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STM Study of the Structure of Sulfur $(2\sqrt{3}x2\sqrt{3})R30^{o}$ Overlayer on Rhenium (0001)

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ABSTRACT

The structure of the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ sulfur overlayer chemisorbed on rhenium(0001) has been studied with scanning tunneling microscopy. The ordered sulfur overlayer was prepared in UHV and then transferred through air to an STM operating at a vacuum of 10^{-7} Torr. The $(2\sqrt{3}x2\sqrt{3})R30^\circ$ sulfur overlayer passivates the rhenium substrate in air. STM images show the atomic structure of the overlayer unit cell to be a hexagonal ring of six sulfur atoms. Defect structures in the two dimensional lattice of sulfur hexagons, overlayer domain boundaries and substrate dislocations were also observed.

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1. Introduction

Sulfur forms ordered overlayers on many metal surfaces, often producing several distinct low energy electron diffraction (LEED) patterns with increasing sulfur coverage. More than one hundred LEED patterns have been reported for sulfur chemisorbed on various crystal faces of at least sixteen metals.[1]

The sulfur chemisorption system is of technical importance since sulfur is a common ingredient of lubricants. Studying the structure of sulfided surfaces may help explain the fundamental mechanisms of friction and lubrication. Sulfur adsorption on molybdenum and rhenium is also important for several industrial chemical reactions.[2,3]

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Scanning tunneling microscopy (STM) has been used to study the atomic structure of chemisorbed monolayers on metal substrates, including oxygen on nickel(110),[4] sulfur on molybdenum(100),[5] iodine on platinum(111),[6] and also benzene on rhodium(111).[7] In this study we extend our previous STM work on sulfur adsorbed on molybdenum (100)[5] and rhenium (0001).[8]

2. Experimental Methods

2.1. STM Imaging

Two different scanning tunneling microscopes were used in this study. The initial experiments were done with a tripod type STM described previously,[9] while the later work was done using a "double-tube" type STM similar to that described by Lyding.[10] The STM's were controlled using electronics developed at LBL, and data were acquired using a PC compatible computer system equipped with a 12-bit 150 KHz analog to digital converter.

All STM measurements were performed at room temperature in a 10^{-7} Torr vacuum. The STM was operated in the topographic (constant current) mode using tips mechanically cut from 1 mm diameter Pt-40%Rh alloy wire. Bias voltages were between 10 and 200 mV and tunnel currents between 0.5 and 15 nA. In this bias range the STM images show no polarity dependence. The tunneling tip was scanned over the surface at velocities of 500 to 6000 Å/sec. Images were recorded with 256 points per line and 256 or 128 lines per image for acquisition times of 10 to 100 sec/image.

2.2. Sample preparation

A rhenium (0001) single crystal substrate was cleaned and prepared in ultra-high vacuum (UHV) using standard surface science techniques. The crystal was sputtered with Ar^+ ions and annealed until no surface contamination was detectable by Auger spectroscopy and a sharp (0001) LEED pattern was obtained.

An ordered sulfur overlayer was formed by heating a Re(0001) single crystal to 800 K and holding it in H_2S gas at $\sim 2 \cdot 10^{-7}$ Torr for a total exposure of $\sim 6 \cdot 10^{-6}$ Torr-sec. H_2S decomposes on the hot rhenium surface and the hydrogen desorbs, leaving chemisorbed sulfur behind. The exact exposure time is not critical since a sulfur coverage of 0.5 monolayers, corresponding to the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ structure, saturates the Re(0001) in UHV. At this coverage the H_2S sticking coefficient drops sharply, greatly reducing the sulfur deposition rate.

The Re(0001) crystal with the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ overlayer was transferred through air to the STM. After mounting the sample the STM was evacuated to 10^{-7} Torr. We believe the structure of the Re(0001)-$(2\sqrt{3}x2\sqrt{3})R30^\circ$ surface is not affected by a brief exposure to atmosphere. This hypothesis was tested by forming the Re(0001)-$(2\sqrt{3}x2\sqrt{3})R30^\circ$ surface in UHV, exposing the surface to room air for one hour, and then analyzing the surface in UHV. The LEED pattern was unchanged by exposure except for a slight increase in background, and the only change in the chemical composition, as determined by Auger spectroscopy, was some slight carbon contamination corresponding to a few percent of a monolayer.[2] A similar passivation property is

observed for the saturation sulfur overlayer on Mo(100).[5]

There are three additional sulfur structures formed on Re(0001) at coverages of 0.25, 0.34 and 0.40 monolayers.[2] These structures are not stable in air, so they cannot be studied with the transfer procedure used for the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ saturation structure. A UHV STM experiment is being prepared to investigate these lower coverage structures.

3. Results and Discussion

3.1. Rhenium substrate structure: steps and dislocations

Large area images of the sulfur passivated Re(0001) surface show atomically flat terraces separated by atomic height steps (figure 1). Step edges are approximately parallel with terraces $\sim$ 200 Å wide. There are few kinks in the step edges, and most steps are one or two atomic layers high. This step density along with the low kink density shows that the rhenium crystal was cut $\sim 1.1^\circ$ away from the (0001) plane close to the $[10\bar{1}0]$ direction. The peak-to-peak noise on the terraces is $\sim$ 0.5 Å.

Substrate defects are seen on the sulfur passivated Re(0001) surface. At the lower left of figure 2, a screw dislocation emerges where two single height atomic steps join together and vanish. Figure 3 shows a detailed view of an isolated dislocation. Again two single-height steps come together and $\sim$ 600 Å later the double-height step disappears. The screw dislocations we have observed end in double-height steps which is

reasonable given the abab stacking of the (0001) planes. The (0001) surface of an hcp crystal will have less in-plane strain for a double-layer screw dislocation than for the single layer case.

