Title
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Permalink
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Journal
Journal of vacuum science and technology B, 9(2)

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Publication Date
1990-10-01

UC-406

LBL-29713
Preprint

Center for Advanced Materials

CAM

Submitted to the Journal of Vacuum Science and Technology

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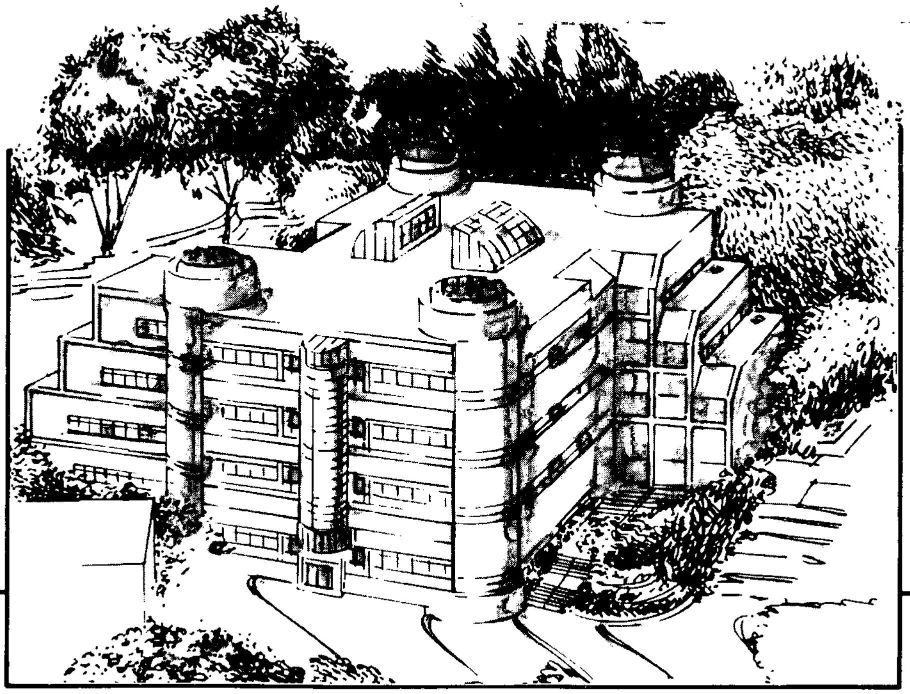

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-29713

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ACKNOWLEDGMENT
This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division, U.S. Department of Energy under contract No. DE-AC03--76SF00098.

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ABSTRACT

Scanning tunneling microscopy has been used to study submonolayer coverages of titanium oxide on rhodium. After reduction with CO, titania is shown to form one atomic layer thick islands $\sim$ 20 Å in size on the Rh(111) surface at sub-monolayer coverages. High resolution filled state images show enhanced contrast at the island perimeter. The "ring shaped" appearance of the islands is related to the electronic structure of the titania overlayer.

October 11, 1990

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1. INTRODUCTION

The interaction of noble metal catalysts with oxide supports is an active area of research in catalysis. This interaction is believed to be responsible for the enhancements observed in many chemical reactions. The strongest effects are observed when the oxide is reducible. The interaction is then known as Strong Metal Support Interaction (SMSI). Some well known reactions involve the activation of CO bonds in molecules like CO, CO_2 and acetone by Pt and Rh supported on TiO_2 to produce methane and alcohols when reacted with H_2. [1-4]

The system we have studied consists of submonolayer amounts of TiO_x deposited on a Rh (111) single crystal. This configuration is the reverse to that used in supported metal catalysis in which the noble metal is dispersed on a TiO_2 support. Previous studies in our laboratory using a variety of surface science techniques, in combination with a high pressure reactor, have shown that it constitutes an excellent model for the real system [5-7]. The model that emerged from these previous studies is that in the activation process, which involves a reduction step (CO or H_2), Ti^{3+} sites are created at the periphery or interface between the oxide and the metal. It is postulated that these are the active sites responsible for the SMSI effect.

