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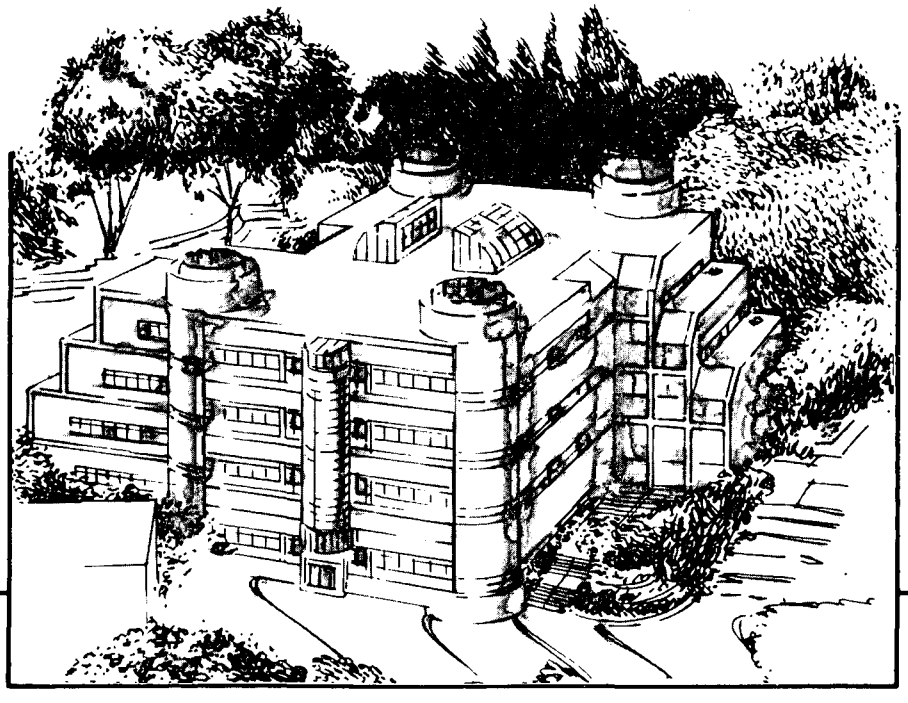

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THE PRESENT STATE OF UNDERSTANDING OF THE ROLE OF SULFUR IN MODIFYING THE FRICTION AND LUBRICITY OF METAL SURFACES

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THE PRESENT STATE OF UNDERSTANDING OF THE ROLE OF SULFUR IN MODIFYING THE FRICTION AND LUBRICITY OF METAL SURFACES

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Recent surface crystallography studies using scanning tunneling microscopy and low energy electron diffraction reveal the coverage dependent changes of the surface structure of sulfur on rhenium surfaces. There is evidence of metal reconstruction as the sulfur metal bonds are formed and there is evidence of clustering of sulfur atoms that form trimers, tetramers and hexamers at increased coverages. Contact experiments using the STM reveal that the elastic properties of the surface are maintained by the protecting S overlayer. The implications of the STM and LEED crystallography findings to tribology and the importance of sulfur monolayers in modifying the mechanical properties of surfaces are discussed.

In recent years the development of the scanning tunneling microscope and the atomic force microscope permits us to obtain real space images of surface atoms and adsorbed molecules and to apply forces in the range of 10^{-9}-10^{-4} Newtons on the atomic scale that are less or slightly more than required to break bonds between atoms. New non linear laser spectroscopy techniques are being developed (SHG and SFG) that are not only totally surface sensitive but provide access to the buried solid-solid or solid-liquid interfaces that are not accessible to electron or ion probes (*1*). Therefore, it is not surprising that the attention of surface scientists is now focusing on phenomena that occur at these solid-solid and solid-liquid interfaces that include mechanical properties such as adhesion, friction and lubrication. Our aim is to understand, on the molecular level, how bonding occurs and how the mechanical properties at these surfaces are determined by the surface structure and surface bonding.

To this end, we undertook studies of the passivating properties of sulfur monolayers on the Mo(001) and the Re(0001) crystal faces. Sulfur forms an ordered monolayer on these metal surfaces and exhibits surprising and diverse structural chemistry as a function of coverage. We studied these sulfur monolayer structures by both LEED and STM (*2-6*). The adsorbate induced restructuring of rhenium has been identified by LEED crystallography (*7*). Substrate mediated adsorbate-adsorbate (sulfur-sulfur) interactions gives rise to clustering in the otherwise already ordered sulfur layer to produce 3, 4 and 6 member sulfur clusters of unique geometry. Sulfur is an important component in many organic and inorganic lubricants. The overlayers that it forms have structural and chemical properties that illustrate many of the reasons for its unique lubricity and passivating characteristics against mechanical or chemical attack on surfaces.