3.2. Atomic structure of the sulfur unit cell

Hexagonal rings of sulfur atoms in the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ overlayer are resolved in figure 4. A double-height step crosses the upper right corner of the image. Atomic resolution is lost over a $\sim$ 35 Å wide region near the step because of multiple-tip effects, implying a tip radius of the same order. Tunneling over the terraces is probably from a single tip atom since details of ¼ of the unit cell spacing or $\sim$ 2 Å are resolved.

The atomic structure for chemisorbed sulfur overlayers has been determined by dynamical LEED structure calculations and a few photoelectron diffraction studies for the low coverage sulfur structures on metal surfaces, including the ¼ monolayer (2x2) and ½ monolayer c(2x2) structures on several (100) surfaces, the ¼ monolayer (2x2) structure on (110) surfaces and the 0.33 monolayer $(\sqrt{3}x\sqrt{3})R30^\circ$ structure on the (111) surface of Ir, Pd, Pt and Rh.[11,12] The sulfur atoms occupy the adsorption site with the highest coordination number, and the sulfur-metal bond lengths range from 2.18 to 2.45 Å. The four solved structures on three-fold symmetrical surfaces are all (111) faces of fcc metals, where sulfur has been shown to adsorb in the triply coordinated "fcc" hollow sites (those without second layer metal atoms below the hollow site) with bond lengths from 2.20$\pm$0.03 Å to 2.33 $\pm$0.03 Å.

Based on our STM data we propose that the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ sulfur overlayer consists of a ring of six sulfur atoms adsorbed in 3-fold hollow sites (figure 5a). The sulfur-rhenium layer spacing would be $\sim$ 1.5 Å for a sulfur-metal bond length of $\sim$ 2.25 Å, which is close to the sum of the metallic rhenium radius and the sulfur covalent radius. We have no direct information on the registry of the overlayer and substrate. The STM data cannot assign sulfur to the fcc or hcp type hollow sites so electron or ion scattering data are needed for a definite conclusion, however the sulfur is probably in the rhenium fcc hollow.

The apparent depth of the trough between two sulfur hexagons is 1 to 2 Å and the hollow at the center of the hexagons at least 0.5 Å (figure 6). Based on a hard sphere model for sulfur on Re(0001) both hollows and troughs should be 1.1 Å deep and only 2 Å wide at the bottom. Its reasonable for the hollows in the STM topographic images to appear shallow compared to the troughs since six neighboring sulfur atoms contribute to the tunnel current in a hollow while fewer contribute in a trough. On most clean surfaces the atomic corrugations measured by STM are significantly smaller than the hard-sphere values (except for the well known giant corrugations observed on graphite).[13,14] Here the high resolution images were recorded with a tunneling gap of 2 to 3 MΩ, where the tip-surface forces may elastically deform the tip or surface and magnify the actual corrugation.[15] We have reduced the gap resistance as low as 20 KΩ for a few msec, producing large tip-surface forces, without apparent tip or substrate damage as shown by identical before and after atomic resolution images.[16,17]

When the sulfur unit cells are displayed at maximum magnification (figure 7) the six-atom sulfur ring appears to be made up of three sub-units, breaking the apparent hexagonal symmetry with a Kekulé type distortion. This distortion may be caused by a geometrical displacement of the sulfur ion cores from the high symmetry hollow sites, by a change in the electronic structure of the adsorbed sulfur that modifies the tunneling current or by some combination of the two. The deeper layers of the rhenium surface have a visible effect on the STM images, since the sulfur overlayer and the topmost rhenium layer have *c6v* symmetry, which is reduced to *c3v* only when the second metal layer is included.

3.3. Disorder in the sulfur overlayer

The sulfur overlayer has a variety of imperfections (figure 8), including distorted and broken unit cells. The disordered regions usually consist of small aggregates of sulfur atoms separated by troughs similar to those between hexagons -- neither isolated sulfur atoms nor large sulfur islands are observed.

Rhombic clusters of four sulfur atoms are common, and sometimes form ordered arrays of "compressed" unit cells as in part of figure 8. Although not reported from LEED studies, a stable 0.44 monolayer sulfur phase of rhombic clusters on a 3x3 lattice may exist (figure 5b).

Non-hexagonal sulfur clusters are often found at anti-phase domain boundaries, which occur when the registry of two overlayer regions differs by a fraction of the overlayer unit cell. Twelve different registries are possible since there are twelve rhenium atoms in the overlayer unit cell, and several types of domain boundaries have been observed. In some cases sulfur is adsorbed in a region too narrow for hexagonal unit cells and compressed unit cells are found at the boundary. In other cases no sulfur is observed at the boundaries, leaving wider gaps between hexagonal unit cells than in the ordered domains.

In one series of images a narrow rift free of sulfur clusters was visible between two ordered hexagonal domains. This rift evolved and changed over the course of an hour, bending and breaking into two separate pieces as sulfur clusters diffused over the surface. Despite a large adsorption energy of ~ 2.3 eV/atom^2 sulfur clusters are mobile at 300 K.

4. Summary

A model of sulfur adsorbed in hexagonal rings of fcc hollow sites is proposed for the $(2\sqrt{3}\text{x}2\sqrt{3})\text{R}30^\circ$ structure on Re(0001). Sulfur forms isolated aggregates or clusters of a few atoms on the surface, which are mobile at 300 K. Unusually large atomic corrugations suggest elastic deformation of the tip and surface during STM imaging. Rhenium screw dislocations are also observed.