In this work we report the first results of our studies on the TiO_2-Rh system using Scanning Tunneling Microscopy (STM) in an Ultra High Vacuum (UHV) environment. We concentrate on the growth and structure of the deposits after oxidation and CO reduction and in particular on the structure of the edges of the oxide islands.

2. EXPERIMENTAL

2.1. Sample preparation

All the experiments were carried out in a UHV chamber with a base pressure lower than $3 \cdot 10^{-10}$ torr. The vacuum system includes a cylindrical mirror analyzer for Auger analysis and a manipulator with an electron bombardment sample heater. The Rh(111) surface was cleaned by heating to 1000° C for a few minutes in UHV. No contamination was detectable by Auger spectroscopy. The orientation of the Rh(111) crystal was determined by LEED in another vacuum chamber.

The titanium oxide overlayer was prepared by evaporating metallic Ti from a wire wrapped on a tungsten filament at the rate of ~ 0.3 ML/min. The sample was then heated to $\sim 300°$ C and oxidized by exposure to $5 \cdot 10^{-7}$ torr of O_2. This oxidizes both Rh and Ti. The oxygen was selectively removed from the Rh(111) surface by introducing CO into the chamber at a pressure of $5 \cdot 10^{-7}$ torr. Previous XPS results [7] show that CO adsorbs only onto the rhodium oxide and that heating to $\sim 500°$ C causes CO_2 to desorb leaving Rh and titanium oxide. The coverage of titanium oxide was estimated using the Ti/Rh Auger peak height ratio calibration of Williams, *et al.* derived from AES and ISS data [6]. Because of the difficulty in comparing Auger peak ratios obtained with different systems our coverage scale may not agree with this previous work [8]. The titania coverage values given below are nominal values. However, relative coverages given in this work should be consistent.

2.2. STM imaging conditions

The UHV compatible scanning tunneling microscope used in this experiment was designed and built in our laboratory and is a "dual tube" scanning head design with a double spring suspension for vibration isolation. The microscope is mounted on a standard 8 inch vacuum flange, similar in design to the one described in Ref.[9].

The STM was operated both in topographic (constant current) and in $\partial I/\partial z$ mode with scan rates of typically 1 sec/line. Sample biases ranged from -1 to +1 volts and tunneling currents were typically 0.1 to 1.0 nA. The tunneling tips were formed from mechanically cut Pt-40%Rh alloy wires. The z piezo was calibrated by measuring monatomic step heights on Rh(111) and on Au(111) films on mica. The xy piezos were calibrated on graphite (0001).

We have performed $I-V$ measurements on the Rh(111)/titania system but we have not yet obtained useful results. An unexpected side effect of this attempt was a significant increase in resolution due to changes in the tunneling tip. With a mechanically cut tip we typically measured a monatomic step width of 20 Å. With the microscope in tunneling range at a current of ~ 0.5 nA and a bias of 1.0 V the feedback loop was disabled and the voltage was ramped from -4.0 to 4.0 V over a few msec, increasing the tunnel current to ~ 20 nA. After this procedure the tip resolution often increased, giving a monatomic step width of 7 Å. This procedure was routinely used to produce sharp tips.

In order to distinguish between oxide patches and clean Rh, we utilized the method of barrier height imaging, which consists in modulating the tip surface distance by a small value at high frequency, while detecting the ac part of the tunneling current with a lock-in amplifier [10]. The output is a contrast signal that is material dependent and can be used to separate the metal and oxide contributions. We were able to prove that metal and oxide could be easily distinguished in that manner. Due to space limitations we will present these measurements in a more extensive account of our work [11].

3. RESULTS AND DISCUSSIONS

Figure 1 shows a 2500 x 2500 Å image of clean Rh(111) consisting of many terraces of triangular shape separated by mostly monoatomic height steps. The most common steps are oriented parallel to the $[\bar{1}10]$ direction, the compact direction in the (111) surface of fcc crystals.

