AD-A199 922

CUMENTATION PAGE

Form Approved OMB No. 0704-0188

UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; Distribution is unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): AFOSR-TR- 88-0988
6a. NAME OF PERFORMING ORGANIZATION: University of Maryland	6b. OFFICE SYMBOL (If applicable):
6c. ADDRESS (City, State, and ZIP Code): Dept of Physics & Astronomy, College Park, MD 20142	7a. NAME OF MONITORING ORGANIZATION: AFOSR/NC
	7b. ADDRESS (City, State, and ZIP Code): Building 410, Bolling AFB, DC 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: AFOSR	8b. OFFICE SYMBOL (If applicable): NC
8c. ADDRESS (City, State, and ZIP Code): Building 410, Bolling AFB, DC 20332-6448	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: AFOSR-85-0042

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2303	A2	

11. TITLE (Include Security Classification): Scanning Tunneling Microscopy as a Surface Chemical Probe

12. PERSONAL AUTHOR(S): Ellen D. Williams

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
FINAL	FROM 12/1/84 TO 5/31/88		19

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The instrumentation needed for combining a new imaging technique, Scanning Tunneling Microscopy (STM), with standard surface analytical methods has been developed. The surface analytical capabilities of the new system have been demonstrated by a study of the Barium-catalyzed oxidation of Ni. The operation of the STM has been demonstrated by a detailed study of the imaging of the graphite surface. The changes in graphite imaging with tunneling voltage have been measured and compared with theoretical predictions of the effect of surface change density and surface deformation on imaging via STM. The combination of STM with the surface analytical probes has been demonstrated in a comparison of LEED and STM measurements of a stepped Si surface. It is shown that LEED is rather insensitive to structural changes that are readily apparent using STM.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Lt Col Larry W. Burggraf	(202) 767-4960	NC

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE: UNCLASSIFIED

Final Report

AFOSR-85-0042

Scanning Tunneling Microscopy as a Surface Chemical Probe

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I. Abstract

The instrumentation needed for combining a new imaging technique, Scanning Tunneling Microscopy (STM), with standard surface analytical methods has been developed. The surface analytical capabilities of the new system have been demonstrated by a study of the Barium-catalyzed oxidation of Ni. The operation of the STM has been demonstrated by a detailed study of the imaging of the graphite surface. The changes in graphite imaging with tunneling voltage have been measured and compared with theoretical predictions of the effect of surface change density and surface deformation on imaging via STM. The combination of STM with the surface analytical probes has been demonstrated in a comparison of LEED and STM measurements of a stepped Si surface. It is shown that LEED is rather insensitive to structural changes that are readily apparent using STM.

II. Overview

When atomic-resolution imaging using STM was first demonstrated [1], it was entirely unclear whether the technique would prove to be a dead-end or whether it would revolutionize the understanding of surface properties. In the intervening six years, progress in the field has been remarkable [2]. The application of STM to surface structural determination is now well established. In addition, a wealth of other applications including lithography, biology, electrochemistry, and magnetic imaging have been discovered and are rapidly being developed [3].

The goal of the work supported under this grant was to develop STM (at that time an unproven technique) as a surface chemical probe. This required developing instrumentation for surface analysis in combination with STM. In the following three sections we describe results obtained demonstrate our surface analytical capabilities, the use of our STM, and the combination of the two. The experience developed in the course of this work, along with the developments in STM in the general scientific community, have led to some conclusions about the directions of research using STM, which are summarized in the final section.

III. Surface Analysis

The most important characteristics of a surface, structure and composition, can be determined using two analytical probes, low-energy electron diffraction (LEED) and Auger Electron Spectroscopy (AES). We have established an UHV system with these capabilities, as well as sample heating/cooling, gas dosing and metal deposition capabilities.

