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Brief Reports

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Formation of sulfur clusters on Re(0001) surfaces observed with the scanning tunneling microscope

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We have studied the various structures formed by sulfur on Re(0001) single-crystal surfaces using a scanning tunneling microscope. At coverages of 0.25 monolayer and below, open lattices formed by single adatoms are formed, mostly with a (2×2) structure. Between 0.25 and 0.5 monolayer, phases consisting of three-, four-, or six-adatom clusters are observed. The sulfur trimers are formed first randomly in the (2×2) regions and then ordered as their coverage increases to saturation at 0.45 monolayer. In all cases sulfur atoms are adsorbed in threefold hollow sites. The formation of sulfur clusters above 0.25 monolayer is interpreted as evidence of substrate-mediated many-body forces.

The forces between atoms and molecules that determine the structure of adsorbed layers can usually be described in terms of pairwise attractive or repulsive interactions. Three-adatom interactions have been combined with pairwise interactions in several cases to model adsorbate structures in Monte Carlo calculations; however, the three-adatom interactions have always been small corrections to the dominant pairwise interactions.[1-3] In this paper we describe a system where three- or more-adatom interactions dominate the adsorbate ordering.

Sulfur and other electronegative elements adsorbed on metal surfaces often form ordered layers characterized by strong repulsive forces between adatoms.[4,5] Sulfur forms an ordered (2×2) overlayer on Re(0001) at a coverage of 0.25 monolayer (ML, defined as one sulfur adatom per substrate unit cell). At coverages between 0.25 and 0.5 ML sulfur adatoms form three-, four-, and six-adatom clusters. Larger clusters are never observed and dimers are rarely seen and are not found in ordered regions. This type of adatom clustering above a critical concentration has never been reported before. It illustrates the effects of three- and more-adatom interactions on adsorbate ordering and the novel adsorbate phases that result.

The sulfur adsorption experiments were carried out in an UHV chamber equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and a scanning tunneling microscope (STM) of our own design.[6] The Re(0001) crystal was cleaned by heating in O_2 until the carbon contamination was removed, then exposed to H_2S gas at or below 10^{-7} Torr while the crystal was maintained at approximately 850 K. Sulfur coverages up to 0.5 ML can be obtained in this manner. The sulfur coverage can be reduced by heating the crystal in vacuum to desorb sulfur. After cooling to room temperature the adsorbate order was checked by LEED then the crystal was transferred to the STM for imaging. STM images were obtained in both topographic and current modes with gap resistances between 20 and 200 MΩ using mechanically cut Pt–40%Rh tips. Varying the sample bias voltage from -1.5 to $+1.5$ V had no significant effect on image contrast. Outside this range the gap became unstable and the image quality deteriorated.

Four ordered structures have been reported for sulfur adsorbed on Re(0001). The LEED patterns, in order of increasing sulfur coverage, are (2×2), $(3\sqrt{3}\times3\sqrt{3})R30°$, $\left(\begin{smallmatrix}3 & 1\\ 1 & 3\end{smallmatrix}\right)$, and $(2\sqrt{3}\times2\sqrt{3})R30°$.[7] We have obtained STM images for these ordered structures, as well as an additional low coverage (0.20 ML) $c(\sqrt{3}\times5)$rect structure that was not detected previously by LEED.[8,9]

The (2×2) sulfur overlayer has a local coverage of 0.25 ML. We propose that sulfur adatoms are adsorbed in threefold hollow sites [Figs. 1(a) and 1(b)]. LEED, surface extended x-ray-absorption fine structure (SEXAFS), and photoelectron diffraction techniques have been used to study (2×2) and $(\sqrt{3}\times\sqrt{3})R30°$ sulfur overlayers on a number of other close-packed metal surfaces, and in all cases sulfur atoms were located in the most highly coordinated sites with sulfur-metal bond lengths of $\sim2.2-2.3$ Å, approximately the sum of the covalent radii.[10,11]