They cross each other at angles of 60° and 120°. The existence of crossing steps is indicative of dislocations due to mechanical stresses that were relieved during annealing. Steps oriented in other directions are also observed with lower frequency. A detailed study of step structure and dynamics will be the object of a separate paper [12].

The images obtained after deposition of one or more complete monolayers of TiO_2 followed by exposure to reducing CO gas reveal a surface that is composed of flat terraces separated by monoatomic steps and is similar to the original clean surface. It is indicative of the good wetting of the oxide layers that is observed even after 3 monolayers. At close range the images did not reveal any atomic scale features within the noise level of 0.3 Å presently the limit of our instrument.

The oxide deposits are found at the bottom of the step edges and grow from there into the lower Rh terrace on the annealed and CO reduced surface. The 2000 x 2000 Å image in figure 2a corresponds to a coverage of 0.7 monolayers. The edges of the Rh terraces are distinguishable by their structure. Step edges are straight and oriented along close packed directions, and usually meet at 120° angles typical of the (111) orientation. Some "holes" in the clean Rh terraces also have hexagonal shapes. They are particularly visible in the upper terrace of the image. In contrast the flat TiO_2 regions have edges that are irregular without any particular preferred orientation. A profile of the surface along the cursor line shown in the figure reveals the step heights of the various terraces (figure 2b). The step found in going from clean Rh to the TiO_2 appears to be 0.7 Å high, whereas that from the TiO_2 to the Rh is 1.5 Å high adding to a total of 2.2 Å, the Rh-Rh interplanar spacing in the [111] direction as measured on the clean surface. Because of the electronic contributions to the tunneling current, the TiO_x island thickness measured by the STM is not necessarily the geometric thickness.

A close look into the TiO_2 region reveals a surface composed of small clusters packed together with sizes of approximately 20 Å. When the x-y resolution of the tip is good (step edges with widths less than 10 Å), the cluster edges are resolved and appear higher than the center of the island giving the surface an appearance of rings as shown in figure 3. The higher elevation of the island edges is an electronic effect. It is only observed at negative sample bias and on samples that have been reduced with the CO treatment. A close view on a ring is shown in figure 4. It appears that the "elevated" island edges are oriented as seen by the angles of 60° and 120° between its sides. The fine structure seen in the image is noise from the digitization process and has no relation with atomic structure.

Our interpretation of these observations is as follows. The CO reduction process disrupts the TiO_2 islands by removing O atoms mostly from the edges. The edges are thus decorated with Ti^{3+} species while Ti^{4+} resides mostly in the interior, as proposed in an earlier work from this laboratory based on XPS and reactivity studies [6]. It is known from photoemission studies of TiO_2 and $SrTiO_3$ that Ti^{3+} near O vacancies has partially filled 3d states near the Fermi level [13-14]. The Fermi level is located very close to the conduction band (n type). In contrast, in its stoichiometric form, the Ti^{4+} has its filled 3d electronic levels at 3 eV below the Fermi level in the valence band [15]. It is the higher density of states at the Fermi level in the island edges that in our model is responsible for the higher tunneling current and thus the higher corrugation observed. The effect should be mostly observed at negative sample bias where filled sample states are imaged. At positive bias both the oxidized and reduced TiO_2 have abundant unfilled states due to the 3d states of Ti^{3+} and Ti^{4+}, both at the bottom of the conduction band, making them similar in terms of tunneling probability.

We are currently continuing these studies to include more spectroscopic characterization of the island edge structure. We are also studying the changes of oxide island structure upon reoxidation in situ. These studies are not easy since the sample has to be removed from the STM head to heat and that prevents examination of the same original area of the surface. Other studies in progress include the structure of the clean Ti deposits before and after oxidation and reduction.