Mechanical Force Needed to Break a Chemical Bond

Consider a surface atom bound to its neighbors by a chemical bond of binding energy of the order of 1eV. We can estimate the mechanical force, F, necessary to break this bond by computing the force needed to displace the atom by 1Å, the order of magnitude of bond lengths. Thus the force needed to stretch the bond is given by F = 1eV/1Å which yields 1.6 x

10^{-9} Newton. We need forces in the range of 10^{-9}-10^{-8}N per atom to break the bond which corresponds to 0.1-1μgm. The atomic force microscope can explore contact forces on the atomic scale. As the microscope tip approaches the surface at distances of 2Å or less, the forces (attractive then repulsive) exerted on the tip by the surface can be measured in the range as small as 10^{-9} Newton and up to 10^{-4} Newton. After applying a force of certain magnitude the area of tip contact is scanned for signs of permanent damage. Using a smooth Au surface (as shown in Figure 1), permanent damage could only be detected at about 10^{-5} Newtons with a tip radius of 10^3Å (*8*). This indicates that the metal surface responds to the approaching metal tip by elastically deforming in the range of up to 1.0 GPa pressure. This is the regime of elastic deformation. Only by applying a pressure greater than 1.0 GPa will plastic deformation commence on Au surfaces accompanied by irreversible displacement of Au atoms as shown in Figure 1. From measurements of this type one can determine the forces needed for elastic or plastic deformation on the atomic scale and to correlate the results with those obtained by macroscopic studies.

Sulfur Structures on Re(0001) Crystal Face. LEED and STM Studies

The structures formed by sulphur on Re(0001) surfaces as a function of coverage θ, have been studied by LEED and AES (*4*). At saturation (θ=0.50) S imparts to the Re(0001) surface passivating properties. In particular it was shown that such a monolayer prevents oxidation of Re upon exposure to air. STM experiments revealed that the S-structure was stable and could be imaged in air (*9*). To study the structures formed at lower coverages, the experiments have to be performed in UHV. We have recently completed studies of the structures formed from around θ=0.25 up to θ=0.50 (*7,8*). The outcome of these studies constitutes a dramatic demonstration of how STM helps solve structures with large unit cells. The capability to study complicated structures is not only an incremental refinement of crystallographic techniques, but uncovers new phenomena, like new phases formed by adsorbate aggregation. We describe now briefly these findings. Up to a coverage of 0.25, S-S repulsive first neighbor pairwise interactions dominates the structure of the absorbed layers. The structure formed is (2x2) and is shown in Figure 2a . As the coverage increases, the next ordered structure of high symmetry that maintains the monomeric form of S is the $(\sqrt{3}x\sqrt{3})R30$ when θ=0.33, as observed on many other single crystal surfaces (*10,11*). Instead, on Re(0001) a new phase forms in which S coalesces into trimers, first near domain boundaries and then at all regions. In these trimers, each sulphur atom sits on the same three-fold hollow site as in the low coverage monomer structures. The fact that dimers do not form except as occasional defects indicates that three-body forces are determinant at this stage. Three body forces were previously introduced as necessary corrections to the dominant pairwise interactions in Monte Carlo simulations of gas lattice dynamics in order to fit the experimental data (*12*). Here, these forces are dominant and cause the local coverage to change abruptly from 0.25 to near 0.45 (the value of θ for the ordered $(3\sqrt{3}x3\sqrt{3})R30^\circ$ structure described below.) Initially, the trimers are identical and have their center in a three-fold hollow site. As the coverage continues to increase, trimers of a different structure form that are rotated 60° relative to the first ones and have their center on a top site. At maximum trimer density an ordered $(3\sqrt{3}x3\sqrt{3})R30^\circ$ structure forms that is composed of trimers of the two types in a 3 to 1 ratio, as shown in Figure 2b. Atom counting indicates that the coverage is 0.45. By adding more sulphur to the surface, the trimers incorporate a fourth sulphur atom and rearrange to form tetramers. The schematic of Figure 2c shows the new structure formed at completion, a (3,1;1,3) in LEED matrix notation. The coverage, determined by counting atoms, is 0.5. This observation came as a surprise. The highest coverage structure (and saturation) was thought to be the one obtained by further sulfur dosing, with a $(2\sqrt{3}x2\sqrt{3})R30^\circ$ structure, where S forms hexagonal units as shown in Figure 2d and in the image at the top of Figure 3. The coverage here is again

0.5. To form this last structure, a higher exposure to H_2S or S_2 is required. By heating this saturation structure to increasingly higher temperatures to desorb sulfur, all the lower coverage ones can be generated, including the tetrameres that coexist with the trimers and defects. The $(2\sqrt{3}x2\sqrt{3})R30^\circ$, structure might be energetically more stable than the (3,1;1,3), but it requires a substantial rearrangement of sulphur atoms in order to break the trimer unit. Thus the tetrameres structure is kinetically stabilized against the more stable hexagonal ring structure.