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Figure Captions

Figure 1 A 1500 Å square region of the sulfur passivated Re(0001) surface after a best-fit plane has been subtracted from the image and the surface illuminated at a low angle to highlight the steps. The brighter lines are double-height steps and the dimmer lines are single-height steps, with a triple-height step at the lower left corner of the image. There are occasional kinks where a multiple-height step splits into two smaller steps and where smaller steps come together to form higher steps.

Figure 2 Another 1200 Å square area of the sulfur-passivated Re(0001) surface showing a distribution of single and double-height steps. In the lower right corner of the image two single-height steps form a "V" where a screw dislocation surfaces.

Figure 3 Close up of the tip of a screw dislocation in a 1700 Å square area of the Re(0001) surface. Two single height steps join to become a double-height step and 600 Å later the step vanishes where the screw dislocation surfaces.

Figure 4 An unprocessed high-resolution image of the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ sulfur overlayer on Re(0001), displayed with a grey scale proportional to height. The image area is 204 x 176 Å, recorded at a sample bias of -18 mV and a tunneling resistance of 2.8 MΩ. The sulfur atoms form hexagonal rings

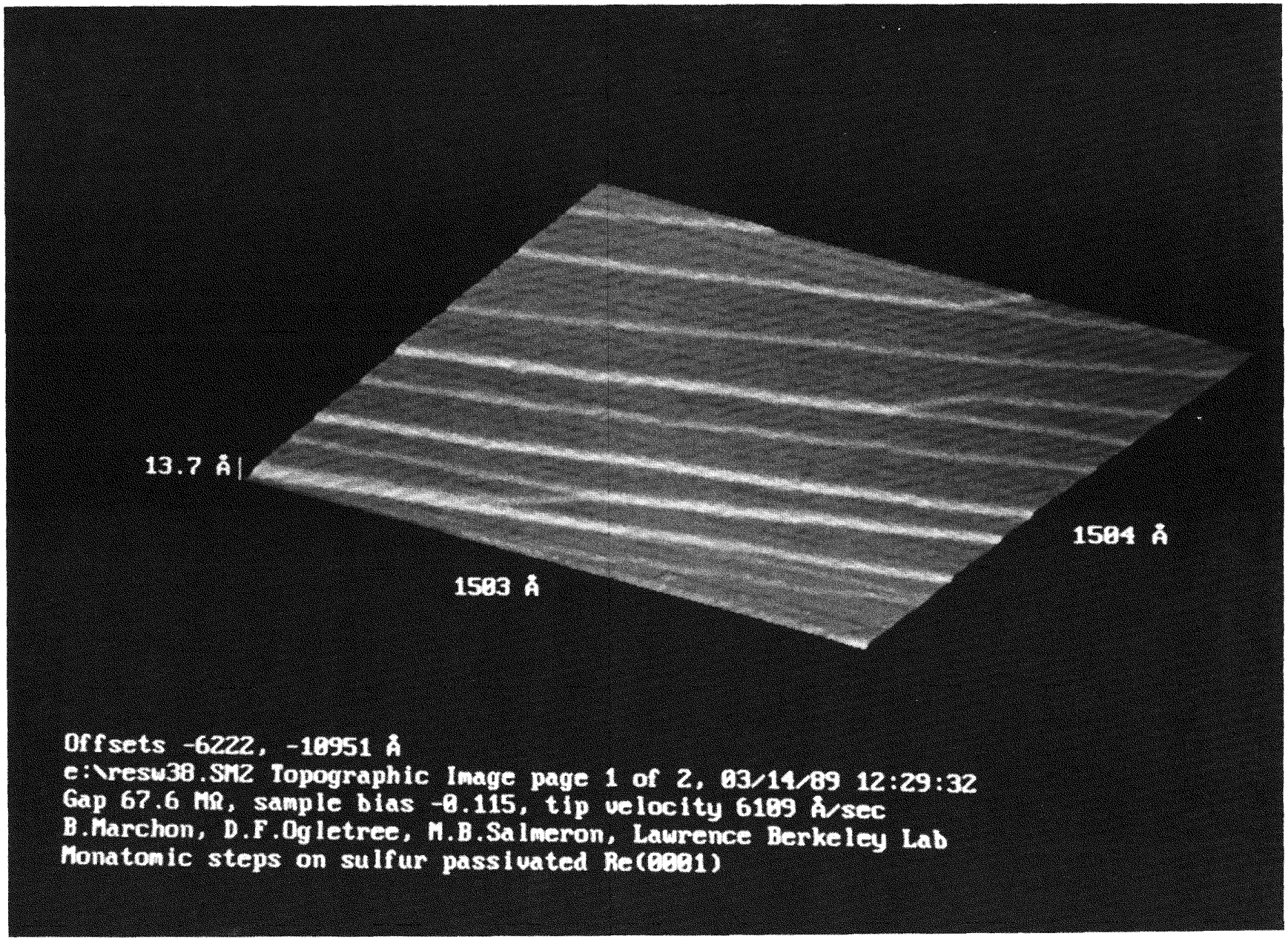
separated by 9.5 Å, and a double-height step crosses the upper right corner of the image. The hexagons are slightly elongated since the X and Y deflections of the piezo scanner tube are not completely orthogonal.

Figure 5 Model structure for the sulfur overlayer. The sulfur and rhenium atoms are drawn to scale. a) The $(2\sqrt{3}x2\sqrt{3})R30^\circ$ sulfur overlayer on Re(0001). b) Model showing "compressed" rhombic unit cells at the left and hexagonal unit cells at right.