4. CONCLUSIONS

We have shown that TiO_2 deposited on Rh(111) surfaces grows atomically flat up to at least 3 layers. These deposits preserve the step structure of the Rh substrate. At submonolayer coverages we have observed the oxide to grow by nucleating at the steps and propagating into the lower Rh terraces. The structure of the oxide regions after CO reduction is discontinuous and formed by clusters of similar size, typically 20 Å. The edges of these clusters appear brighter (more conductive) at negative sample biases. Our proposed interpretation of these observations is consistent with a model based on previous XPS studies where the oxide islands are edged with Ti^{3+} species that give rise to higher tunneling conductivity.

Acknowledgements

The authors would like to acknowledge the assistance of H. C. Galloway in preparing this manuscript. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Additional support was provided by a contract from the Dow Chemical Company, Midland, MI.

FIGURE CAPTIONS

1) Topographic 2500 x 2500 Å image of clean Rh(111) showing intersecting step structures along the $[\bar{1}10]$ directions, the compact direction on the (111) surface. Crossing steps are formed when stresses of dislocations are relieved by annealing. Sample bias is -0.1 V and tunneling current is 1.0 nA

2) (a) Topographic image corresponding to 0.7 ML of TiO_x on Rh in a 2000 x 2000 Å area. Steps alternate between the angular type step observed on the substrate and an irregular step formed by the oxide layer that nucleated at the Rh steps. (b) The cross section shows two alternating step heights of 1.5 Å and 0.7 Å respectively. The monoatomic step height of clean Rh is 2.2 Å. Sample bias is -1.0 V and tunneling current is 0.1 nA.

3) 200 x 200 Å image of an oxide region showing several ring shaped islands of approximately 20 Å in size. The variations in the ring height range from 0.2 to 1.5 Å. Notice that the rings do not appear to coalesce into larger islands. Sample bias is -0.1 V and tunneling current is 0.4 nA.

4) High resolution image of a single TiO_x island 15-20 Å in diameter. Sides appear to meet at 60° and 120° following the orientation of the underlying substrate. The fine structure is noise and has nothing to do with the atomic structure. Sample bias is -0.94 V and the tunneling current is 0.4 nA.