The Role of Coadsorption and Strongly Adsorbed Monolayers During Tribological Change (Friction, Lubrication)

High coverages of chemisorbed molecules exhibit decreasing heats of adsorption indicating the weakening of the average adsorbate-substrate bond. This effect is due to the adsorbate-adsorbate interaction that often forces the molecule onto new adsorption sites. The coadsorption of two different molecules, one an acceptor the other a donor to the metal substrate, leads to ordering into a mixed layer due to attractive adsorbate-adsorbate interaction. One example of this is the surface structure that forms upon the coadsorption of carbon monoxide and ethylene (*13*). The coadsorption of two donors or two acceptors yields disordered monolayers as indicated by several studies (*14*). However, there are many examples indicating that one of the chemisorbed species during coadsorption can also restructure the substrate. Chemisorbed potassium restructures iron oxide (*15*), oxygen or alumina restructures iron (*16*) and sulfur or carbon restructures nickel and rhenium (*7*). Thus, the chemisorbed coadsorbed species exert their chemical influence not only by altering the adsorbate-adsorbate bond but also through restructuring of the substrate. This effect is particularly noticeable during catalytic reactions and could be very important during lubrication. A monolayer of strongly chemisorbed atoms, sulfur for example, can act as a lubricant markedly decreasing the friction coefficient of the surface. The good lubricating properties of S compounds derive in our opinion from the strong S-metal bonds formed at the surface. The strength of these bonds is such that S-covered surfaces are chemically passivated against chemical attack, even when the new bonds to be formed by the reactive species are stronger than those formed by S. The reason for this is kinetics, not thermodynamic equilibrium. At saturation S-coverages, oxidation by air exposure, for example, is inhibited by the lack of empty or exposed Re sites that are necessary to dissociate the attacking O_2 molecule.

During mechanical contact, S overlayers can thus prevent the formation of metal-metal bonds between the contacting bodies. The situation can be compared to that of layer compounds such as MoS_2. Cleavage along the Van der Waals layers, that are separated by 2 sulfur layers, is easy and does not disrupt bonds within the layers.

We have performed studies to illustrate these ideas by studying the elastic contact between a PtRh tip (probably covered with S) and a Re(0001) surface that is also saturated with S. We describe the results in the next section.

Elastic Properties of Sulfur Monolayers on Metals

In order to study the tip-surface contact, we measured the changes in tunnel current as a function of tip displacement over the sulfur covered Re(0001) surface (*17*). An ordered $(2\sqrt{3}x2\sqrt{3})R30^\circ$ sulfur overlayer was first prepared in UHV and the sample was afterwards transferred through air to an STM operating in a 10^{-7} Torr vacuum.

In the experiments presented here, the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ sulfur structure was first imaged in the topographic mode at a gap resistance of 20MΩ and a -16mV sample bias (Figure 3). The tip was then positioned in the middle of the image, the feedback loop was disabled, and the tip was advanced until a predetermined current I_{max} was obtained. Currents as large as 900 nA

were obtained after z piezo displacements of 20Å, as shown in Figure 3. The gap resistance reached values as low as 20 kΩ, on the order of the Sharvin point contact resistance. However, no changes were seen in atomic resolution images of the sulfur overlayer recorded before and after tip approach, indicating that only elastic deformations of the tip or sample took place during the contact. Advances larger than 20Å and 900nA did however result in irreversible disruption of the surface.

Tip-surface forces could not be directly measured in these STM experiments. However, if we assume that most of the 20Å displacement is due to elastic deformations of tip or sample, we can get to an estimate. First, we assume a rigid gap and a deformable tip and/or surface with increasing area of contact as the tip advances. The increase in current would then be proportional to the increase in contact area and we can treat the measured gap resistance as the Sharvin resistance $R = 4\rho l/3\pi a^2$. Here ρ is the specific resistivity of the material, l is the electron mean free path, and $a = a(z)$ is the radius of the circular contact area as a function of tip displacement z. It depends on the tip shape as the only parameter. Indeed, we obtain a good fit to the data of Figure 3 by implying a conical tip (solid line). Using the elastic moduli of Re and PtRh and a radius of 100Å for the tip (estimated from the observed step widths in the STM image), the initial compressive force is estimated to be of the order of 10^{-6} N and the maximum gap pressure ≈10GPa.

