O Atom Induced Gradual Deconstruction of the 23 × $\sqrt{3}$ Au(111) Surface[†]

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Received: July 27, 2007; In Final Form: September 25, 2007

He diffraction has been used to investigate changes in the surface morphology of reconstructed Au(111) when small quantities of O atoms are adsorbed. It is proposed that the electronegative oxygen removes charge from the surface, which causes the surface to revert to the (111) structure. The extent of this deconstruction is dependent on the initial O coverage and the surface temperature. These results further delineate and emphasize the delicate interplay of adsorbate coverage and surface structure for the oxygen−gold system, a topic of current high interest due to the remarkable and technologically relevant catalytic properties of gold interfaces and clusters spanning atomic through nanoscale dimensions.

Introduction

Gold surfaces have both technologically useful and scientifically interesting properties. For instance, Au based catalysts have been shown to oxidize CO at, or below, room temperature.[1,2] Au based catalysts have also been shown to create useful reaction intermediates through partial oxidation at low temperatures, an example being the epoxidation of propene.[3,4]

Au is also interesting because the close-packed (111) face undergoes an extensive reconstruction.[5−9] The reconstructed Au(111) surface forms a superstructure having a rectangular 22 × $\sqrt{3}$ unit cell (or equivalently a 23 × $\sqrt{3}$ unit cell and a 4.4% compression) with the long axis along the $\langle 110 \rangle$-type azimuths. On an even larger scale, this structure is modulated by a regular array of kinks where the orientation is rotated by 120°. This produces the herringbone pattern clearly seen in scanning-tunneling microscopy (STM) images.[6,7]

This reconstruction is easy to modify by changing the effective surface charge. Adsorbing alkali metal atoms under ultrahigh vacuum (UHV) conditions results in the top layer of Au becoming even more densely packed, with ordered, hexagonally arranged domains.[10] Adsorbing the electronegative species O and S has been shown to lift the herringbone reconstruction.[11,12] In electrochemical cells, it is possible to cause the unit cell to revert to that of the unreconstructed (111) surface by imposing a positive surface charge.[13−15]

In this paper, we discuss experiments involving the change in the surface structure while adsorbing small amounts of oxygen under UHV conditions at surface temperatures (T_s) between 200 and 400 K. O_2 does not adsorb on the Au surface under these conditions. O_2 can be chemisorbed at elevated temperatures and pressures ($T_s \approx 750$ K and $P = 1$ bar), leading to short- and long-range surface reordering.[16,17] At $T_s = 900$ K and a lower O_2 pressure of 5×10^{-6} mbar, a change in the surface structure was attributed to the formation of an AuO_x overlayer.[18] For adsorption near room temperature under UHV conditions, it is necessary to use more reactive forms of oxygen, for example, O_3[19] or O atoms produced by decomposing O_2 on a hot filament.[20] These experiments involved dosing at 300 K and monitoring the surface structure with low-energy electron diffraction (LEED). For O coverages of less than 0.1 monolayer (ML), the diffraction rods due to the reconstruction disappeared, and only features corresponding to the (111) surface remained. As the coverage was increased, bright streaks became apparent between the integral order spots, indicative of some additional superstructure that is ordered in one dimension. Also, the incoherent background increased in brightness with additional O coverage, indicating that the surface was becoming disordered.

In this paper, the deconstruction of the reconstructed Au(111) surface will be discussed as a function of oxygen coverage and surface temperature for low coverages (<0.1 ML) of randomly adsorbed oxygen. A low-power radio frequency source was used to create a beam of ground state O(^{3}P) atoms. To investigate the ordering, a well-collimated supersonic beam of He atoms was scattered from the surface, which has an advantage over LEED in that it is exclusively surface sensitive. For random coverages of <0.1 ML of oxygen atoms adsorbed at $T_s = 200$ K, there is a change in the diffraction spectra, which we interpret as the beginning of the surface reverting to the unreconstructed (111) face, involving some of the Au atoms moving away from their reconstructed hcp sites to fcc sites. The surface returns to the reconstructed structure upon heating to room temperature, well below the temperature at which oxygen normally desorbs from Au.

Experimental Procedures

The experimental apparatus and methods have been covered elsewhere, so only a brief description will be presented here.[21,22] The experiments were performed in a UHV molecular beam scattering machine that contained an independently rotatable crystal manipulator and differentially pumped quadrupole mass spectrometer detector with an angular resolution of ∼1° fwhm. The Au crystal was cut and polished within 0.5° of the (111) plane and cleaned by Ar$^+$ sputtering (1.5 kV, $T_s = 1000$ K). Cleanliness was checked by Auger electron spectroscopy. Ordering was achieved by annealing for several days at ∼1200 K, occasionally sputtering as impurities diffused out of the selvedge.