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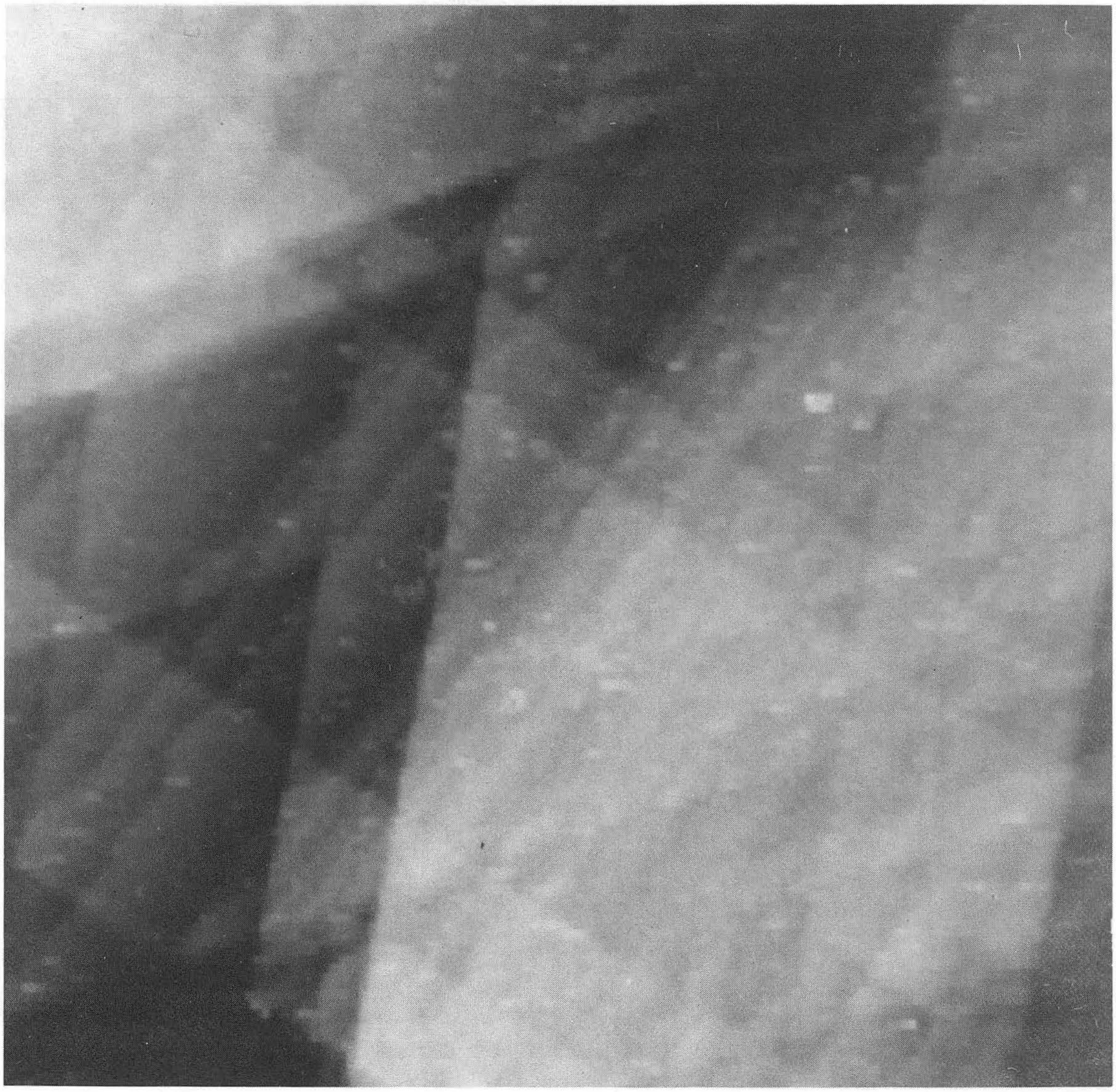

