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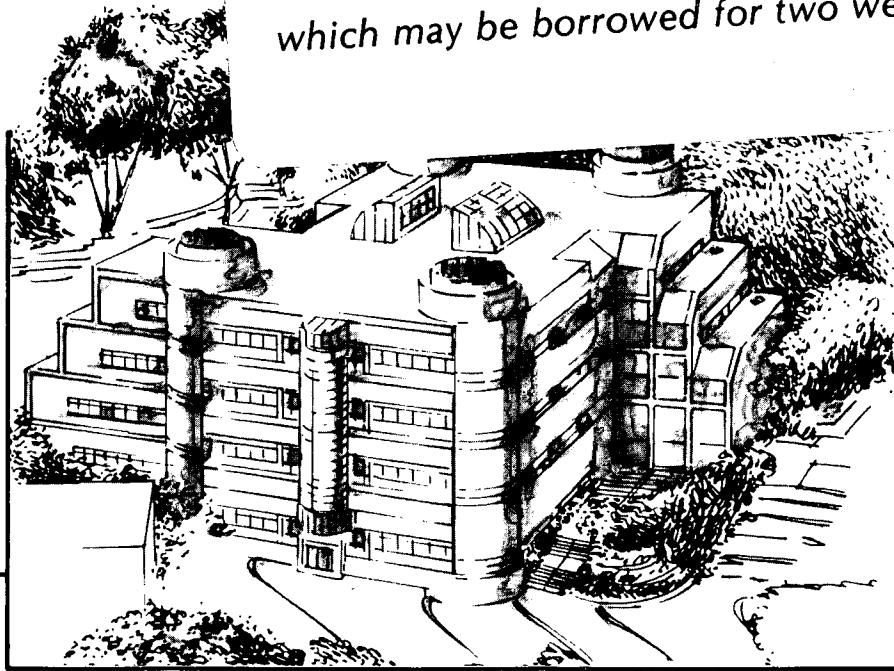**Center for Advanced Materials**

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ATOMIC ARRANGEMENT OF SULFUR ADATOMS ON Mo(001) AT ATMOSPHERIC PRESSURE: A SCANNING TUNNELING MICROSCOPY STUDY

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The study of the geometric and electronic structure of surfaces at elevated pressures is of great importance to understand the behaviour 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 Ultra High 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] and recently Au(111)[4] with atomic resolution.

Whereas several studies have shown the effect of the adsorbates on the surface reconstruction[5-7], and surface roughening[8] of surfaces, to our knowledge, only one paper by Baro et al.[9] concerning oxygen atoms chemisorbed on Ni(110) has reported atomic resolution imaging of adsorbates on a metal surface.

In a previous paper[10], we reported an STM study of the sulfur-Re(0001) system in air, where atomic-like features, tentatively attributed to sulfur atoms, could be imaged. The lack of long range order prevented a conclusive statement to be made at that time. In the present study, we show for

the first time 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 Low Energy Electron Diffraction (LEED) experimental results have already been published[11,12]. At a saturation coverage of one monolayer, the sulfur overlayer shows an ordered pattern, as described by a $p(2 \times 1)$ superlattice. The 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 using 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[12]. 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 hours and subsequently reexamined by LEED and Auger Spectroscopy after pump-down 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

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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[13]. The tips utilized in this study were prepared by mechanically cutting a 1 mm diameter 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 megaohms, 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 Angstroms per second. Images obtained at different bias voltages (below 0.2 volts), polarities and gap resistance, 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 cut-off, 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

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ϕ:

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

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

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

Measuring $\delta(I)$ at each point for a given $\delta(s)$ and I_t^0, allows the recording of the barrier height image. It must be emphasized that the signal obtained in this way might contain some contribution of the local topography as Binnig et al. have pointed out[14]. In our case, however, the atomic flatness of the surface should not make this effect too crucial. Also, it should be kept in mind that this simple picture is for an idealized case of two infinite, flat, structureless surfaces. It is, therefore, over simplified when it is applied to 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 topo-

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graphic mode. In the present experiments, typical modulation frequencies were 4 kHz, and the amplitude of z-piezo oscillation was approximately 0.6 Angstroms as determined by the voltage modulation applied to it.

In figure 1a we show the barrier height image of a 60×30Å region. It should be emphasized that this image is the raw data, without any filtering and/or processing. The pseudo hexagonal arrangement of bright spots has the 1×2 symmetry of the sulfur overlayer which was observed by LEED at low pressures[11,12]. The shortest atom-atom distance on this image is 3.4Å, which, within the precision of the piezo calibration, corresponds to the sulfur-sulfur distance of 3.1Å along the [100] direction, in the model proposed by Clarke[11] (figures 1b and 1c). In other regions of the crystal, not shown here, the pattern was rotated by 90 degrees, corresponding to 2×1 domains. Single scan profiles along the rows of sulfur atoms in the [100] and [120] directions are reproduced in figures 2a and 2b. The lateral resolution as estimated from the half-width at half maximum of the corrugation peaks is approximately equal to 1.4 Angstroms. The images taken in the topographic mode were of lower quality than those taken in the barrier height mode and are not reproduced here. Some topographic line profiles through the rows of sulfur atoms along the [010] and the [120] directions could be measured, and are shown in figures 2c and 2d. The horizontal resolution in this case is also close to 1.5 Angstroms. The corrugation in both

