neutral electrolyte. The capability of the technique was later confirmed by another group [12], who has studied the same Au(110) surface in an acidic electrolyte. However, their results are inconsistent both with ours and with previous studies, as will be discussed below.

We present in this Letter a *real-time monitoring* by RAS of the transitions between reconstructions of Au(110) in a liquid. The RA spectra for the unreconstructed 1 × 1 surface of Au(110) and for the reconstructed 1 × 2 and 1 × 3 ones, immersed either in acidic (H_2SO_4) or in neutral (Na_2SO_4) electrolytes, are identified for specific values of the applied potential. Our results demonstrate that the driving force of the reconstructions is indeed the charging of the surface induced by the applied potential, as theoretically proposed [1,7], and clears up the apparent contradiction between previous studies. Recording the RA signal as a function of the potential allowed us to study in *real time* the transitions between the reconstructions and to determine the energy barriers that the atoms have to overcome during their displacements, by use of a kinetic model.

RAS was performed on the gold sample placed in a homemade three-electrode electrochemical cell, through a strain-free fused quartz window. Special care was taken in order to minimize possible contamination of the working compartment. Potentials reported here are given with respect to the Ag/AgCl reference electrode. Before each set of experiments, the Au(110) surface was flamed and slowly cooled in air for cleaning and to obtain the 1 × 2 surface [1]. The sample was then placed in the cell and held under potential control for an hour in the electrolyte solution, which was purged from dissolved oxygen by argon circulation. The RAS spectrometer, built following Aspnes' setup [13], delivered the RA signal defined by $\mathrm{Re}\{\Delta r/r\} = \mathrm{Re}\{(r_{[1\bar{1}0]} - r_{[001]})/r\}$, where the $[1\bar{1}0]$ direction is parallel to the atom rows of Au(110); r is the mean value of the reflectances of light along both crystalline orientations: $r_{[1\bar{1}0]}$ and $r_{[001]}$.

Figures 1 and 2 show two sets of RA spectra obtained at different potentials, measured in acidic (0.1 M H_2SO_4) and neutral (0.1 M Na_2SO_4) electrolytes, respectively. In the former case, the potential ranged from −0.2 to 0.6 V, i.e., between hydrogen evolution and the beginning of oxidation. In the second case, the neutrality of the solution allowed us to extend the range to more negative potentials. Two different spectral regions can be distinguished when dealing with the optical response of gold [14]. The RA signal measured below the onset $\hbar\omega_i$ of the interband transitions, around 2.4 eV, has been accounted for by an anisotropy of the Drude parameters for the free electrons in the region close to the reconstructed surfaces [6]. Above $\hbar\omega_i$, the interband transition from the filled *d* bands to empty states, above the Fermi level, play the major role. The anisotropy in this region has mainly two different origins. One is the local-field effect, long-range order, which has been treated theoretically by use of the so-called "swiss-cheese" model [15] and has permitted to grossly reproduce the shape of the spectra for Au(110), Ag(110), and Cu(110) surfaces [10,16]. The second effect, short-range order, is the anisotropy of the bulk band structure in the vicinity of the surface, which has been accounted for by *ab initio* treatments [17]. The main features are indeed observed close to the structures related to the interband transitions, in particular around 2.5 and 3.5 eV. The surface microscopic order is obviously expected to have an important effect on the intensities of the RA signal at the corresponding energies, being apparently the most important at 2.5 eV.

We have identified previously, by *in situ* STM [6], the reconstructions of Au(110) in Na_2SO_4 for the following applied potentials U: 1 × 3 ($U \approx -0.6$ V), 1 × 2 ($U \approx 0.0$ V), and 1 × 1 ($U \approx 0.6$ V). When Au(110) is in H_2SO_4, it has been shown by others [4] using also STM that both 1 × 2 and 1 × 1 surfaces can be obtained, for potentials below 0.05 V and above 0.25 V, respectively. From these STM results, and from the similarity of the RA spectra obtained either in Na_2SO_4 or in H_2SO_4 for the same potentials, we conclude that the spectra obtained at 0.0 and 0.6 V, drawn in thicker lines in Figs. 1 and 2, can be considered as the *optical fingerprints* of the 1 × 2 and 1 × 1 surfaces of Au(110), respectively. The slight variations between these RA spectra in both electrolytes, are likely due to some differences in the quality of the surfaces, caused by a nonperfectly reproducible preparation procedure of the samples. For Au in Na_2SO_4, the RA spectra measured at −0.6 V, and drawn in thicker line in Fig. 2, is the optical fingerprint of the 1 × 3 surface. RA spectra between −0.6 and 0.0 V correspond to intermediate surface orders, composed by 1 × 3 and 1 × 2 domains. The