Summary

The combination of surface structural studies on well characterized surfaces using LEED and STM and measurements of the mechanical properties by AFM appear promising for studies of tribological properties (friction, lubrication) on the molecular scale. There are many surprises along the way as demonstrated by studies of the S/Re(0001) system. There is ordering in the chemisorbed S layer, chemisorption induced restructuring and complex adsorbate-adsorbate interaction among the sulfur atoms leading to clustering (S_3, S_4 and S_6). Many of the properties of the S/Re(0001) interface system identified in these investigations and in particular the very strong S-Re bonds that allow effective blocking of Re sites to further chemical attack, contribute to make sulfur a premier ingredient in lubricants and lubricating systems.

Acknowledgment

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FIGURE CAPTIONS

Fig. 1. Atomic Force Microscopy images of an oriented Au film on mica. Before each image the tungsten tip was pressed against the surface in the center of the image. Permanent indentations were only observed above 6.5×10^{-5} Newtons. The tip radius is estimated from the diameter of the indentation to be close to 1,000Å. After Blackman and Mate (*8*).

Fig. 2 Schematic diagram showing the S structures formed on Re(0001) as a function of coverage. The position of the S atoms (grey circles) was determined by LEED I-V analysis in the case of the (2x2) structure (a). (b), (c) and (d) show the various ordered S aggregate structures that were detected by STM. The adsorption site was determined by a combination of LEED and STM *(5,6,9)*.

Fig. 3. (Top) STM topographic image showing the $(2\sqrt{3}x2\sqrt{30})R30^\circ$ sulfur structure. Hexagonal rings of sulfur constitute the unit cell and are clearly visible in the image, along with defects and a domain boundary running diagonally. The blurred region is a step, two atoms high, separating two terraces. The compression of the distance scale along the diagonal is the result of thermal drifts.

(Bottom) Tunnel current and gap resistance as a function of tip displacement over a surface similar to that of the image shown on top. Tip displacement is measured relative to the initial tunneling conditions of 8 nA and -16mV sample bias. The symbols show different runs from the same sample and tip and the solid line is calculated by assuming the current increase is due solely to an increase of the area of contact for a conical tip.