The results of a surface study of the enhancement of surface oxidation of Ni are shown in Figs. 1 and 2. AES is rather insensitive to Ba, as shown in Fig. 1. Therefore we used appearance potential spectroscopy (APS),

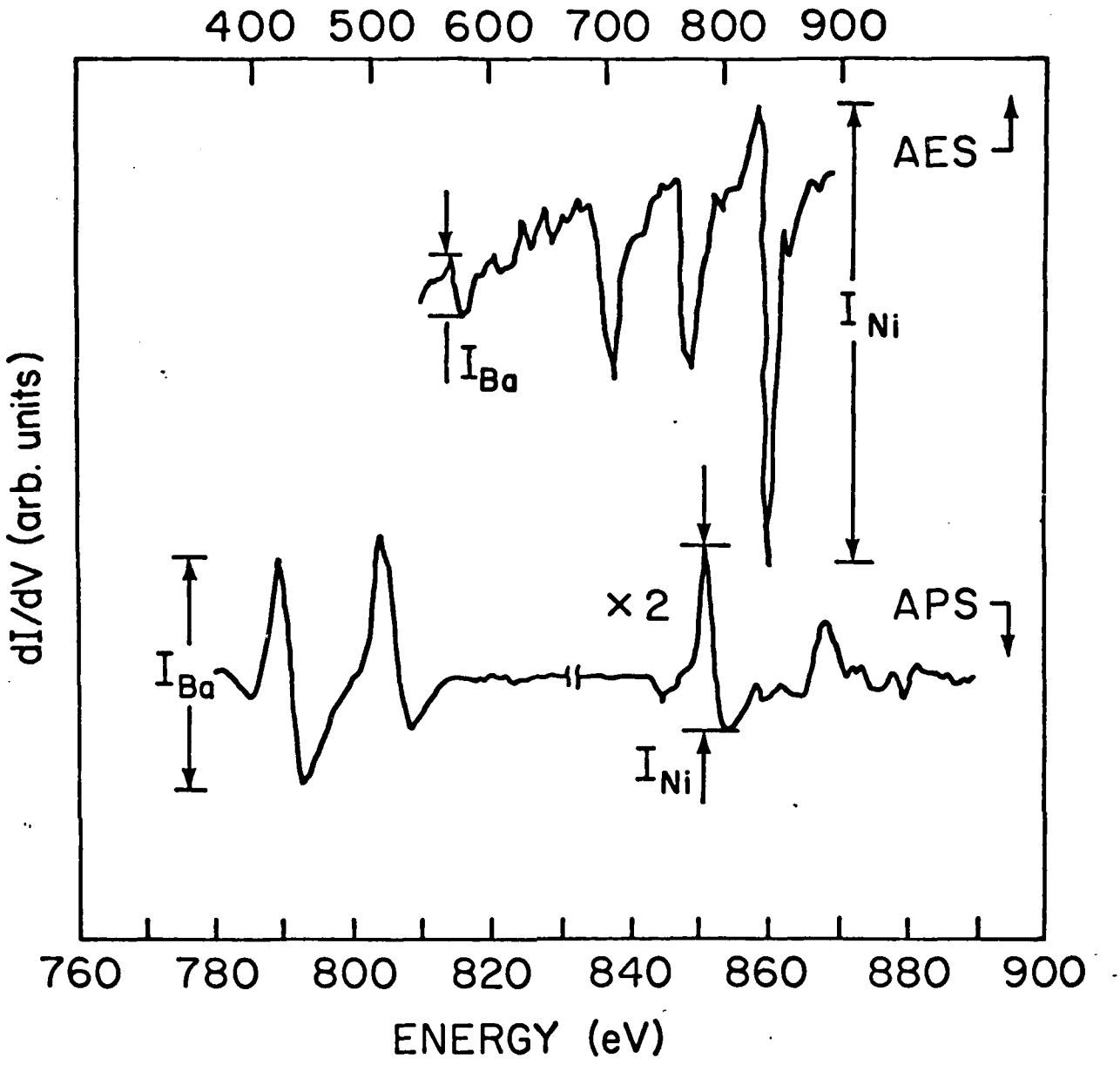