When high lateral resolution was attained (depending on tip condition), STM topographs of the (2×2) and $c(\sqrt{3}\times 5)$rect overlayers showed small protrusions between the sulfur adatoms corresponding to the positions of those substrate rhenium atoms not bound to sulfur atoms.[8] Although this allows us to identify the sulfur adsorption site as a threefold hollow site, we cannot determine from the STM data if this is a hcp hollow site (above a second layer Re atom) or a fcc hollow. Preliminary results of LEED structure calculations for the (2×2) overlayer on Re(0001) favor the hcp site.[12]

Although the adatom maxima typically appear as round bumps, they sometimes have a triangular appearance, as in Fig. 2(a). In some cases adjacent triangles almost overlap, giving a "honeycomb" appearance in the STM images.

When the sulfer coverage is greater than 0.25 ML, corresponding to the idea (2×2) structure, sulfur adatoms must occupy sites closer together than twice the Re(0001) lattice spacing. The next closest packed simple overlayer would be the $(\sqrt{3}\times\sqrt{3})R\,30°$ lattice, where sulfur atoms are separated by $\sqrt{3}$ or 1.73 times the Re(0001) lattice spacing. This (2×2) to $(\sqrt{3}\times\sqrt{3})R\,30°$ phase change is observed for Ru(0001), Pt(111), Ni(111), and Cu(111). In addition the $(\sqrt{3}\times\sqrt{3})R\,30°$ structure has been reported on Ir(111), Pd(111), and Rh(111).[10,11,13]

We saw no evidence for formation of the $(\sqrt{3}\times\sqrt{3})R\,30°$ structure on Re(0001). Instead three-atom sulfur clusters (trimers) form in a disordered way inside areas with the (2×2) structure, as shown in Fig. 2(a). Large area images show that the trimers nucleate preferentially near domain boundaries. Careful observations of the registry of the trimers relative to the (2×2) structure show that the sulfur atoms occupy the same type of threefold hollow sites in trimers as in the (2×2) lattice. The sudden formation of trimers for any excess S above 0.25 monolayer, while the $(\sqrt{3}\times\sqrt{3})R\,30°$ is not formed and dimers are not formed either, is indicative of the existence of three-body forces that are not reducible to sums of pairwise interactions. The trimer tunnel

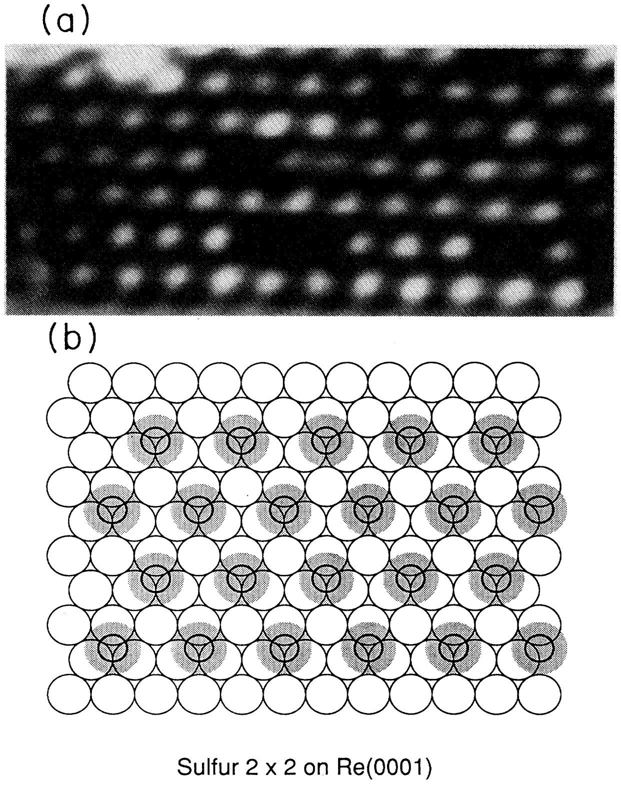

FIG. 1. (a) STM current image of a 35×70-Å^2 region of the (2×2) sulfur overlayer on Re(0001). The dim spots in the image are not vacancies, they are less intense maxima in the (2×2) lattice positions. (b) Model structure for the (2×2) sulfur overlayer on Re(0001). The shaded areas show the van der Waals radii of the sulfur atoms (1.8 Å) and the smaller circles show the covalent radii for sulfur adsorbed on close-packed metal surfaces (0.9 Å).