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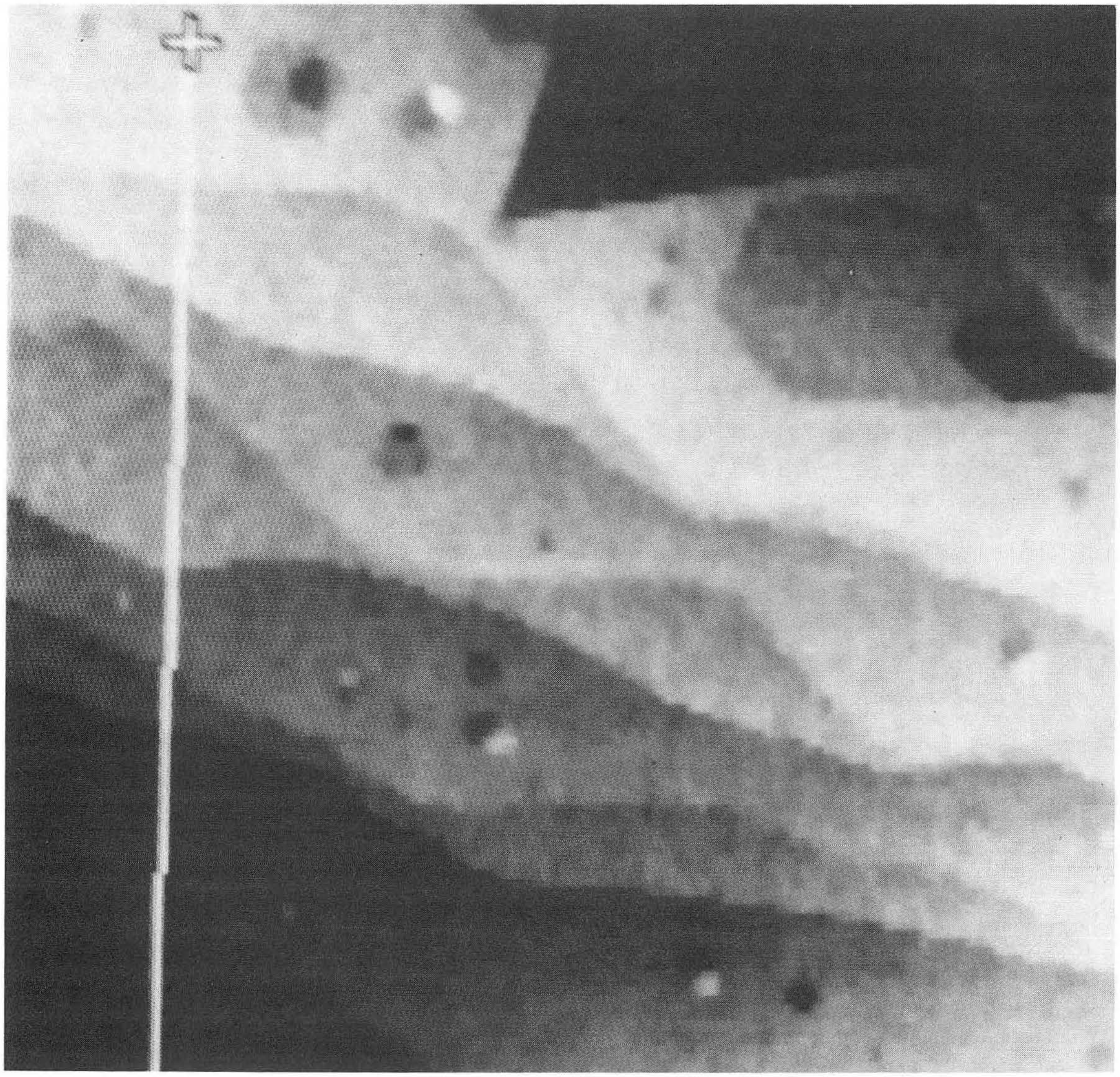