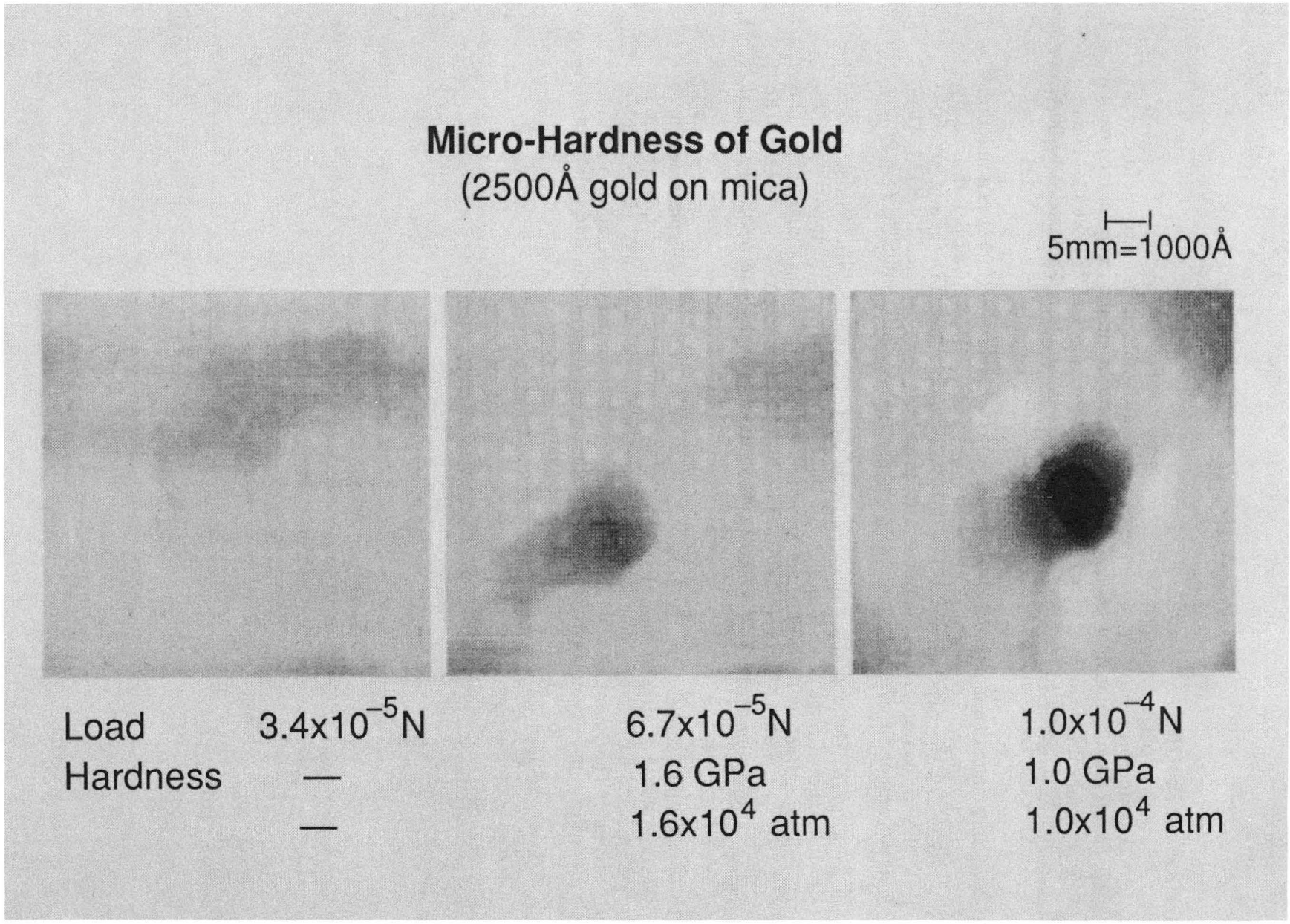

Figure 1

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