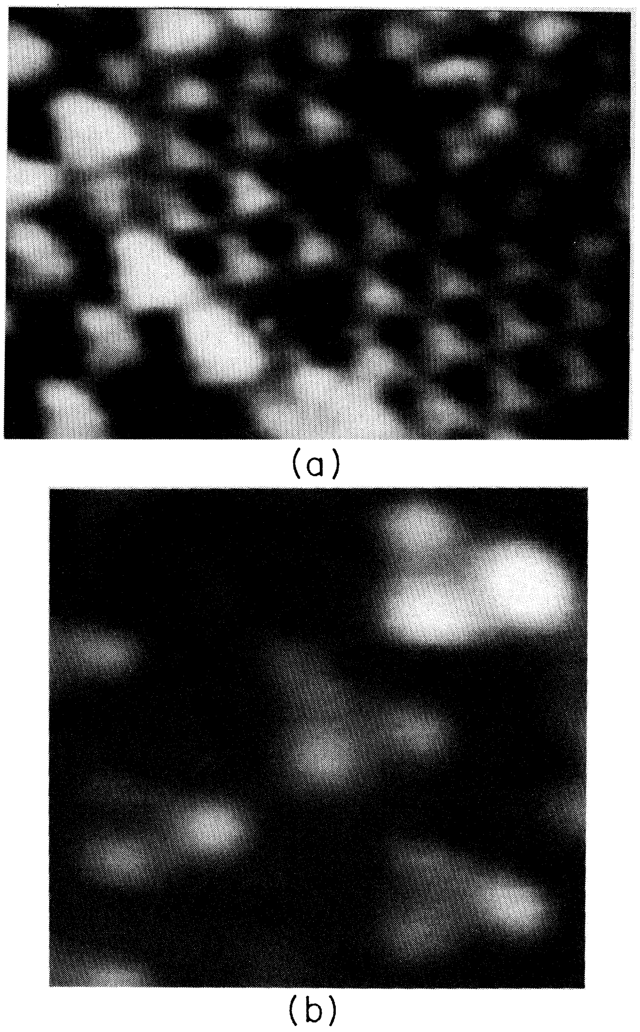

FIG. 2. (a) Current image of a 40×40-Å^2 region showing coexisting (2×2) areas (dim) and trimers (bright). Notice the triangular trimers are all pointing in the same direction (upward in the image). In this image the sulfur adatoms in the (2×2) regions also have a triangular appearance. (b) Current image closeup of a few sulfur trimers (13×13 Å^2).

current in this image and the trimer height in topographic images is always greater than in the (2×2) regions. Figure 2(b) shows a closeup of a few trimers with their individual components resolved.

As the sulfur coverage increases, more trimers are added to the (2×2) structure until an ordered $(3\sqrt{3}\times3\sqrt{3})R30°$ structure is formed (Fig. 3). Sulfur monomers surrounded by trimers and tetramers are found at domain boundaries. This structure, observed by both LEED and STM, corresponds to a local coverage of 0.45 ML. Two distinct types of trimers are present. The first type is a "hollow site" trimer where three sulfur atoms in adjacent equivalent hollow sites form a triangle around a dissimilar hollow site (hcp if sulfur occupies the fcc site or vice versa). The second type of trimer is a "top site" trimer where three sulfur atoms in adjacent equivalent hollow sites form a triangle around a top layer Re atom. The two types of trimers can be distinguished since one type is rotated 60° relative to the other [Fig. 3(b)]. When isolated trimers coexist with (2×2) regions, hollow site trimers outnumber top site trimers by at least ten to one. Top site trimers are seen in significant numbers only near the completion of the $(3\sqrt{3}\times3\sqrt{3})R30°$ structure, where there are three hollow site trimers for each top site trimer. We did not observe any significant difference in STM contrast between top site and hollow site trimers in either topographic or current images.