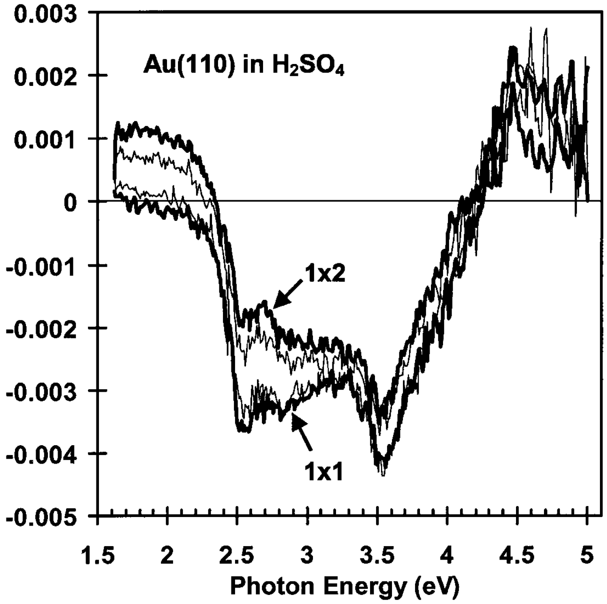

FIG. 1. RAS spectra for Au(110) in H_2SO_4, for applied voltages equal to 0.0, 0.2, 0.4, and 0.6 V (highest curve to lowest curve). The spectra drawn in thicker lines correspond to the 1 × 2 and 1 × 1 reconstructions, obtained for applied potentials of 0.0 and 0.6 V, respectively.

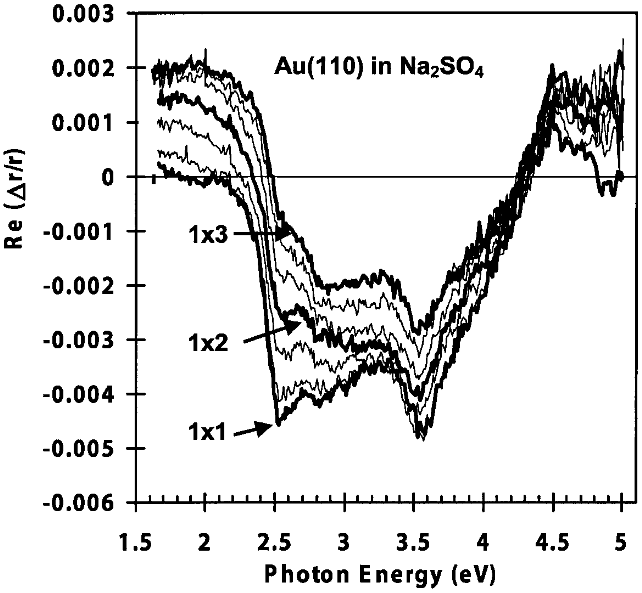

FIG. 2. RAS spectra for Au(110) in Na_2SO_4, for applied voltages ranging from −0.6 to 0.6 V (highest curve to lowest curve). The spectra drawn in thicker lines correspond to the 1 × 3, 1 × 2, and 1 × 1 reconstructions, obtained for applied potentials of −0.6, 0, and 0.6 V, respectively.

