Atomic Arrangement of Sulfur Adatoms on Mo(001) at Atmospheric Pressure: A Scanning Tunneling Microscopy Study

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An ordered monolayer of chemisorbed sulfur adatoms on a Mo(001) surface is imaged in air, by means of scanning tunneling microscopy. The $p(2\times1)$ overlayer is observed, in agreement with low-energy electron-diffraction studies. The adsorption sites of the sulfur atoms on the molybdenum substrate are clarified, on the basis of the measured corrugation amplitudes. Atomic resolution has also been obtained in the barrier-height mode, by use of an ac synchronous detection, and with a better signal-to-noise ratio than in the constant-current (topographic) mode.

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The study of the geometric and electronic structure of surfaces at elevated pressures is of great importance to an understanding of the behavior and properties of real materials in catalysis, corrosion, passivation, and other areas of science and technology. Until recently, most surface-sensitive techniques have been restricted to ultrahigh-vacuum (UHV) environments. The pressure gap of some 10 orders of magnitude makes it difficult to infer explanations of surface phenomena at high pressures from information obtained in UHV. The advent of scanning tunneling microscopy (STM)[1] has provided the opportunity to rectify this situation. Several studies carried out at atmospheric pressure have already demonstrated the capability of STM to image inert surfaces such as graphite,[2] layered compounds,[3,4] and recently[5] Au(111) with atomic resolution.

Whereas several studies have shown the effect of the adsorbates on surface reconstructions,[6-11] to our knowledge, only one system concerning oxygen atoms chemisorbed on Ni(110) has reported atomic-resolution imaging of adsorbates on a metal surface under UHV conditions.[12,13]

In a previous paper,[14] we reported an STM study of the sulfur-Re(0001) system in air, where atomiclike features, tentatively attributed to sulfur atoms, could be imaged. The lack of long-range order prevented a conclusive statement from being made at that time. In the present study, we show in a clearcut fashion that a monolayer of ordered adsorbate atoms on a reactive metal surface can be imaged with atomic resolution, and that these images can be obtained in an atmospheric-pressure environment.

The system we chose was the sulfur-Mo(001) system for which extensive experimental results, including low-energy electron diffraction (LEED), have already been published.[15-18] At a saturation coverage of one monolayer, the sulfur overlayer shows an ordered pattern, as described by a $p(2\times1)$ superlattice. Although some speculations have been made that sulfur atoms occupy both fourfold hollow and twofold bridge sites,[17,18] no real structural data on this system are available in the literature. Also, an important point about this surface is that it appeared to be completely inert towards the adsorption of the most common atmospheric reactants: CO, H_2O, O_2, etc.

A Mo(001) single crystal was prepared by standard metallographic techniques. The sample was cleaned and annealed in UHV until a well-defined LEED pattern was obtained. It was subsequently dosed with sulfur as described in a previous publication.[16] At the saturation coverage of one monolayer, a sharp LEED pattern was obtained that revealed a two-domain structure with (2×1) and (1×2) symmetries. The surface so prepared was exposed to air for a period of 14 h and subsequently reexamined by LEED and Auger spectroscopy after pumpdown to pressures below 10^{-6} Torr. The LEED pattern was as sharp as the initial one, while the Auger spectrum revealed insignificant amounts of carbon and oxygen. The sulfur-to-molybdenum Auger-peak intensity ratio indicated no loss of sulfur after this exposure to air. The sample was then inserted into the STM apparatus which operates at atmospheric pressure and has been described in a previous publication.[19] The tips utilized in this study were prepared by our mechanically cutting a 1-mm-diam Pt-Rh(60:40%) alloy wire without any further treatment. The imaging conditions were as follows. A bias voltage of 21 mV was applied to the sample at a gap resistance of 2 MΩ, corresponding to a tunnel current of 11 nA. Images composed of 128 lines of 256 data points each were recorded with a tip velocity of 650 Å/sec. Images obtained at different bias voltages (below 0.2 V), polarities, and gap resistances were found to be similar.