Figure 6 A cross section through several hexagonal sulfur unit cells, indicated by the white line on the top-view image. The vertical range is 3 Å and the horixonal range is 50 Å. The trough between hexagons is $\sim$ 1 Å deep and the hole at the center of the hexagon is $\sim$ 0.4 Å deep.

Figure 7 A magnified view of a few unit cells shows the pairing of sulfur atoms that breaks the hexagonal symmetry in a Kekulé type distortion.

Figure 8 Image of the sulfur overlayer illustrating various defects, including antiphase boundaries, distorted and broken sulfur hexagons and clusters. Note the row of rhombic sulfur clusters indicated in the lower left quadrant of the image.



XBB 896-5073

Fig. 1

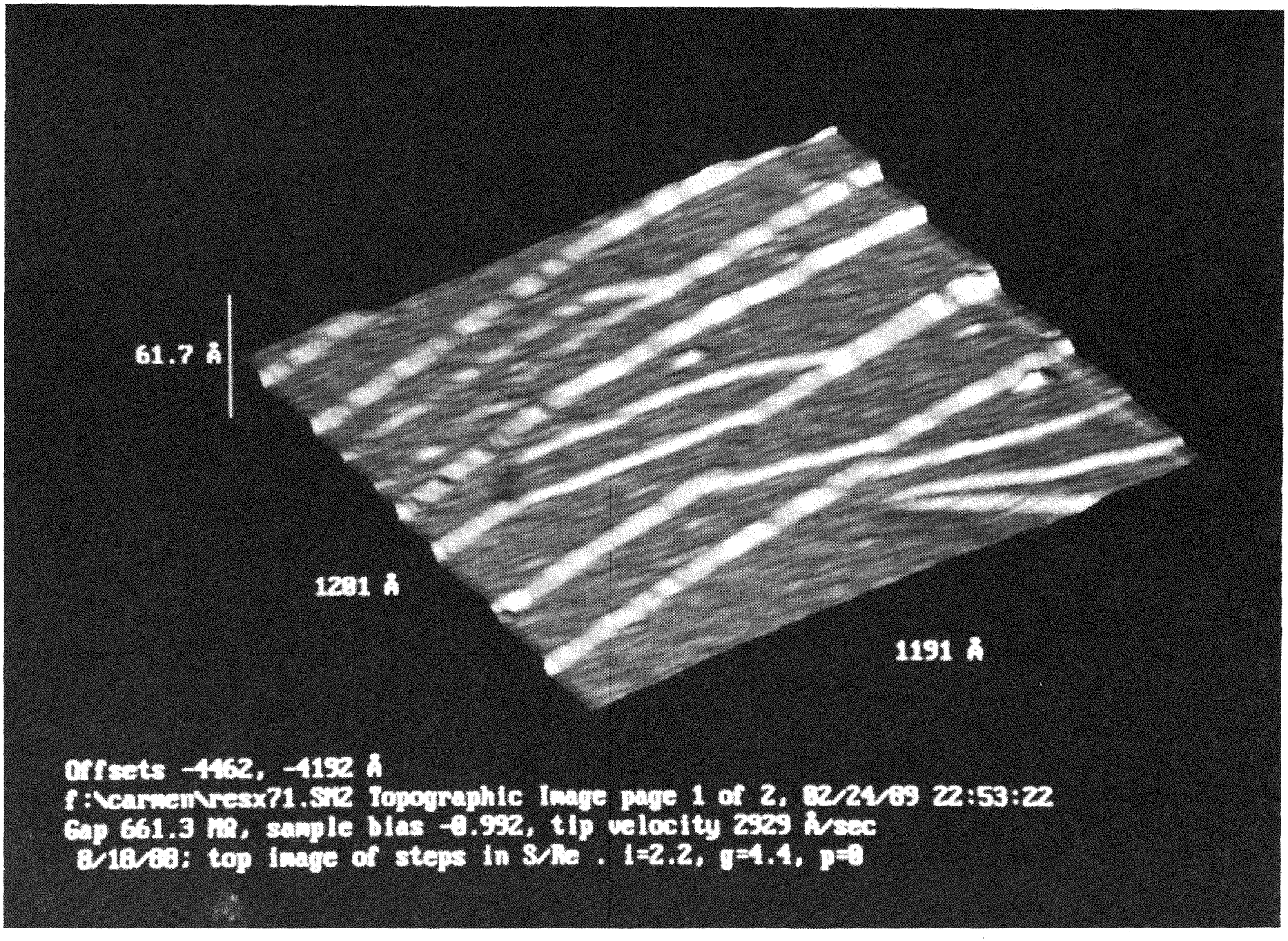


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Fig. 2

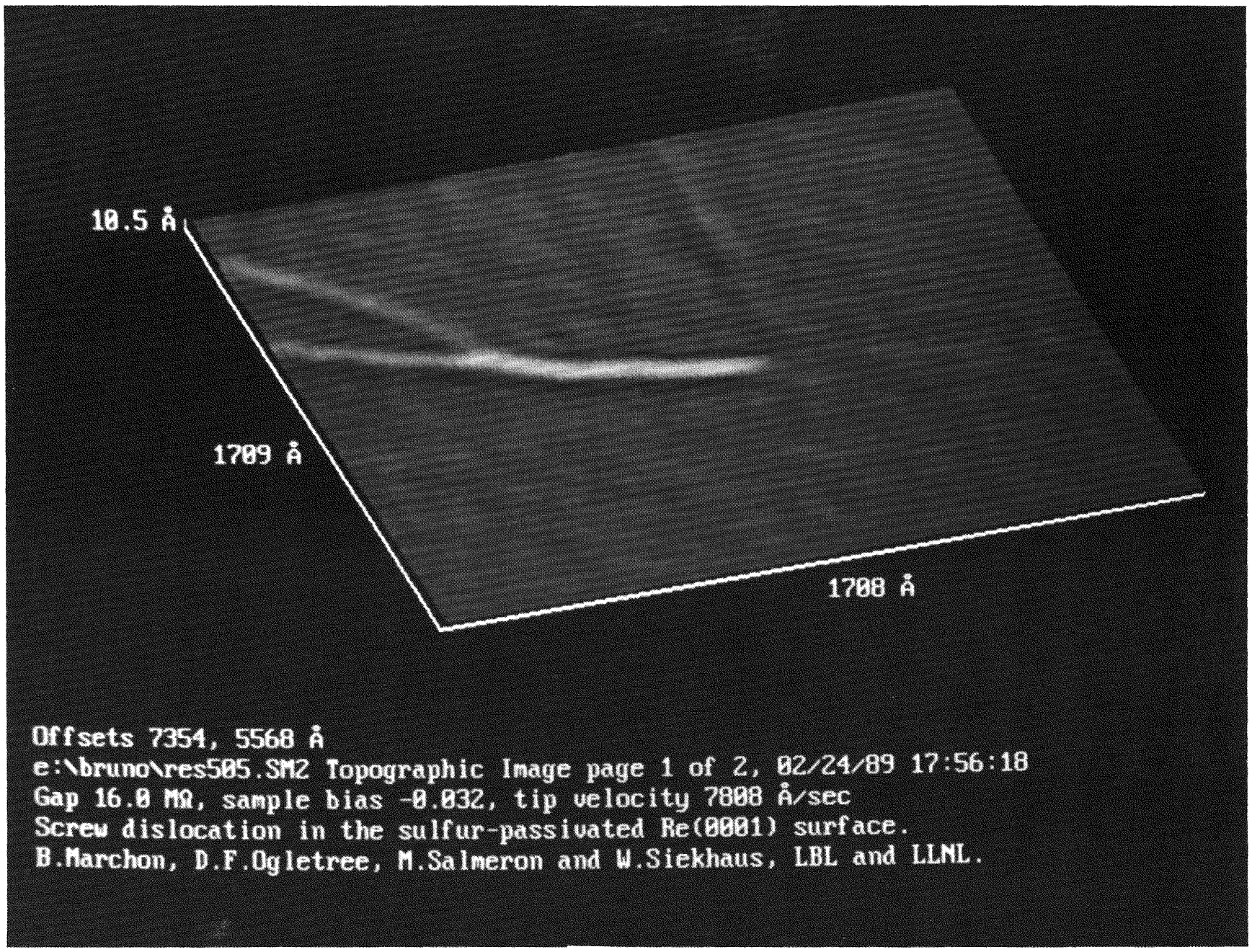


Fig. 3

XBB 897-5400

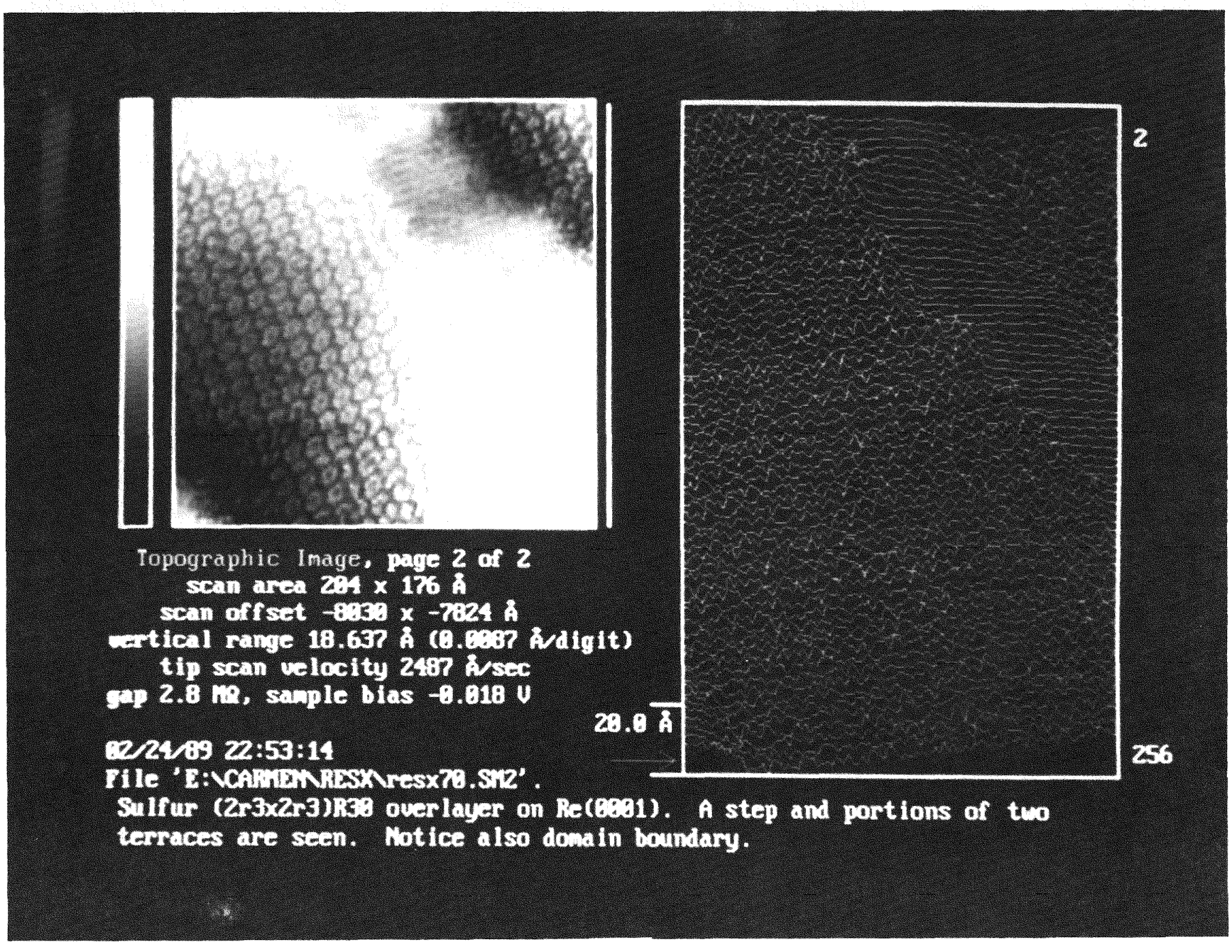
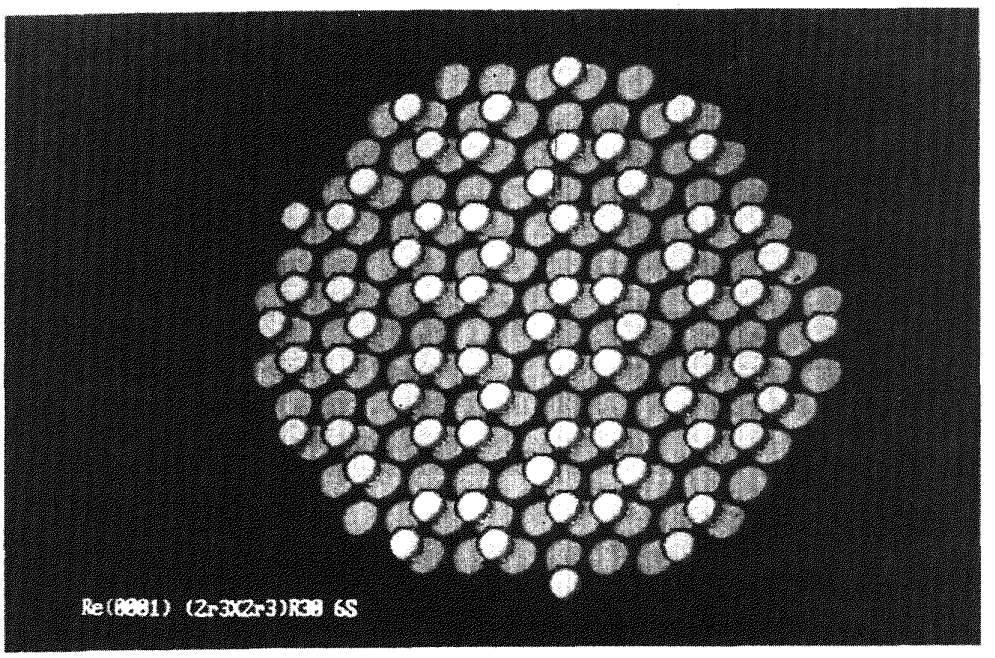