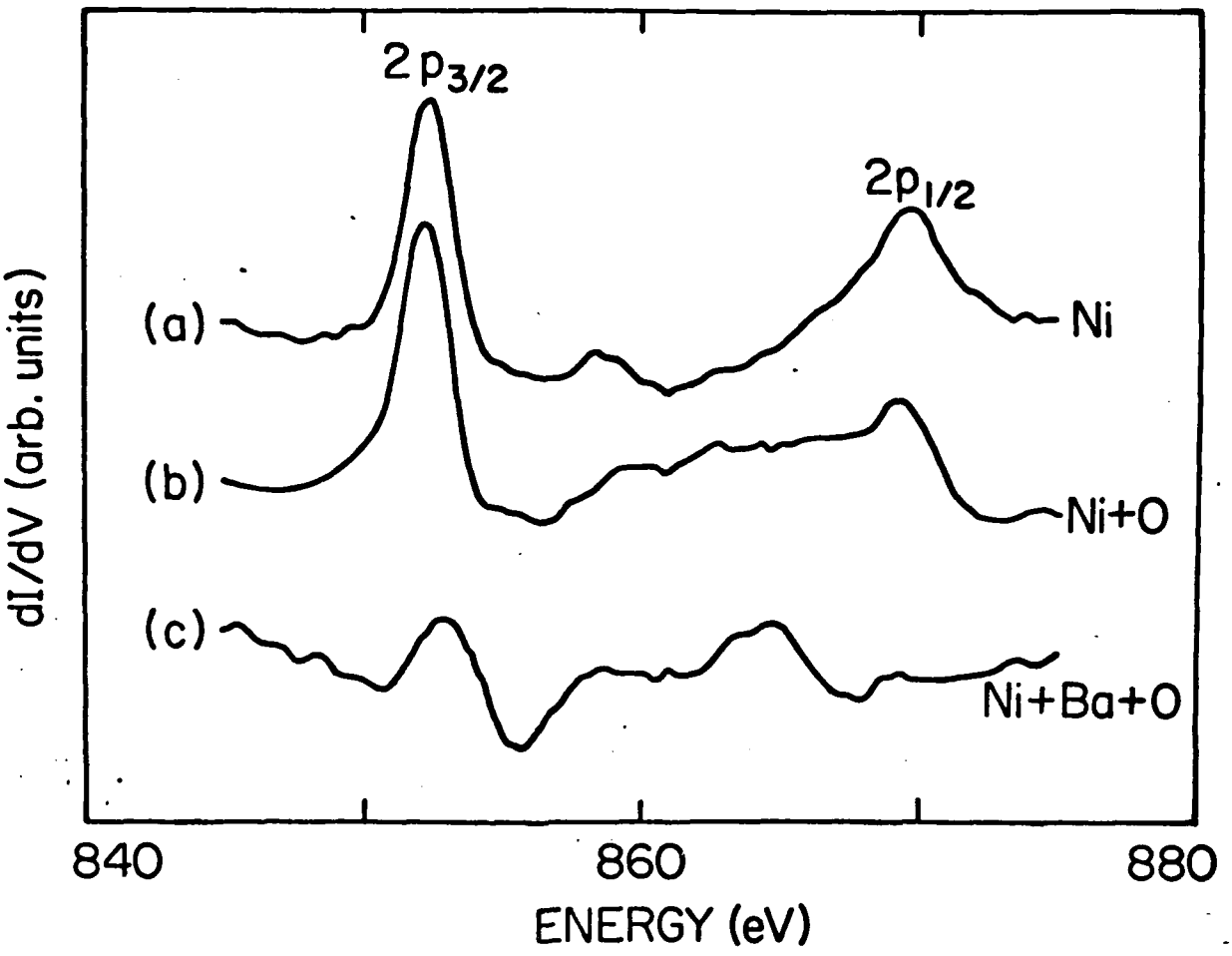


Figure 1. AES and AEAP spectra of Ni with 0.1 ML Ba overlayer. The ratio of the Auger Ni LVV and Ba MNN peak-to-peak heights are compared with AEAPS ratio of Ba $3d_{5/2}$ and Ni $2p_{3/2}$ peaks to obtain the AEAPS sensitivity of Ba relative to Ni.