Two methods of imaging were utilized. The first one is the most commonly used in STM imaging, i.e., the topographic mode. In this mode, the tip-to-surface distance is kept constant and the topography of the charge-density contour is displayed. The second method is the local barrier-height mode. In this mode, the tip-to-surface gap distance is modulated at a frequency above the feedback loop cutoff, such that the mean distance and, therefore, the mean value of the tunneling current is maintained constant. The amplitude of the ac part of the instantaneous tunnel current, as measured by a lock-in amplifier, is directly related to the square root of the local barrier height according to the simple model currently utilized to relate the tunneling current I_t to the gap distance s and the barrier height ϕ:

$$I_t \propto e^{-\lambda\sqrt{\phi}s}. \qquad (1)$$

For $s = s_0 + \delta(s)\cos(\omega t)$, the amplitude $\delta(I)$ of the first harmonic of I_t becomes

$$\delta(I) = -\lambda I_t^0 \delta(s)\sqrt{\phi}.$$

Measurement of $\delta(I)$ at each point for a given $\delta(s)$ and I_t^0 allows the recording of the barrier-height image. The modulation amplitude $\delta(s)$ used in our experiment was approximately 0.6 Å.

It must be emphasized that the signal obtained in this way might contain some contribution of the local topography, as Binnig and Rohrer have pointed out.[20] In our case, however, the topographic gradient on the slope of the sulfur atoms is less than 12°. Therefore, its contribution to the barrier-height images can be estimated at 2%, i.e., negligible. In addition, this influence would appear at double periodicity. Also, it should be kept in mind that the expression (1) of the tunneling current applies to the ideal case of two infinite, flat, structureless surfaces. It is, therefore, oversimplified for the case of a real material with spatially varying properties. It does not explicitly include the changes in the local density of states (LDOS) at the Fermi level along the surface, nor its gradient normal to the surface. For these reasons, while we will continue to use the barrier-height description throughout this paper, we shall not attach a strict meaning to it at present. Aside from these considerations, this imaging mode, which involves an ac synchronous detection, has the inherent advantage of providing a higher signal-to-noise ratio than a dc measurement as performed in the topographic mode. Binnig and Rohrer have used such a technique on the Si(111)(7×7) reconstructed surface,[21] but reported no significant spatial change in the value of ϕ within the unit cell. Since then, no atomic-resolution results have been published with this type of imaging. In the present experiments, typical modulation frequencies were 4 kHz,and the amplitude of z-piezo oscillation was approximately 0.6 Å as determined by the voltage modulation applied to it.

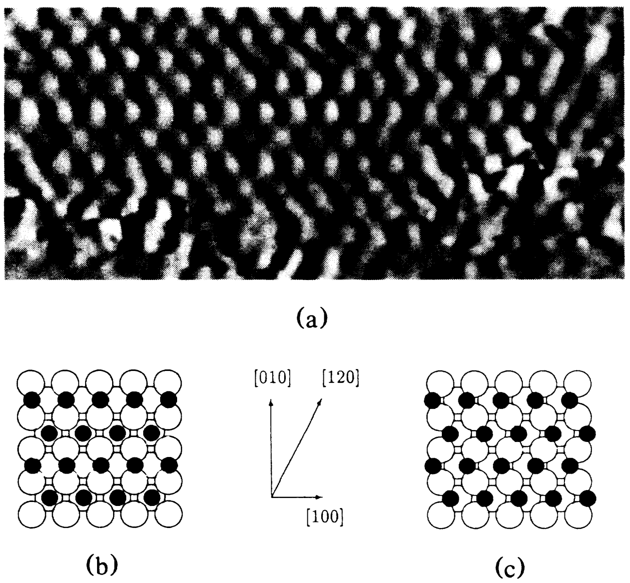

FIG. 1. (a) STM image, recorded in the barrier-height mode, of a 55×25-Å^2 region of a Mo(001)-S(100%)$p(1\times2)$ surface. (b),(c) Possible models for the $p(1\times2)$ sulfur superlattice on Mo(001).