Fig. 4

XBB 896-5080



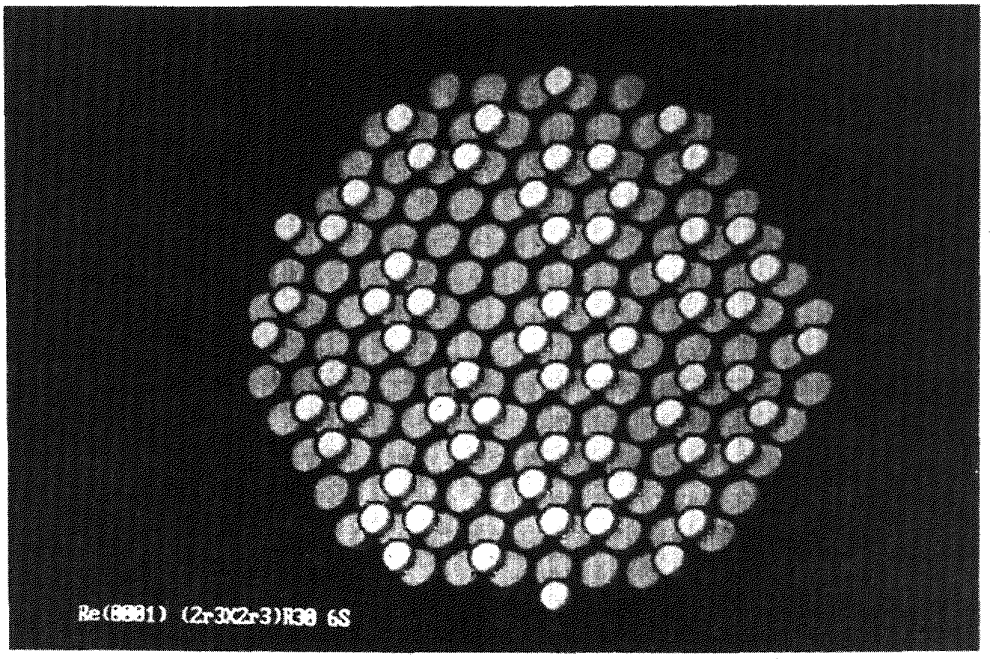


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Fig. 5