The surface diffraction was measured with a He beam produced from a liquid N_2 cooled source. This beam had an

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[†] Part of the “Giacinto Scoles Festschrift”.

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10.1021/jp0759729 CCC: $37.00

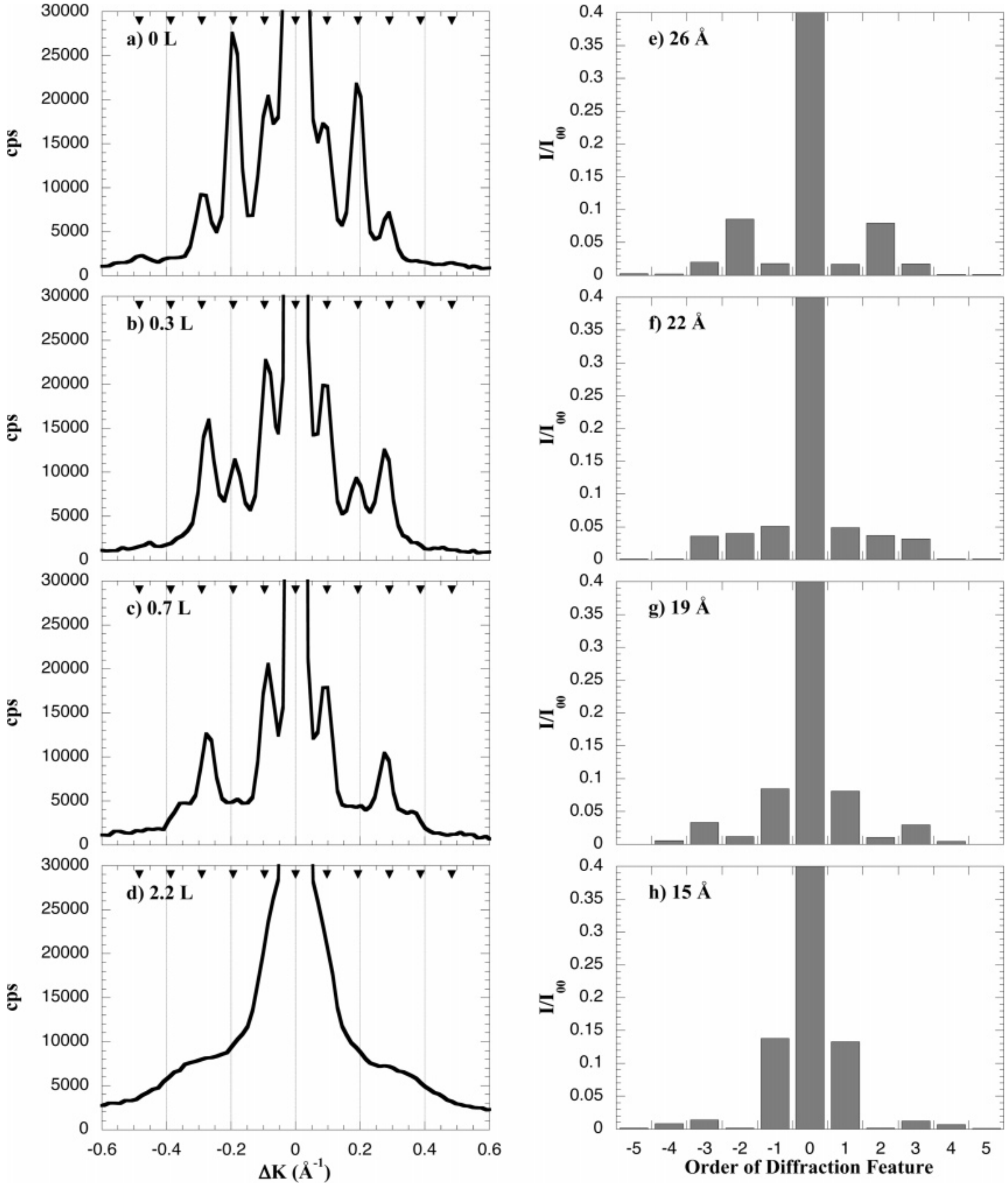

Figure 1. Panels a−d show He diffraction spectra in the $\langle 10\bar{1}\rangle$ direction after progressively longer exposures to O(^{3}P): $\Theta_i = 45°$ and $T_s = 180$ K, with the position of the diffraction orders indicated by the arrowheads at the top of each figure. Exposures are given in Langmuirs (1.4 × 10^{15}/cm^2). Dosing was done at $T_s = 200$ K. Panels e−h show diffraction intensities from the eikonal approximation using the model explained in the text (eq 2), along the $\langle 10\bar{1}\rangle$ azimuth with $a = 63$ Å and normal amplitude of 0.15 Å. The distance given in each of the figures is r(Å), the width of the double row.

energy of ∼20 meV and a $\Delta v/v \approx 1\%$ fwhm. O(^{3}P) was produced by a low-power, low-pressure radio frequency (RF) discharge nozzle beam source, using pure O_2 and having a dissociation of ∼15%. The average energy of the O atoms was 70 meV, with a fwhm of 35−115 meV and a flux of ∼0.04 ML/s O(^{3}P) (1 ML = 1.4 × 10^{15}/cm^2) at $\Theta_i = 45°$, the incident angle for dosing.