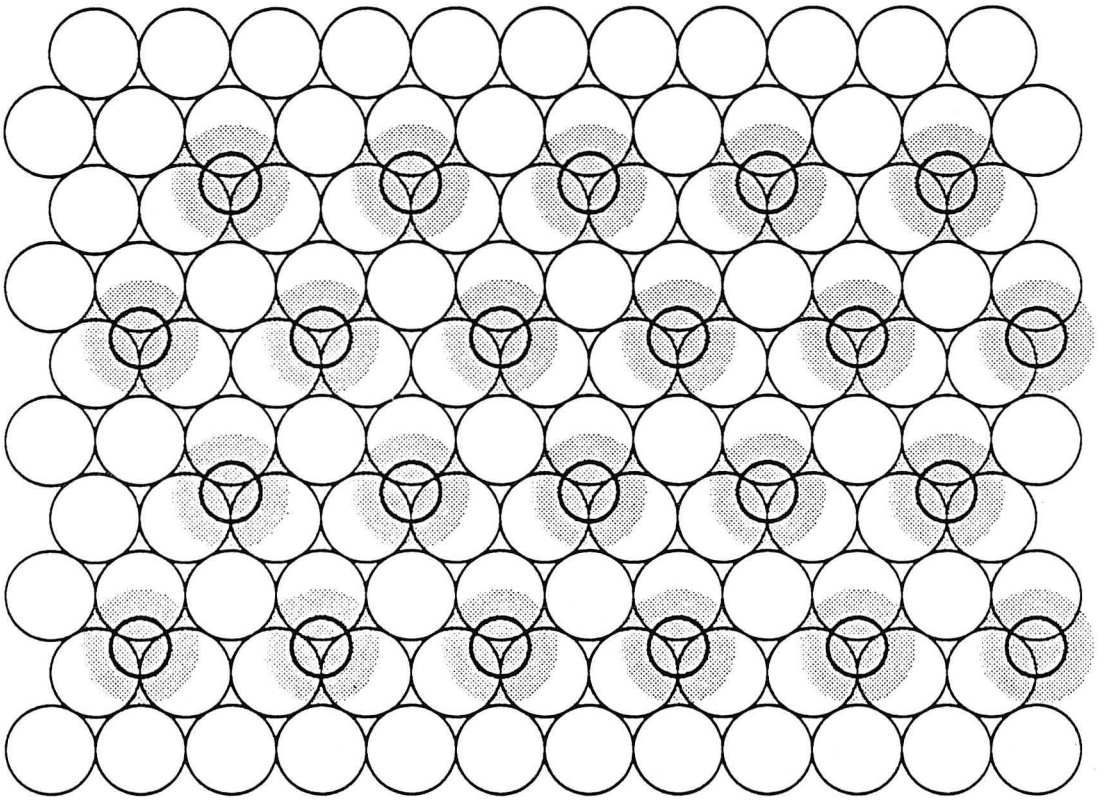
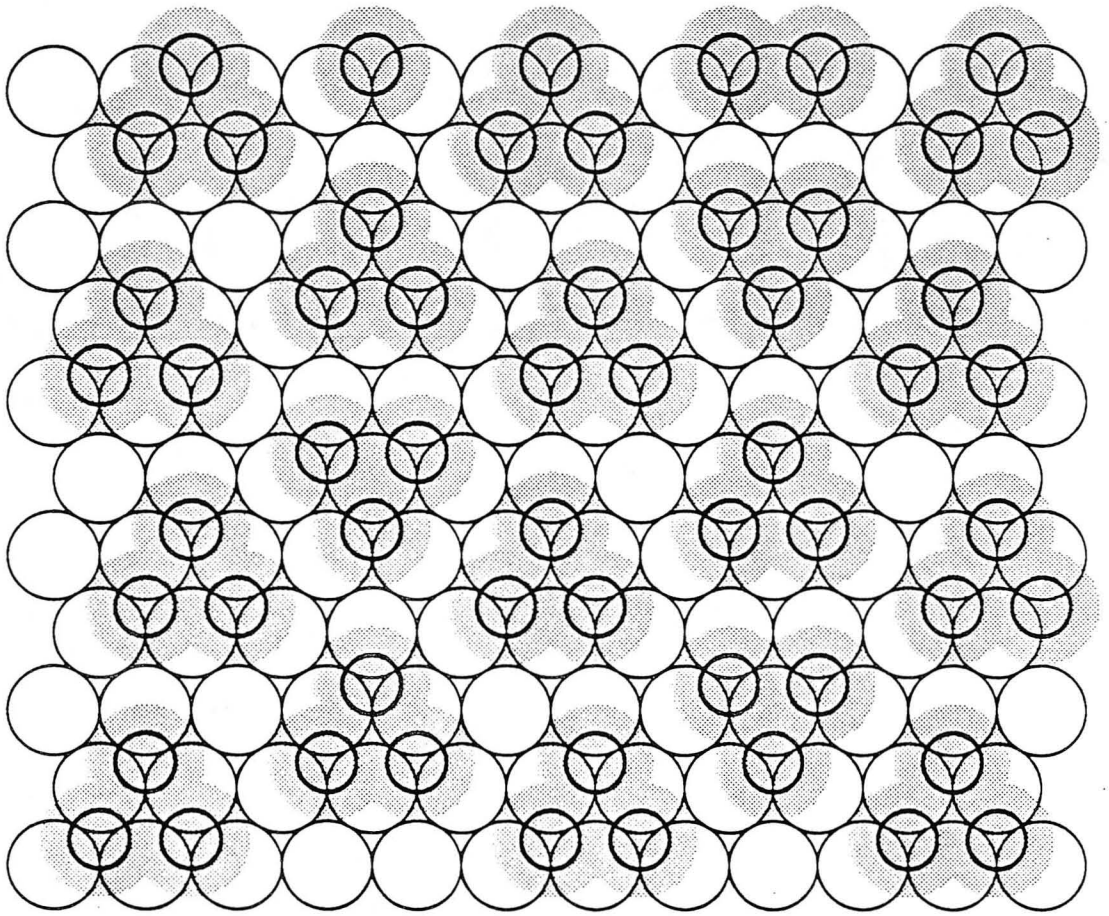