In Fig. 1(a) we show the barrier-height image of a 55×25-Å^2 region. The pseudohexagonal arrangement of bright spots has the 1×2 symmetry of the sulfur overlayer which was observed by LEED at low pressures.[15-18] The shortest atom-atom distance on this image is 3.4 Å, which, within the precision of the piezo calibration, corresponds to the sulfur-sulfur distance of 3.1 Å along the [100] direction, in the model proposed by Clarke[15] [Figs. 1(b) and 1(c)]. In other regions of the crystal, not shown here, the pattern was rotated by 90°, corresponding to 2×1 domains. Single-scan profiles along the rows of sulfur atoms in the [100] and [120] directions are reproduced in Figs. 2(a) and 2(b). The width of the corrugation peaks is approximately equal to 1.4 Å, which is indicative of the lateral resolution achieved in this experiment. The images taken in the topographic mode had a higher background than those taken in the barrier-height mode and are not reproduced here. Topographic line profiles through the rows of sulfur atoms along the [010] and the [120] directions were measured, and are shown in Figs. 2(c) and 2(d). The width of the corrugation peaks in this case is also close to 1.5 Å. The corrugation in both directions is approximately 0.4 Å which is close to the value predicted by Lang[22] for a single sulfur atom imaged with a tip made of a sodium atom. The model proposed by Clarke[15] in which sulfur atoms occupy twofold and fourfold sites is reproduced in Fig. 1(b). However, as this author pointed out, a displacement by a quarter of a unit cell along the [100] axis [Fig. 1(c)] produces a structure where all sulfur atoms occupy equivalent sites. This structure would give rise to the same LEED pattern. Such bonding sites can be viewed as threefold sites, tak-

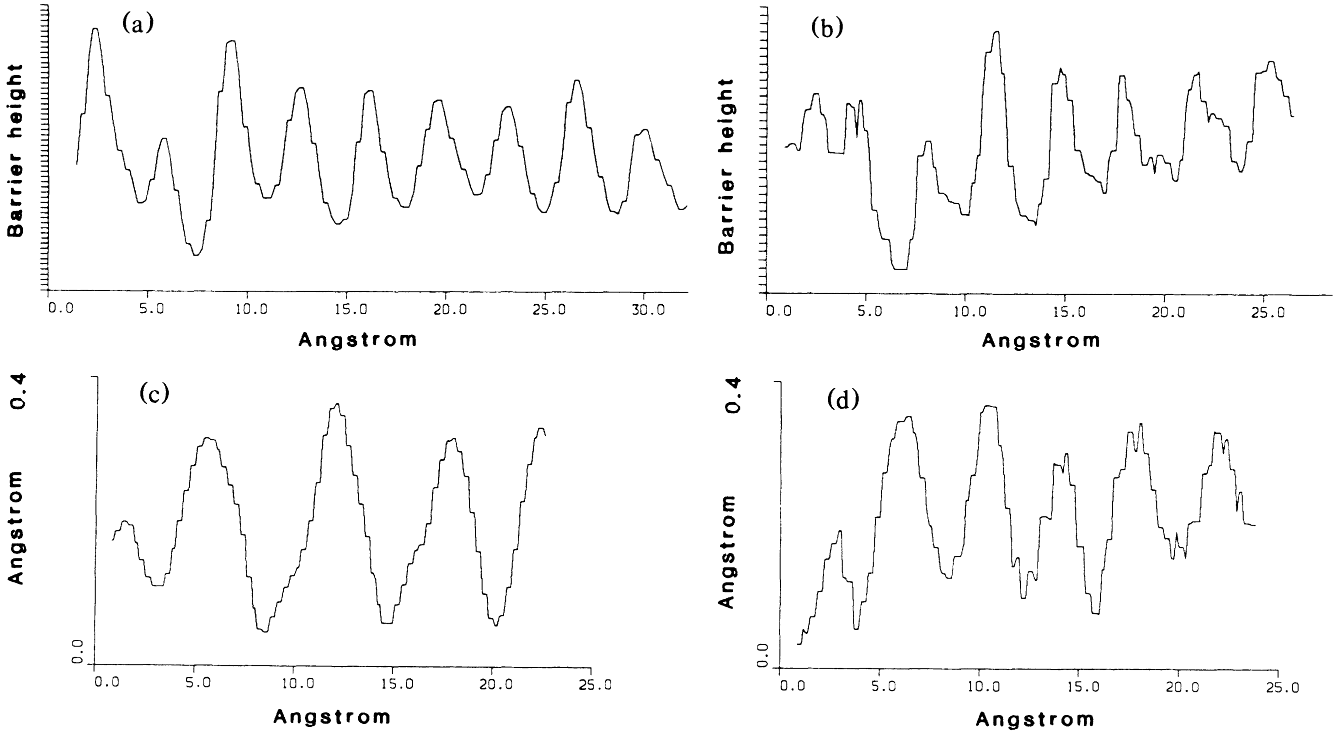

FIG. 2. Line-scan profiles along the (a) [100] and (b) [120] directions of Fig. 1(a) (barrier height mode), (c) on a topographic image, along the [010] direction where the period is twice the one in the [100] direction, and (d) along the [120] direction.