TABLE 1: Relative Diffraction Probabilities, I_G/I_{00}, in the $\langle 10\bar{1}\rangle$ Azimuth

order	clean	0.3 L	0.7 L
−5	0.0015	0.0010	
−3	0.013	0.046	0.045
−2	0.042	0.022	
−1	0.011	0.041	0.061
1	0.0088	0.032	0.046
2	0.031	0.018	
3	0.0073	0.034	0.034
5	0.0010		
relative specular intensity	1	0.55	0.34

Results and Discussion

Figure 1 shows the diffraction spectra along the $\langle 10\bar{1}\rangle$ azimuth after successive exposures of the Au surface to O(^{3}P) at $T_s = 200$ K, and Table 1 lists the fitted intensities normalized by the specular intensity. Figure 1a is the spectrum of the clean surface, and the diffraction features show the relative intensities typical of a clean, reconstructed surface. The accepted structure is a rectangular 23 × $\sqrt{3}$ unit cell with a 4.4% uniaxial compression along the $\langle 10\bar{1}\rangle$ and symmetrically related azimuths, leading to a lattice constant of ~63 Å.[5−7] During the course of this study, the positions of the diffraction features were consistent with a unit cell length of 65 ± 1 Å. With increasingly small O(^{3}P) exposures, the relative intensities of the diffraction features undergo large changes. The diffraction features also move closer to $\Delta K = 0$, leading to the conclusion that the unit cell length has increased by ~2−3 Å. As expected, these changes only occurred when the O(^{3}P) source was powered; exposure to O_2 alone caused no changes in the He scattering.

We also looked along the $\langle 11\bar{2}\rangle$ azimuth and clearly see the diffraction peak due to the hexagonal ordering expected for the (111) face. As in the Harten et al. study,[5] this peak is broadened, but due to our poorer angular resolution, individual features around the expected position could not be resolved, making it difficult to draw any conclusions about structural changes along this azimuth.

Two methods are available to estimate the oxygen coverage: the thermal desorption yield and the attenuation of the He specular scattering intensity. Previous work with O adsorption on Au(111) under UHV conditions shows that the oxygen desorbs as O_2 above 500 K,[19,20] in agreement with our observations. Assuming a saturation coverage of 1.2 ML,[19] we should have been able to easily detect 0.1 ML, but for no exposures as short as those discussed in this paper was there any detectable O_2 desorption upon heating the crystal.

He scattering attenuation is a particularly sensitive probe for a low coverage of randomly adsorbed atoms, a reasonable possibility for the conditions of these experiments. In this case, the coverage as a function of specular scattering attenuation is given by[23]

$$\frac{I}{I_0} = (1 - \Theta)^{n\Sigma} \tag{1}$$

where Θ is the adsorbate coverage, n is the number of Au atoms per unit area (0.14/Å^2), and Σ is the scattering cross-section for the adsorbate. With a reasonable value of Σ, between 75 and 150[23] Å^2, the indicated Θ was between 0.03 and 0.06 ML for 0.3 L (Langmuir) exposure and 0.05−0.1 ML for 0.7 L exposure. These results are consistent with our estimate of an oxygen coverage on the order of hundredths of a monolayer, certainly less than 0.1 ML.

To determine the structural changes responsible for the observed scattering differences, we carried out simple scattering calculations using the eikonal approximation.[24,25] This has already been shown to work qualitatively for the reconstructed surface.[5] For the normal corrugation of the surface due to the reconstruction, we used the double Gaussian model

$$0.15\left(\exp\left[-0.5\left(\frac{x-0.5(a-r)}{5}\right)2\right] + \exp\left[-0.5\left(\frac{x-0.5(a+r)}{5}\right)^2\right]\right) \tag{2}$$

where a is the unit cell length, and r is the inter-row distance. The half-width is twice that used by Harten et al.,[5] although it is in closer agreement with the STM results.[6,7] However, the most important parameter for determining the diffraction spectrum is r. Figure 1e−h shows the results for this calculation, where the value of r is varied. Figure 1e uses a value of 26 Å, which is the value determined from the previous He scattering results, which is larger than the value of ~20 Å determined from the STM experiments.[6,7] However, both STM and calculations have a good qualitative structural agreement. As the value of r is decreased, the evolution of the relative diffraction intensities is qualitatively like the change in the experimental data with increasing O(^{3}P) exposure.