Sulfur 2 x 2 on Re(0001)

XBL 907-6444

Figure 2a



Sulfur $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ on Re(0001)

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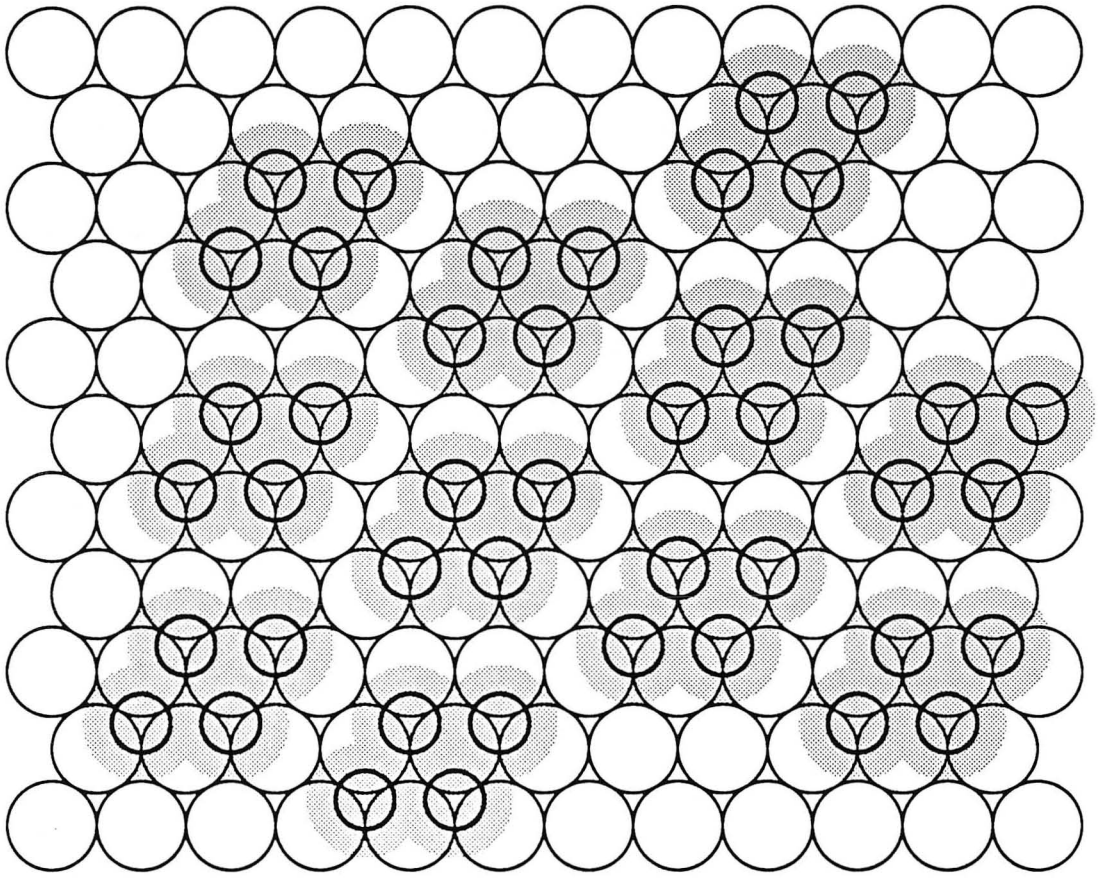
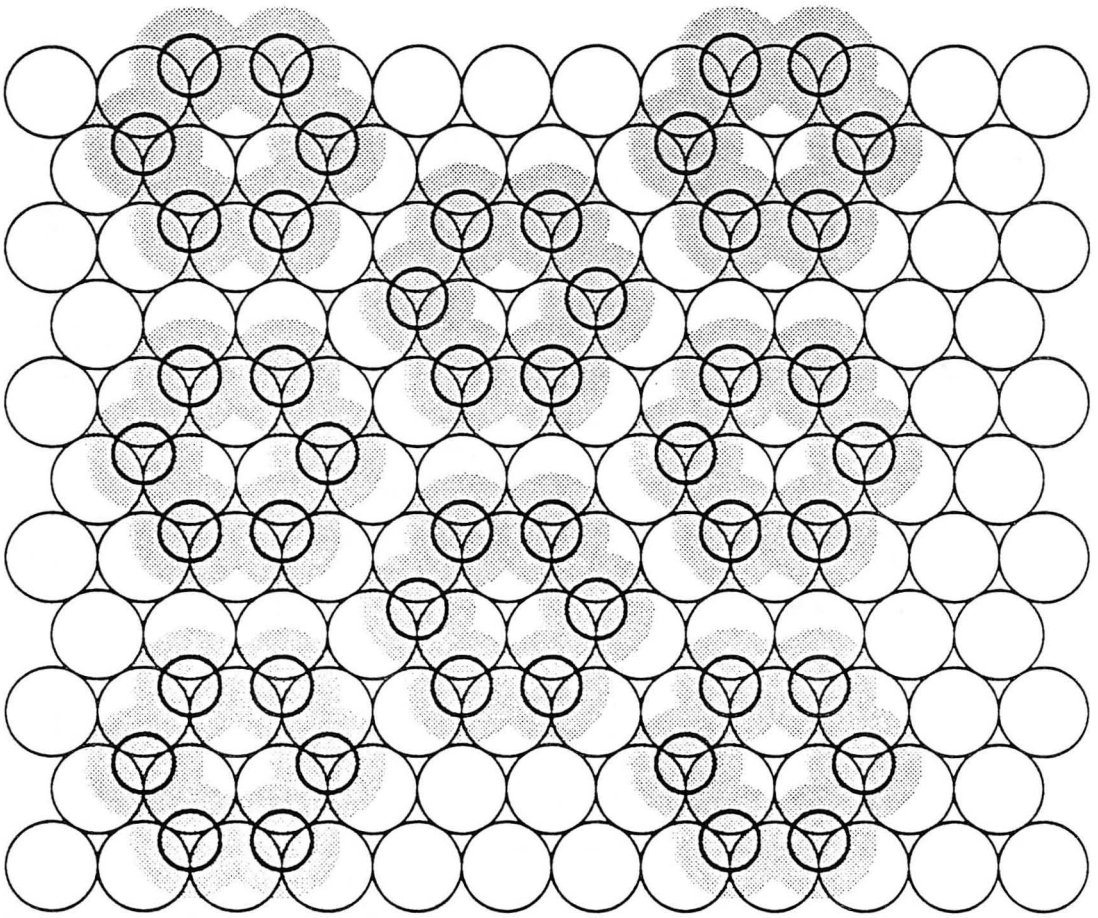
Figure 2b



Sulfur $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ on Re(0001)