AP spectra of Ni with (a) no presorbed Ba or oxygen at room temperature, (the Ni spectrum in the presence of 0.1 ML of Ba is identical.) (b) no preadsorbed Ba after exposure to 470 L of oxygen at room temperature, and (c) 0.1 ML preadsorbed Ba after 30 L oxygen exposure. This shows the enhancement of oxygen uptake of Ni with a slight Ba coverage.

Fig. 2

demonstrating its tenfold greater sensitivity for Barium. This allowed us to monitor the effect of coverages as low as 0.01 ML of Ba on the oxidation of Ni. As shown in Fig. 2, hundreds of Langmuirs exposure of clean Ni to oxygen causes no appreciable oxidation (Fig. 2b). However in the presence of Ba, only 30 L oxygen exposure causes the complete oxidation of the Ni surface.

IV. Implementation of STM

The design, electronics, computer interface and graphics used for our STM have been discussed in previous reports. Here we present results measured in air on the surface of highly-oriented pyrolytic graphite. There has been some controversy in the literature regarding the observed "giant-corrugations" of graphite [4,5]. We have undertaken a systematic study to address these questions.

The most naive picture of STM is that the tip moves over the surface like a ping-pong ball moving at constant height over a tray of marbles. However, a familiarity with the principles of tunneling easily show that this is incorrect [6]. The STM tip will move over contours of constant density of states, which may be very different at different tunneling voltages. However, in the case of graphite, corrugations in the STM scans have been observed that are very much larger than the predicted corrugations on the charge density of the surface [7-9]. A theoretical suggestion has been made that a deformation of the surface due to Van der Waals interactions with the tip is responsible for this effect.

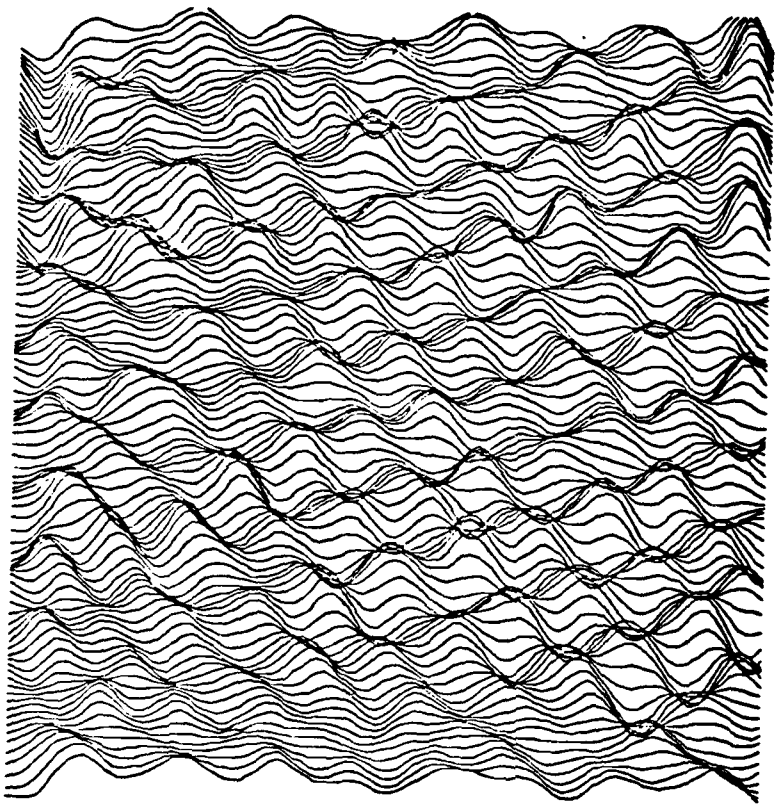
We have investigated this problem by measuring the STM image of the graphite surface in two different ways. In the constant-height mode, the vertical position of the tip is held constant while it is scanned parallel to the surface. The surface structure is imaged in the variations in the tunnel current. Because the Van der Waals force is averaged over an area of the