directions is approximately 0.1 Angstrom. The model proposed by Clarke[11] in which sulfur atoms occupy two- and four-fold sites is reproduced in figure 1b. However, as this author pointed out, a displacement by a quarter of a unit cell along the [100] axis (figure 1c) produces a structure where all sulfur atoms occupy equivalent sites. This structure would give rise to the same LEED pattern. Our results seems to favor the latter model, in view of the uniform corrugation that is observed along the [120] direction, for either type of imaging (figure 2). In the model depicted in figure 1b, the [120] direction would contain sulfur atoms in alternating bridge and four-fold hollow sites. This should lead to a corrugation close to 0.8 Angstrom, assuming a hard-sphere model for the sulfur atoms. This value is far greater than what can be deduced from our STM measurements reproduced in figure 2d. 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 regions spots were attributed to the top of the sulfur atoms. Feibelman et al. have calculated the LDOS at the Fermi level for sulfur on Rh(100)[15]. 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

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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 adsorption of an isolated sulfur atom on a jellium substrate has been calculated by Lang[16]. 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 using STM, and moreover, it does not necessitate an UHV environment. To our knowledge, it is also the first time that an atomically resolved structure has been imaged in the barrier height mode. 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 figure 1a 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 metals can be observed with spatial resolution in the Angstrom range with STM. The advantages of operating 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 chemisorbed layers is achievable in an atmospheric pressure environment. This opens the way for detailed, *in situ* studies of the structure of catalytically important surfaces operating at high pressure.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1 - a) STM image recorded in the barrier height mode, of a $60 \times 30 \mathring{A}$ region of a Mo(001)-S(100%) $p(1 \times 2)$ surface. This image is is a raw, un-processed STM image. b) and c) Possible models for the $p(1 \times 2)$ sulfur superlattice on Mo(001).
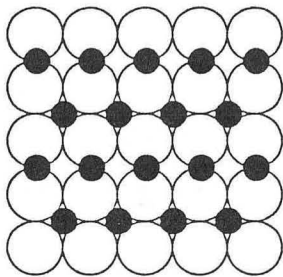
Figure 2 - Line scan profiles along the a) [100] and b) [120] lines shown by the arrows on figure 1a (barrier height mode). c) On a topographic image, along the [010] direction where the period is twice the one in the [100] direction and d) along the [120] direction.
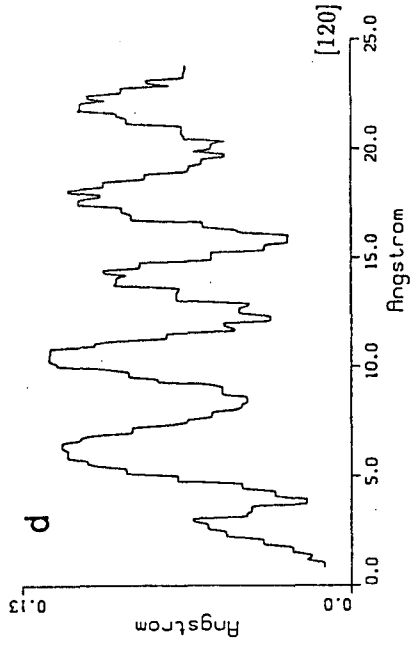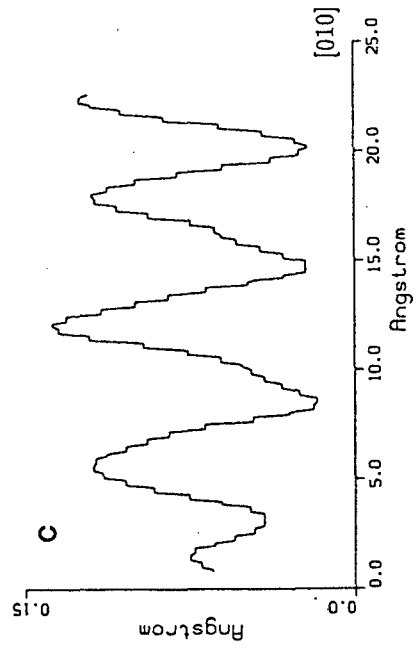
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(a)

(b)   (c)

[010]   [120]