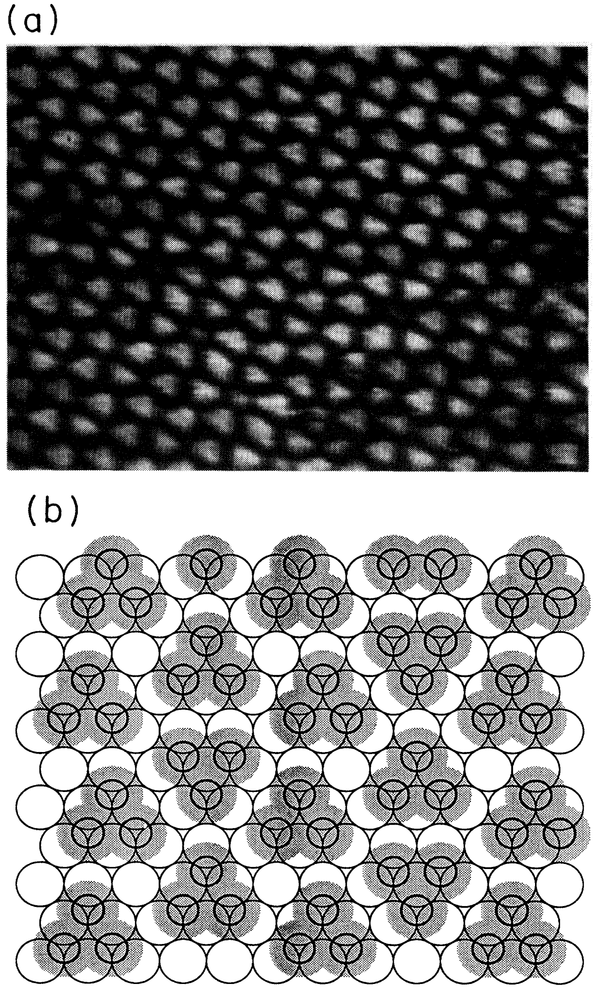

FIG. 3. (a) Topographic 100×90-Å^2 image of the ordered $(3\sqrt{3}\times3\sqrt{3})R30°$ structure (sulfur coverage 0.45 ML) formed of sulfur trimers. Three-fourths of the trimers point in one direction and the remaining one-fourth point in the opposite direction. Sulfur monomers surrounded by trimers and tetramers can be seen at a domain boundary toward the left side of the image. (b) Schematic model of the $(3\sqrt{3}\times3\sqrt{3})R30°$ lattice. The "hollow site" trimers are pointing up, and the "top site" trimers are pointing down.