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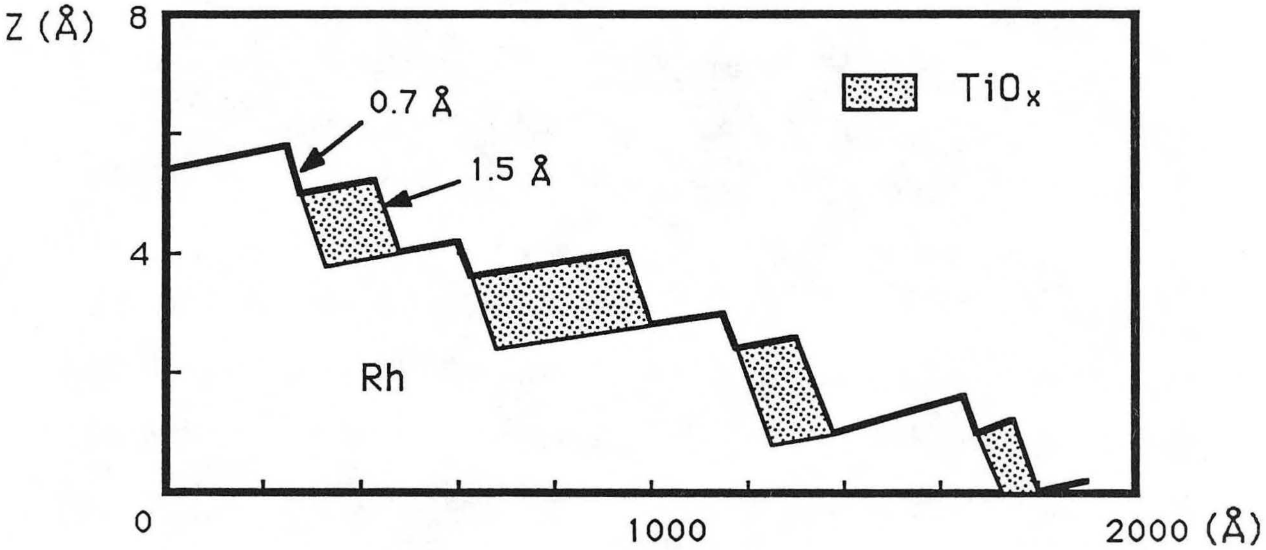
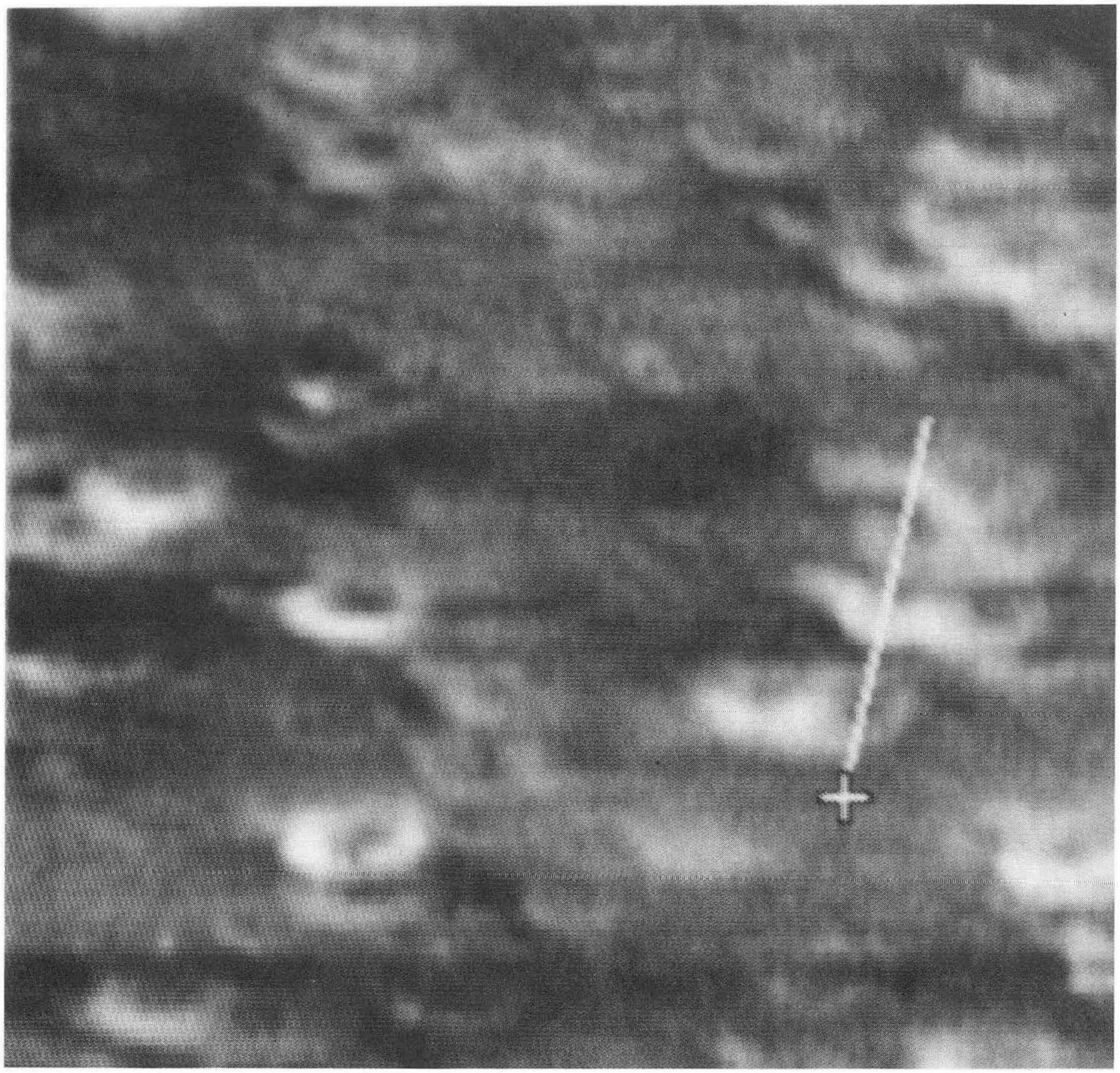