results obtained in H_2SO_4 (Fig. 1) show that increasing the voltage from −0.2 and 0.4 V leads to a well-defined surface transition from the 1 × 2 phase to the 1 × 1 one (the spectrum at −0.2 V, not drawn here, is identical to the 0 V one). When the potential is settled back to −0.2 V, the initial spectrum measured at −0.2 V is restored, which shows that the transition is reversible. These results are in excellent agreement with STM studies by Magnussen *et al.* [4], who showed that the 1 × 2 order is obtained below 0.05 V, and the 1 × 1 surface above 0.25 V. On the contrary, the work by Sheridan *et al.* using RAS for Au(110) in H_2SO_4 [12], is inconsistent with ours: Their RA spectrum displays no change when the potential is increased from 0.0 to 0.6 V, and is assigned to the 1 × 2 surface. This conclusion is in disagreement with both the STM results [4] and ours, as the shape of this spectrum is very similar to the one we obtain at and above 0.4 V, for the 1 × 1 surface. These authors eventually observe a change in the spectrum when increasing the potential to 0.8 V, that they assign to the transition from the 1 × 2 to the 1 × 1 surface, which is also in contradiction with the above results. The effect that they observe is most likely due to surface roughening, or microfaceting, caused by oxygen adsorption at 0.8 V, as it has been pointed out by Magnussen *et al.* by STM [4] and by Pettinger *et al.* by SHG [9].

In order to monitor the transitions between the reconstructions of Au(110), we have measured in real time the intensity of the RA signal at 2.5 eV during the cycling of the potential from negative values to positive ones, and reverse, either in H_2SO_4 or in Na_2SO_4, with a sweep rate of 1 mV/s. Starting from negative potential U, where the surface is reconstructed (either 1 × 2 in H_2SO_4 at $U = -0.3$ V or 1 × 3 in Na_2SO_4 at $U = -0.9$ V), the potential linearly increased to 0.6 V where the surface is unreconstructed, then decreased to the initial potential. Figures 3 and 4 show the change of the signal as a function of the voltage for both electrolytes. The arrows indicate the direction of the scan. The curve in Fig. 3 displays a clear hysteresis shape, with predominance of the 1 × 2 order between −0.3 and 0.1 V in the forward half-cycle (upper part), and predominance of the 1 × 1 order between 0.6 and 0.2 V in the reverse half-cycle (lower part). In Fig. 4, the predominances of the 1 × 3 and 1 × 2 surface orders are seen as plateaus in the forward part of the curve, between −0.9 and −0.5 V, and between −0.2 and 0.2 V, respectively. In the reverse half-cycle, no plateau can be seen, which is due to kinetic effects leading to a longer time for getting the reconstructions than for removing them. This three-step transition is in contradiction with a previously reported study in other salt electrolytes, where a direct 1 × 3 ↔ 1 × 1 transition was obtained between −0.2 and 0.0 V, without getting the 1 × 2 phase [8]. We explain this by the fact that halide anions, present in these electrolytes, adsorb on Au at smaller potentials than $SO_4{}^{2-}$, destroying the reconstruction at a potential where the 1 × 2 phase should be stable. Such an important effect of the type of electrolyte, both on the reconstructions and on the transition potential, has been already stressed by Kolb [1].

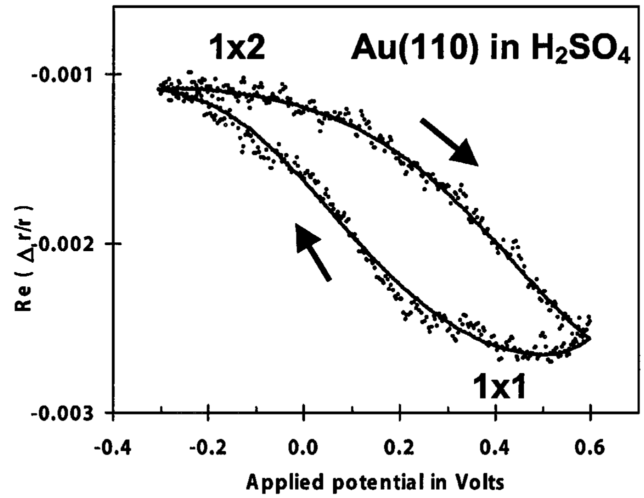

FIG. 3. RA signal measured at 2.5 eV during potential cycle from −0.3 to 0.6 V for Au(110) in H_2SO_4. Points: experiment; continuous line: calculation.