[100]
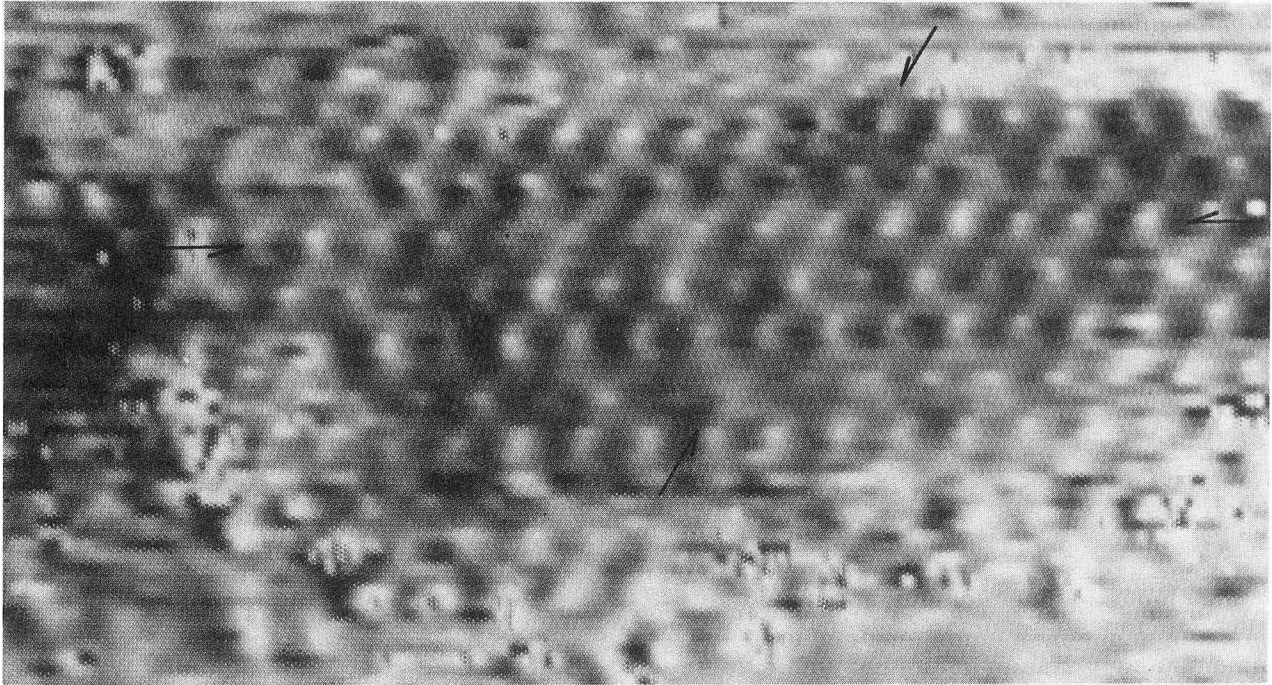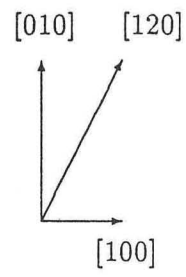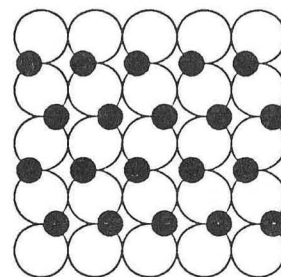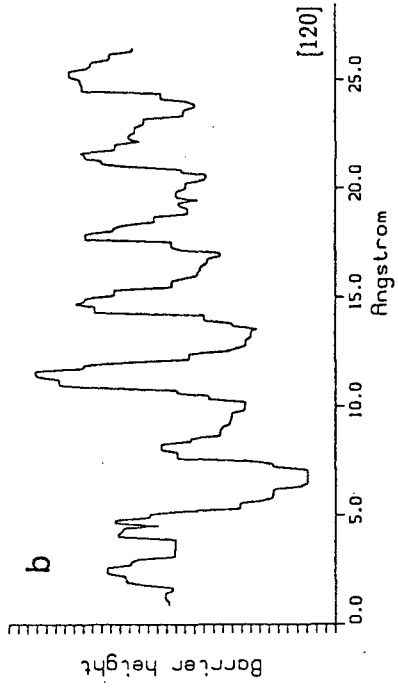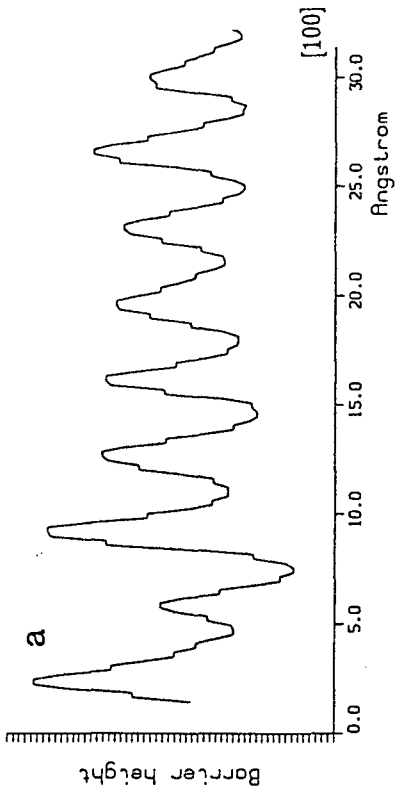
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