Figure 2(b)



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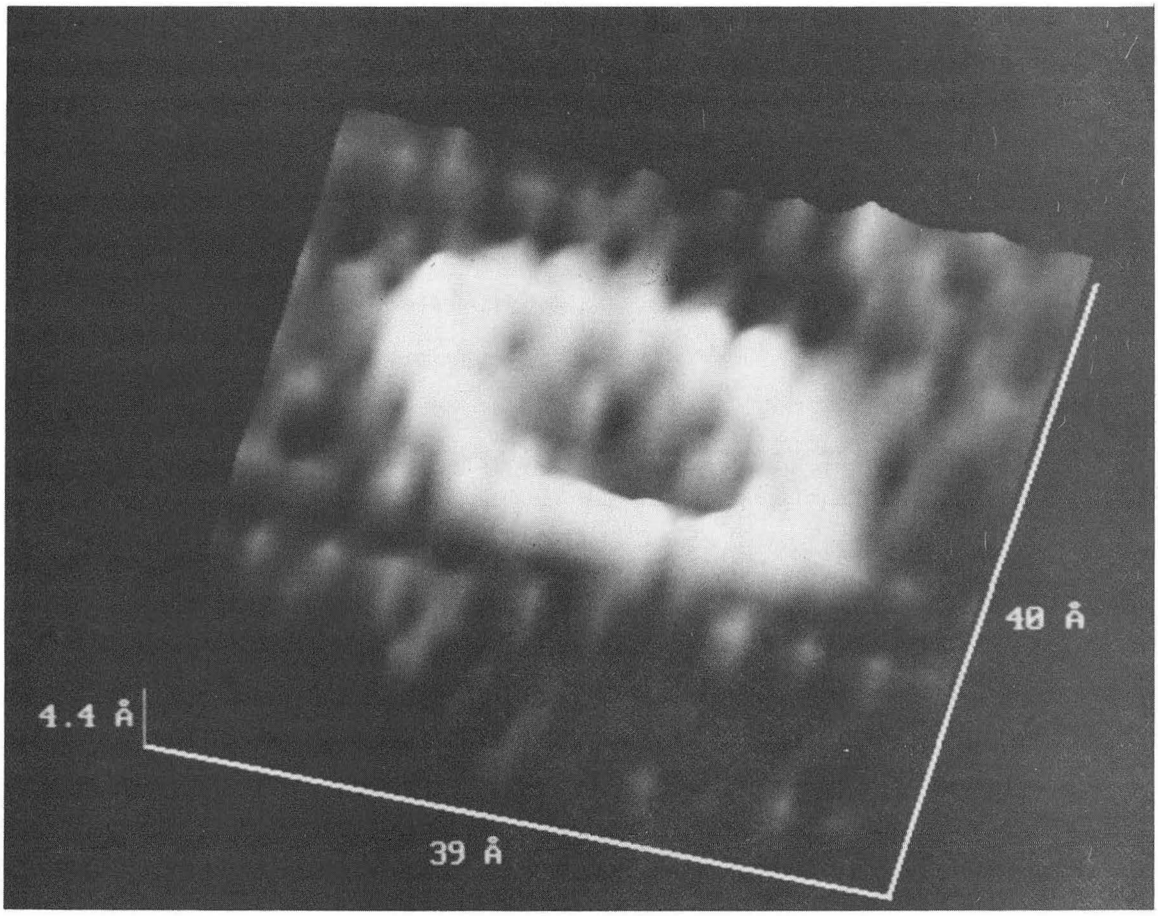

Figure 4 CBB907-5326

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