XBL 907-6446

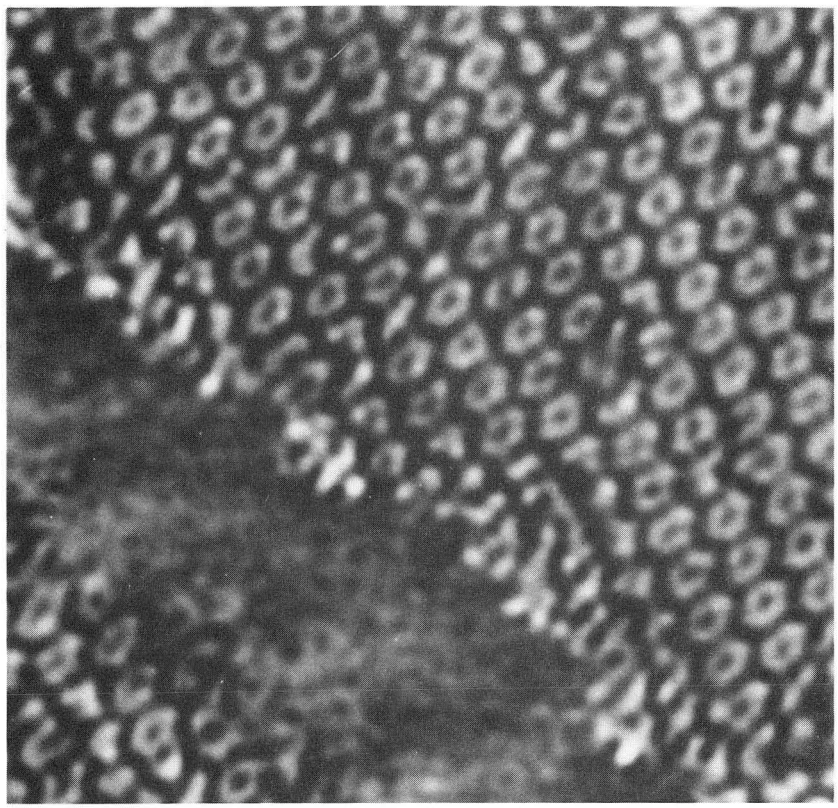
Figure 2c



Sulfur $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ on Re(0001)

XBL 907-6447

Figure 2d



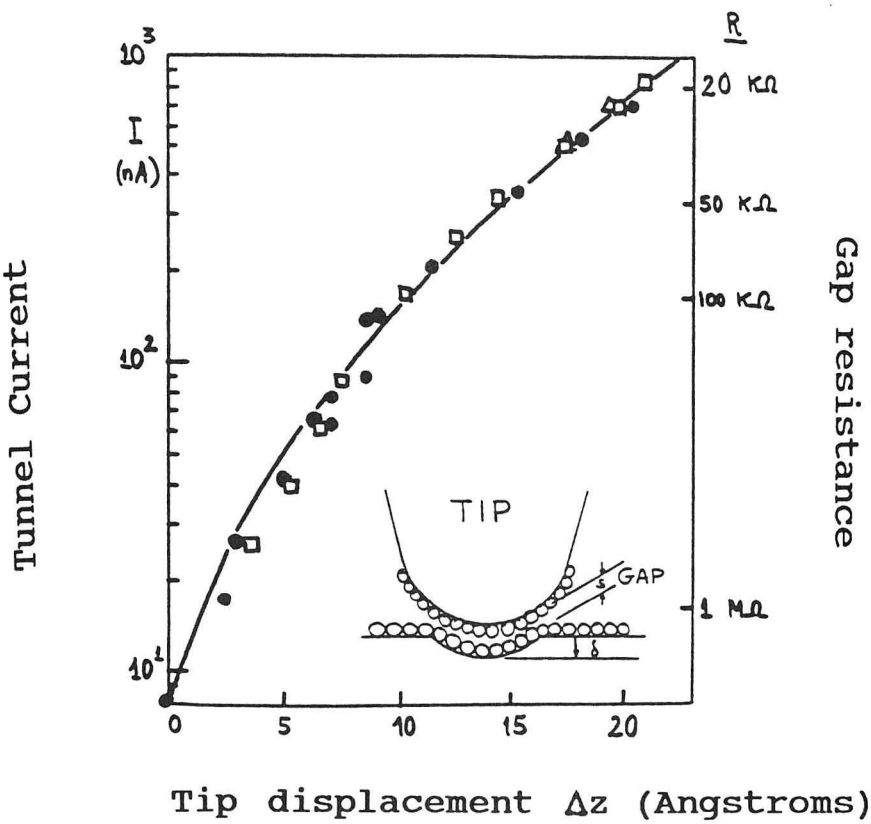


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Figure 3

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