ing into account the second layer on the molybdenum atoms. Our results seem to favor the latter model, in view of the uniform corrugation that is observed along the [120] direction, for either type of imaging (Fig. 2). In the model depicted in Fig. 1(b), the [120] direction would contain sulfur atoms in alternating bridge and fourfold hollow sites. This should lead to a variation close to 0.8 Å for the peak heights of twofold and fourfold sulfur atoms, respectively, in a hard-sphere model. Line profile measurements along the [120] direction, reproduced in Fig. 2(d), show a corrugation difference not greater than 0.1 Å for the two kinds of sulfur atoms. This conclusion, however, must be taken with some caution, as the line profiles show the corrugation of the LDOS at the Fermi level and at some distance from the surface.

In the barrier-height images described above, the bright, high-barrier-region spots were attributed to the tops of the sulfur atoms. Feibelman and Hamann have calculated the LDOS at the Fermi level for sulfur on Rh(100).[23] From their calculations, it appears that both the contour of the LDOS and its gradient normal to the surface show maxima at the position of the sulfur atoms. This higher gradient would increase the amplitude of the tunneling current in a modulation experiment. Unfortunately, their calculations do not extend to distances of the order of typical tip-to-surface distances of STM experiments (5 to 10 Å). The change of the electrostatic potential $\delta\phi_0$ caused by the absorption of an isolated sulfur atom on a jellium substrate has been calculated by Lang, Holloway, and Nørskov.[24] This calculation indicates that $\delta\phi_0$ attains its maximum on top of the atom, which also favors our interpretation.

The important result of this paper is that it proves that atomic-resolution imaging for adsorbate atoms on metals can be achieved with STM in both the topographic and the barrier-height modes, and moreover, it does not necessitate an UHV environment. In the present study, atomic resolution could be attained in some regions of the sample even after the crystal was exposed to the atmosphere for four days. After this long period, reinsertion in UHV indicated that the crystal had accumulated substantial amounts of oxygen and carbon, while the initial S/Mo Auger peak ratio was maintained. A large part of the crystal surface was not atomically resolved in this experiment. This could be explained by the presence of partially conductive contaminants and/or highly oxidized spots on the surface. The area around the ordered structure in Fig. 1(a) is an example of an unresolved region. Other ordered structures of various symmetries were also observed on different areas and will be discussed in a more extended paper, along with observations of the rotated domains.

In conclusion, we have shown that chemisorbed atoms on a metal can be observed with spatial resolution in the angstrom range with STM operating in the topographic or in the barrier-height mode. The advantages of operation in the barrier-height mode are demonstrated in the superior signal-to-noise ratio it provides. We have also demonstrated for the first time that atomic-resolution imaging of surfaces with a chemisorbed layer is achievable in an atmospheric-pressure environment. This opens the way for detailed, *in situ* studies of the structure of catalytically important surfaces, obtained under reaction conditions.

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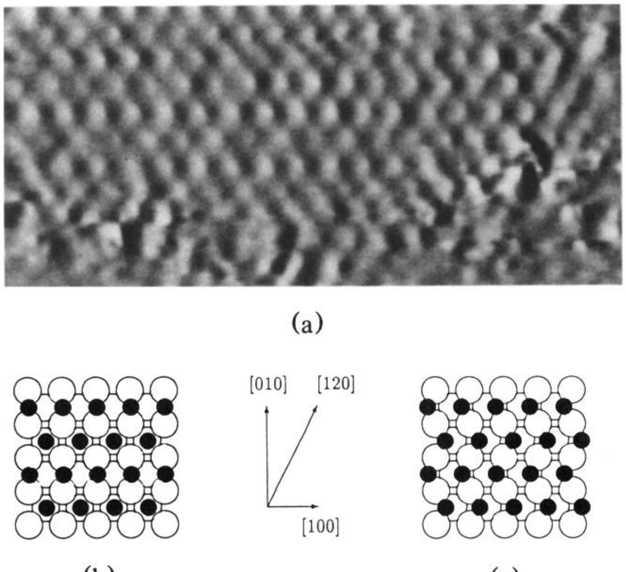

(a)

(b)

(c)

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