At still higher sulfur coverages diamond-shaped tetra-

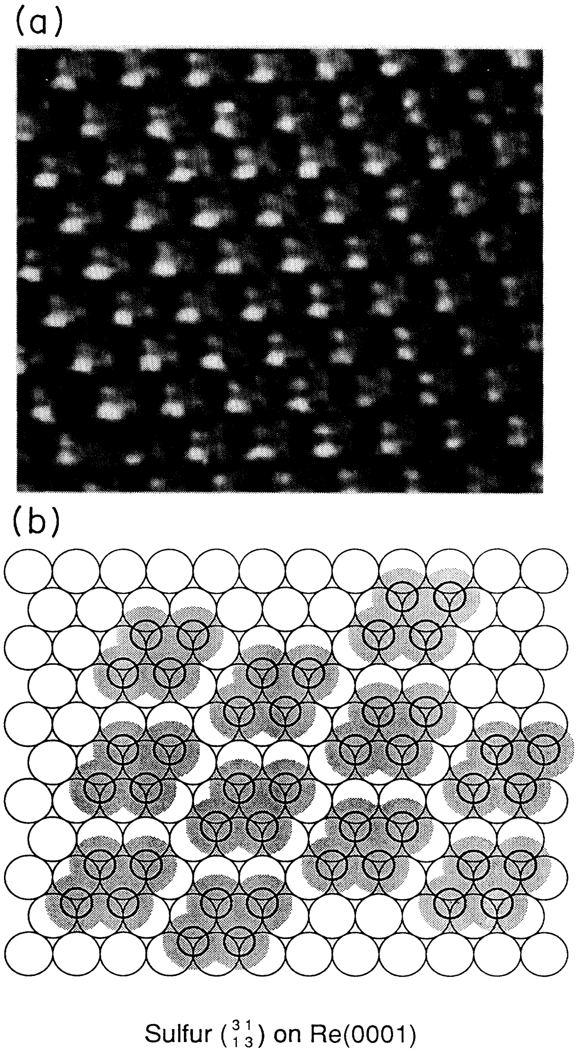

FIG. 4. (a) STM current image of a 68×68-Å^2 square $\left(\begin{smallmatrix}3&1\\1&3\end{smallmatrix}\right)$ region (coverage 0.5 ML), showing diamondlike sulfur tetramers with their long diagonal pointing in the $[1\bar{1}00]$ direction. The long diagonal is the only mirror plane, as can be seen from the non-uniform intensity distribution within the tetramer. (b) Schematic model of the $\left(\begin{smallmatrix}3&1\\1&3\end{smallmatrix}\right)$ lattice.

mers form in ordered domains of the $\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$ lattice. The local coverage of this structure is 0.5 ML. The long diagonal of the tetramer is along the $[1\bar{1}00]$ direction (the crystal orientation was determined by LEED). It constitutes the only symmetry element, a mirror plane. Because of the symmetry of the Re(0001) substrate, the short diagonal of the tetramer along the $[01\bar{1}0]$ direction is not a mirror plane. An image of this structure is shown in Fig. 4(a). The intensity distribution within the tetramers reflects the symmetry of the unit cell just discussed.

We have previously obtained STM images of another sulfur structure, the $(2\sqrt{3}\times 2\sqrt{3})R\,30°$ consisting of hexagonal rings of six sulfur adatoms.[8,9] The local coverage of this structure is 0.5 ML, exactly the same as the $\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$. In order to generate the $(2\sqrt{3}\times 2\sqrt{3})R\,30°$ structure, the sample must be exposed to a high partial pressure of H_2S ($>10^{-7}$ Torr in our case). The thermodynamics of the two 0.5-ML structures is not understood at present. It may be that the $\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$ structure is more stable at coverages below 0.5 ML since tetramers are easily converted into trimers at intermediate coverages, while the average coverage of the $(2\sqrt{3}\times 2\sqrt{3})R\,30°$ structure cannot be reduced without completely disrupting the hexagon pattern.

In conclusion, we have shown that substrate-mediated three- and more-adatom interactions are present in chemisorbed sulfur on Re(0001). At coverages above 0.25 ML, these forces lead to the formation of phases made of clusters of adsorbed atoms. We know that these forces are substrate mediated, since the sulfur atoms in the clusters are separated by the substrate lattice spacing of 2.74 Å (there may be small relaxations in the adatom positions of $\sim 10-20\%$ which cannot be resolved by STM), much larger than sulfur-sulfur bond lengths (1.89 Å for S_2 and 2.07 Å for S_8). To our knowledge the phenomenon of aggregate clustering above a critical coverage has not been observed before. We should emphasize that this clustering is not simply dictated by the need to pack more sulfur on the surface. A substantially higher packing can be achieved by forming the $(3\sqrt{3}\times 3\sqrt{3})R\,30°$ structure with a coverage of 0.33, or by the formation of dimers. However, neither of these structures is observed.

These results illustrate also the power of STM as a structural tool. A study of the adatom arrangement using other structural tools would have been rather difficult in view of the complicated structures that the STM has resolved.