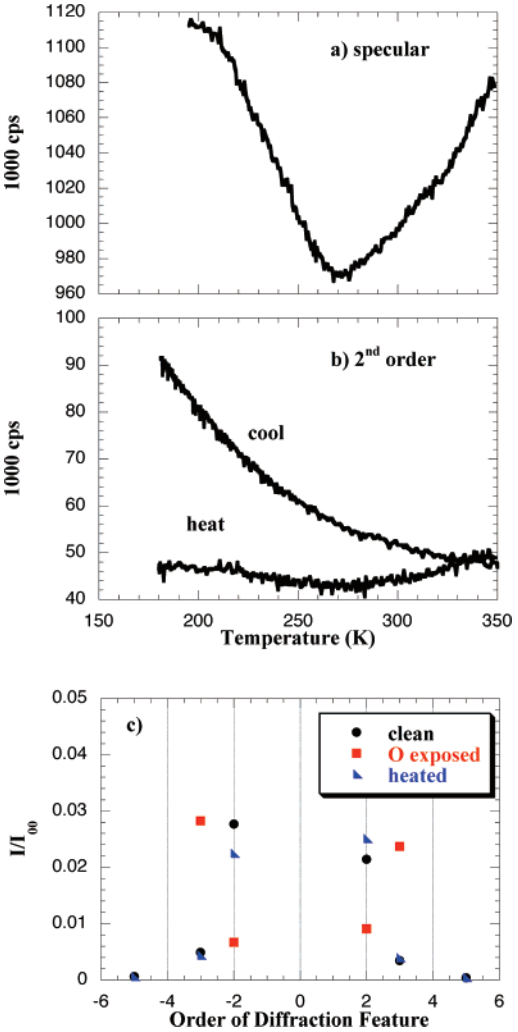

Figure 2. Intensities of some diffraction features along the $\langle 10\bar{1}\rangle$ azimuth as a function of T_s while heating and cooling the sample after exposure to 0.4 L of O(^{3}P) at $T_s = 200$ K: $\Theta_i = 45°$ and heating rate was 1 K/s. Panel a is the specular intensity while heating, and panel b is the second-order diffraction peak while first heating and then cooling. Panel c shows the normalized diffraction intensities at $T_s = 180$ K of the clean, O(^{3}P) dosed, and heated and then cooled surface.

In simplified terms, the surface atoms within the area between the maxima of the Gaussians of dimension r are in a region of hcp stacking. In the larger regions, the surface atoms are in a position consistent with the fcc sites expected for an unreconstructed Au(111) surface. The decrease in r indicates that the region of hcp stacking is becoming smaller; the surface atoms are reverting to their unreconstructed positions. One possibility is that the adsorption of the electronegative O atoms withdraws charge from the surface, causing the surface to begin reversion, or deconstruction, to a (111) structure. The precedence for this is seen in electrochemical studies, where the $23 \times \sqrt{3}$ to (111) conversion is accomplished by inducing a positive potential on an Au(111) electrode.[13−15]

Figure 2 shows what happens when an O(^{3}P) dosed surface is heated above room temperature. At first, the intensity of the specular and small second-order diffraction peaks decrease with increasing surface temperature, probably Debye−Waller attenuation. At ~275 K, this trend is reversed. Upon cooling this surface from 350 K to 180 K, both relative and absolute intensities are almost identical to those of the clean reconstructed surface. Since oxygen desorption takes place above 500 K, a reasonable explanation is that the randomly adsorbed oxygen diffuses across the surface to become trapped at defects or steps. This leaves the features responsible for the ordered diffraction spectra, the large terraces, oxygen-free and capable of reconstructing.

Conclusion

In this study, we investigated changes in the surface structure of reconstructed Au(111) when small quantities of O atoms are adsorbed, randomly, using O(^{3}P) produced from an RF beam source and He diffraction to measure the structural changes. The surface reverts to the (111) structure, possibly because the electronegative oxygen removes charge from the surface. For much less than 0.1 ML of O adsorbed at 200 K, the He diffraction spectra indicate that this deconstruction is only partially complete, and the surface quickly returns to the totally reconstructed structure upon heating to room temperature. This is probably caused by the O diffusing away from the terraces and becoming trapped at steps or defects.

These results further delineate and emphasize the delicate interplay of adsorbate coverage and surface structure for the oxygen−gold system, a topic of current high interest due to the remarkable and technologically relevant catalytic properties of gold interfaces and clusters spanning atomic through nanoscale dimensions. These results also reinforce the view that such catalytic interfaces should be treated as structurally dynamic systems, sensitive to adsorbate coverage and temperature, especially in the presence of electronegative chemisorbing species such as atomic oxygen.

Acknowledgment. This work was primarily supported by the Air Force Office of Scientific Research. We also received funding through the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, and the NSF-MRSEC at the University of Chicago, Grant NSF-DMR-0213745.

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