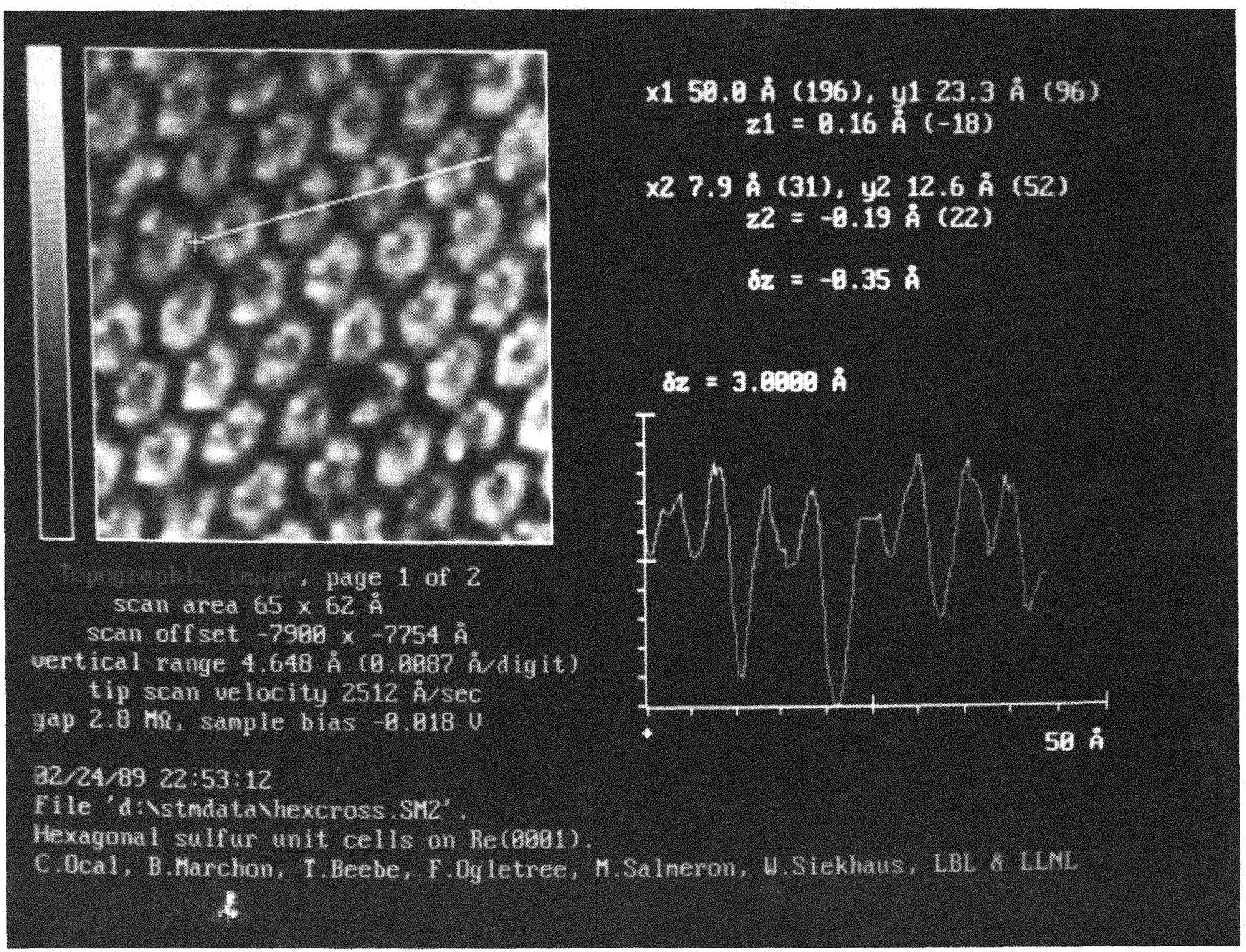

Fig. 6

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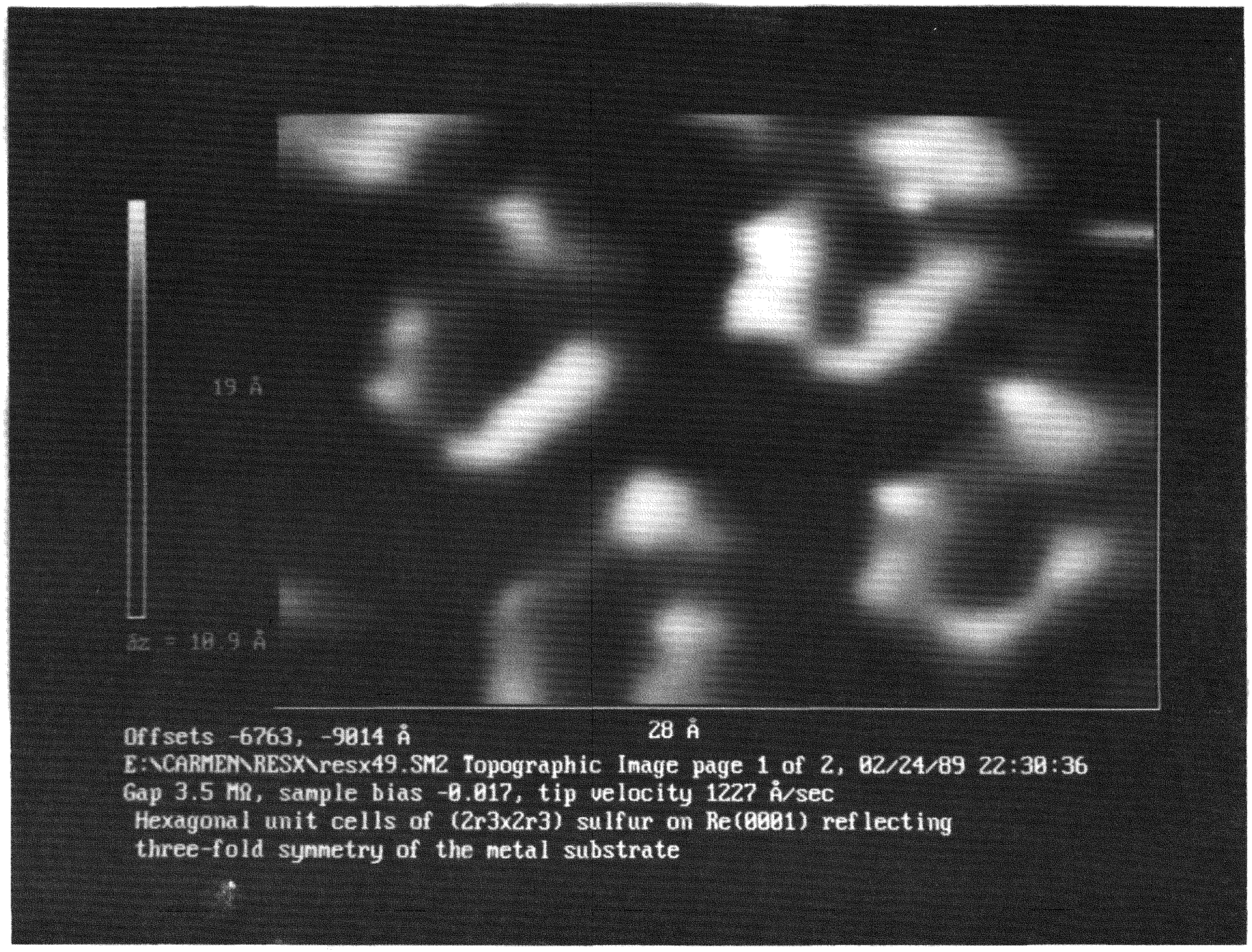