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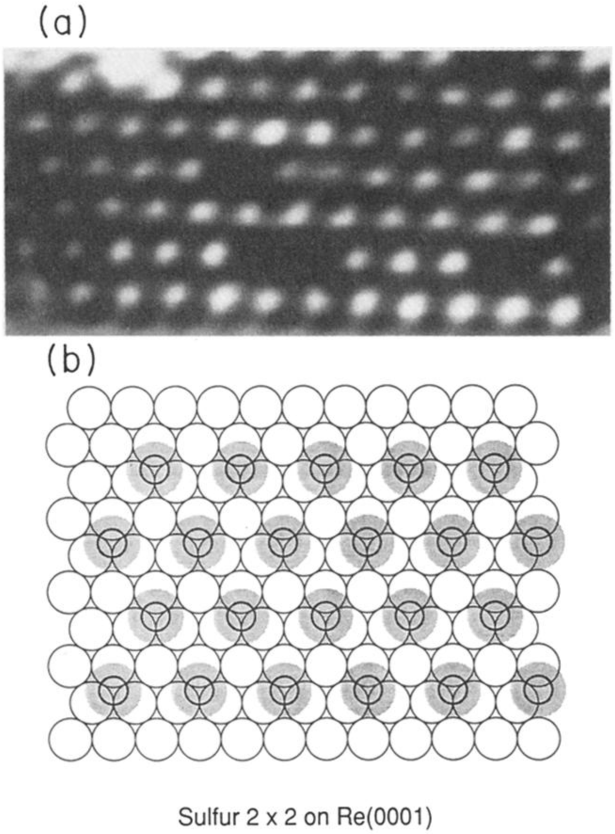

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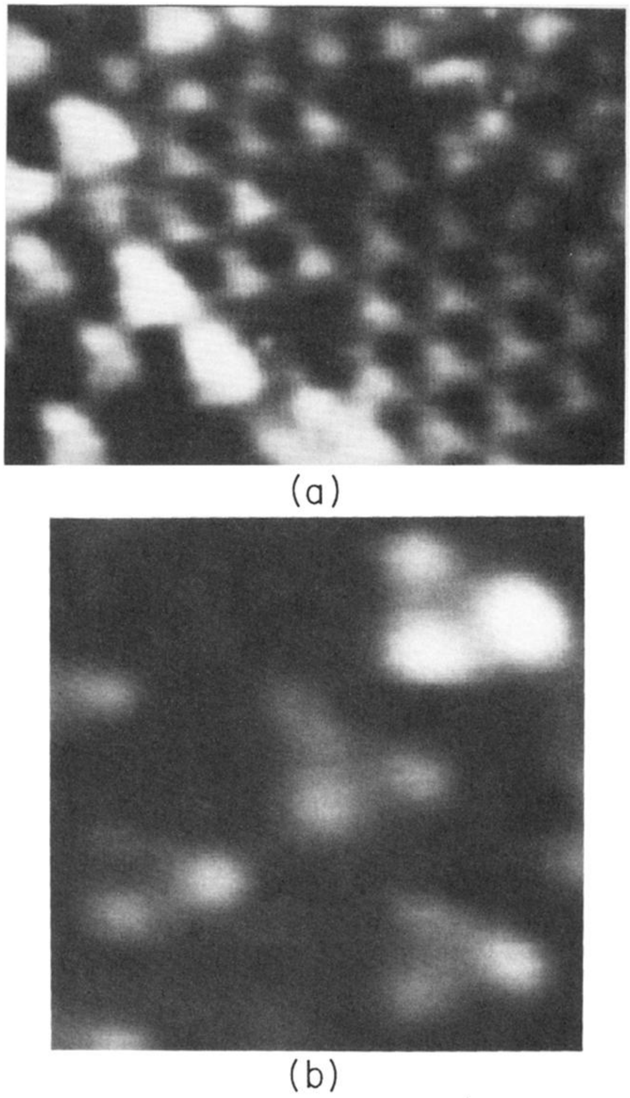