It has been shown by first-principle calculations [1,7] that the Gibbs free energy of the three orders for Au(110) indeed depends on the charge of the surface. The 1 × 2 phase is predicted to be stable for the uncharged surface, while the 1 × 3 phase is stable for more negative charging, and the 1 × 1 one is stable for more positive charging. Our results confirm clearly these predictions, and show that the surface order is determined by the applied potential, therefore by the surface charge [18], unless specific adsorption of anions or cations occurs. The transitions between the different surface orders require bond breaking and transport of Au atoms, which have to involve activation energy barriers [1]. This explains the hysteresis

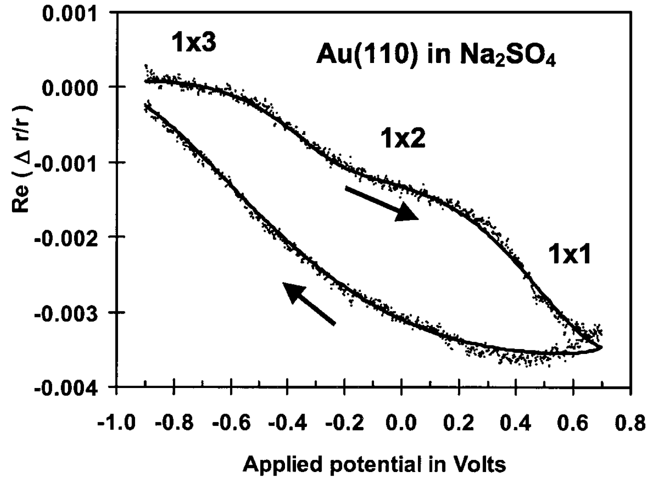

FIG. 4. RA signal measured at 2.5 eV during potential cycle from −0.9 to 0.6 V for Au(110) in Na_2SO_4. Points: experiment; continuous line: calculation.

curve of Fig. 3, and also the shape of the curve in Fig. 4 which indicates that the removal of the reconstructions is much easier than their restoring. In order to reproduce these observed cycles, we have developed a kinetic model, which describes the transitions. STM studies have shown that there is coexistence of regions with different reconstructions, for intermediate potentials [4,5,8]. For a given potential V, we therefore describe the surface by adjacent regions with reconstructions A (1×3), B (1×2), and C (1×1), with coverage fractions $a(V)$, $b(V)$, and $c(V)$, linked by $a(V) + b(V) + c(V) = 1$. If we define the intensity of the RA signal at 2.5 eV for each surface order by I_A, I_B, and I_C, the RA intensity at a given potential reads $I(V) = a(V)I_A + b(V)I_b + c(V)I_c$. The following kinetic equations are then used for the transitions: $A \xleftrightarrow{k_{-1},k_1} B \xleftrightarrow{k_{-2},k_2} C$

$$da/dt = -k_1 a + k_{-1} b, \qquad dc/dt = k_2 b - k_{-2} c,$$

where $k_{\pm i}$ are the kinetic factors of the direct $(+)$ or reverse $(-)$ transitions, written as

$$k_{1,2} = \exp\{-[G^*_{1,2}(V) - G_{A,B}(V)]/k_B T\} \quad \text{and}$$
$$k_{-1,-2} = \exp\{-[G^*_{1,2}(V) - G_{B,C}(V)]/k_B T\},$$