Fig. 7

CBB 896-5090

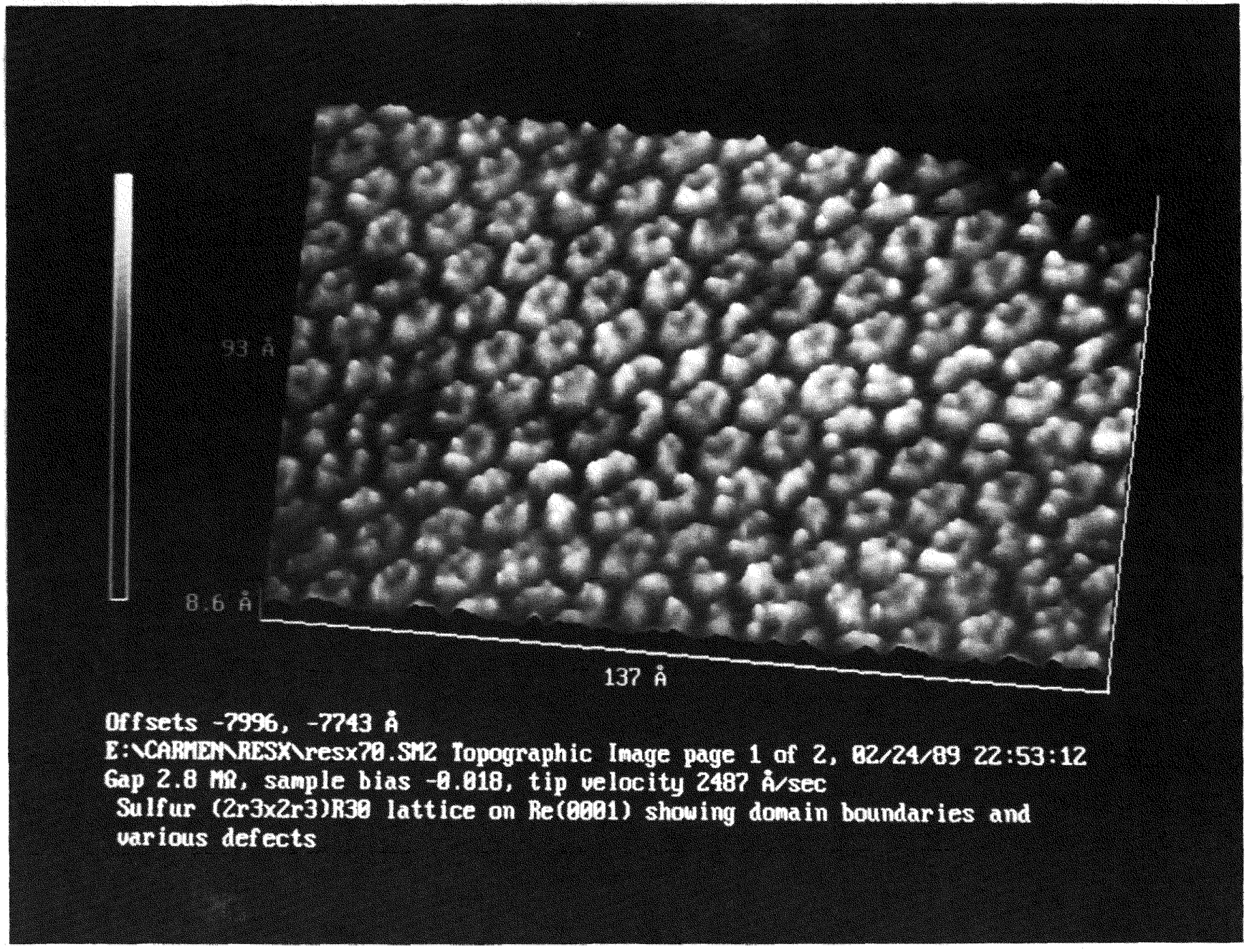

Fig. 8

CBB 896-5092