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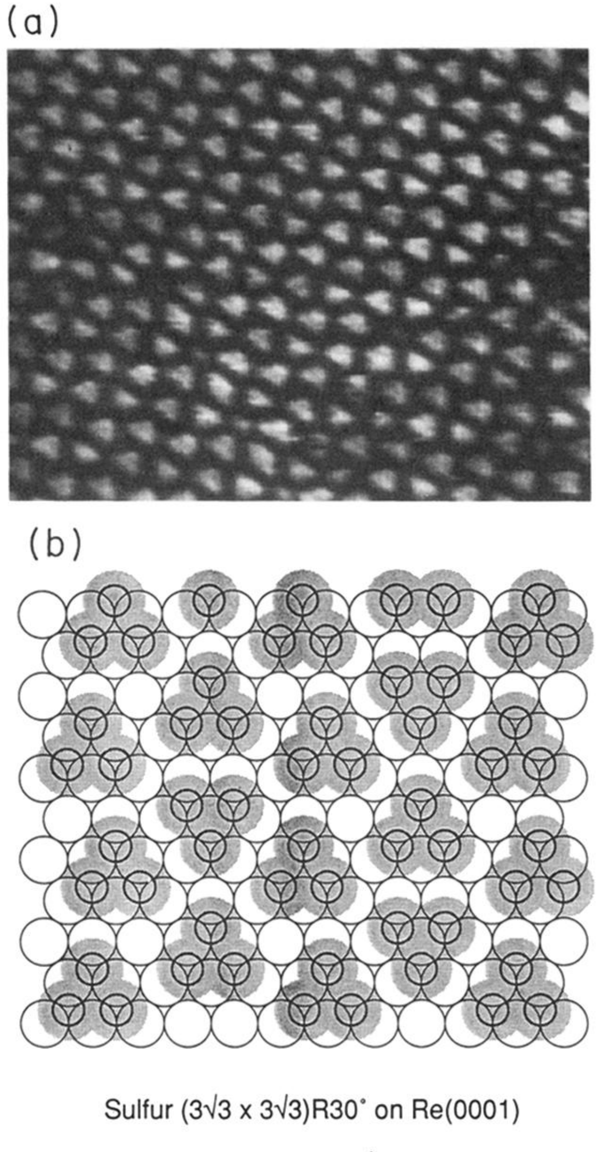

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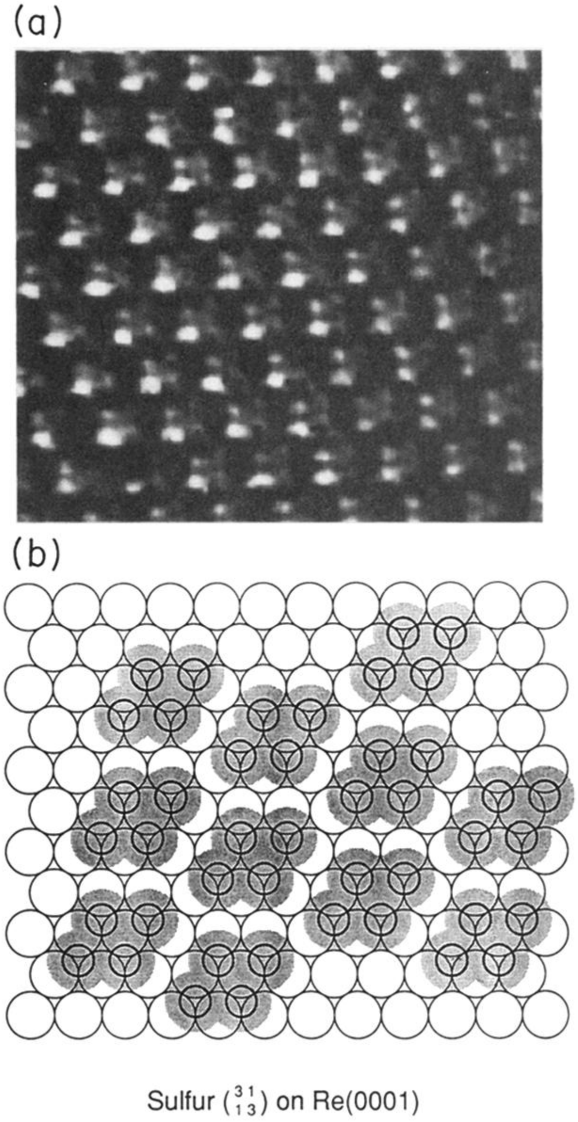

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