where $G_A(V)$, $G_B(V)$, and $G_C(V)$ are the free energies of the A, B, and C reconstructions. $G^*_1(V)$ and $G^*_2(V)$ are the energy barriers between the states A and B, and the states B and C, respectively. By using a simplified linear dependence upon V for G_A, G_B, and G_C, and for G^*_1 and G^*_2 [19], we could reproduce well the cycles given in Figs. 3 and 4 (continuous lines). The so-determined transition potential $V_{1\times1\leftrightarrow1\times2}$ is 0.24 V, when Au(110) is in H_2SO_4, and 0.1 V when Au(110) is in Na_2SO_4. This small difference is probably due to the different natures of the cations, which can have some influence on the stability ranges of the surface orders [1]. These values are in excellent agreement with the above-discussed results obtained by STM [4]. The transition potential $V_{1\times2\leftrightarrow1\times3}$ is found here equal to -0.56 V. Finally, the average activation barriers per atom were found to be 0.15 eV (respectively, 0.09 eV) for the $1 \times 2 \leftrightarrow 1 \times 1$ transition in H_2SO_4 (respectively, in Na_2SO_4) and 0.2 eV for the $1 \times 3 \leftrightarrow 1 \times 2$ transition in Na_2SO_4 [20]. The smaller activation energy for the $1 \times 2 \leftrightarrow 1 \times 1$ transition than for the $1 \times 3 \leftrightarrow 1 \times 2$ transition is likely due to different local mechanisms for both transitions [3,5]. The former transition can involve migration along the rows only, leading to antiphase 1×2 regions, while the second one requires also migrations across the rows, whose energy barrier is expected to be larger. As pointed out from STM studies, the microscopic mechanisms of the surface transformations are in fact probably much more complicated, involving also defects such as steps, kinks, and microfacets [4]. These activation barriers are of the same order, although smaller, than the ones obtained from effective medium theory for the surface diffusion of atoms on Au(110) in vacuum (0.27 eV along the rows and 0.67 eV across the rows) [21], which indicates that these values are realistic.

We are grateful to A. Tadjeddine and B. Croset for helpful discussions and advice. We thank R. G. Barrera for valuable comments and criticism of the manuscript, and W. Sacks for a critical reading of the manuscript.

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[1] D. M. Kolb, Prog. Sur. Sci. **51**, 109 (1996).
[2] M. Sturmat, R. Koch, and K. H. Rieder, Phys. Rev. Lett. **77**, 5071 (1996).
[3] X. Gao, A. Hamelin, and M. J. Weaver, Phys. Rev. B **44**, 10 983 (1991).
[4] O. M. Magnussen, J. Wiechers, and R. J. Behm, Surf. Sci. **289**, 139 (1993).
[5] X. Gao *et al.,* Surf. Sci. **318**, 1 (1994); X. Gao and M. J. Weaver, Surf. Sci. **313**, L775 (1994).
[6] V. Mazine, Y. Borensztein, L. Cagnon, and P. Allongue, Phys. Status Solidi (a) **175**, 311 (1999).
[7] K. M. Ho and K. P. Bohnen, Phys. Rev. Lett. **59**, 1833 (1987); C. L. Fu and K. M. Ho, Phys. Rev. Lett. **63**, 1617 (1989).
[8] B. M. Ocko *et al.,* Phys. Rev. Lett. **69**, 3350 (1992).
[9] B. Pettinger, S. Mirwald, and J. Lipowski, Appl. Phys. A **60**, 121 (1995); C. Bilger and B. Pettinger, Chem. Phys. Lett. **294**, 425 (1998).
[10] Y. Borensztein *et al.,* Phys. Rev. Lett. **71**, 2334 (1993); W. L. Mochan *et al.,* Physica (Amsterdam) **207A**, 334 (1994).
[11] P. Hofmann *et al.,* Phys. Rev. Lett. **75**, 2039 (1995); K. Stahrenberg *et al.,* Phys. Rev. B **58**, R10 207 (1998).
[12] B. Sheridan, D. S. Martin, J. R. Power, S. D. Barrett, C. I. Smith, C. A. Lucas, R. J. Nichols, and P. Weightman, Phys. Rev. Lett. **85**, 4618 (2000).
[13] D. E. Aspnes *et al.,* Appl. Phys. Lett. **52**, 21 (1988).
[14] F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972).
[15] J. Tarriba and W. L. Mochan, Phys. Rev. B **46**, 12 902 (1992).
[16] J. K. Hansen, J. Bremer, and O. Hunderi, Phys. Status Solidi A **170**, 271 (1998).
[17] S. Bouarab *et al.,* Phys. Rev. B **63**, 195409 (2001); P. Monachesi and R. Del Sole, Phys. Rev. B **64**, 115421 (2001).
[18] The point of zero charge is -0.04 V for Au(110)-(1×2) and -0.02 V for Au(110)-(1×1), after Ref. [1].
[19] The linear dependence of G^*_1 upon V is included in the one of G_A and G_B, and eventually G^*_1 is taken constant.
[20] Referred to a complete surface (110) monolayer.
[21] P. Stoltze, J. Phys. Condens. Matter **6**, 9495 (1994).