surface around the tip, we expect no variations in the force as a function of lateral position as long as the tip height is constant. Thus in the constant height mode, no "giant" corrugations should occur. The second method of imaging is the constant-current mode. In this case a feedback is used to maintain a constant current by varying the tip height as it moves across the surface. In this case, as the tip moves, the Van der Waals force will cause a corresponding motion of the surface. Thus a large displacement of the tip will be required to cause a small change in the tip-surface separations. The apparent corrugation of the surface in this case will be "giant".

In measuring the surface corrugation, it is important to use only images of high quality. Low quality images contain a large amount of noise that could be mistakenly analyzed as corrugations. To check the quality of our images we used both graphical display and Fourier transform. Some good data is shown in Fig. 3. It is important the 2-D symmetry can be observed as shown. Scans showing only 1-D features indicate a blunt tip and cannot be trusted to give a true measure of the corrugation.

The results of the corrugation measurements are shown in Figs. 4 and 5. In the constant height mode, the corrugation is independent of V_T. However, in the constant current mode, large corrugations of approximately 3Å are observed at the smaller values of V_T. A full understanding of the results requires a measurement of the effective work function which we are now completing. In Fig. 6, we show the variation of the tip position with respect to the tunneling voltage. The change of nearly 100Å over only 100 mV change in tunnel voltage is consistent with the deformation of the surface due to a tip-surface interaction force.

STM IN CONSTANT CURRENT MODE:
OBSERVATION OF GIANT
CORRUGATIONS IN GRAPHITE



SCAN SIZE: 25 X 25 $Å^2$
AVERAGE AMPLITUDE: 6 Angtroms
TIP VOLTAGE: −20 mV
TUNNEL CURRENT: 3 nA

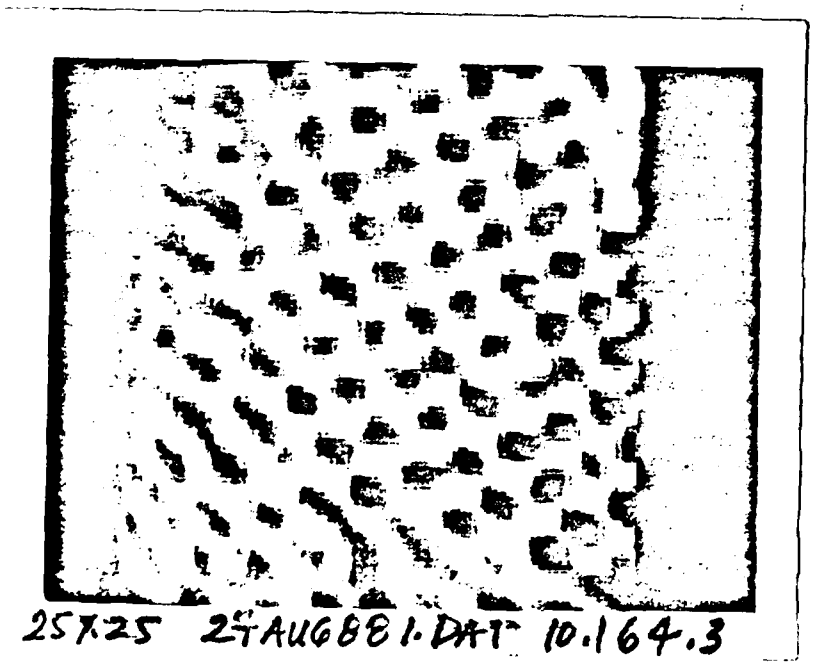


Fig. 3. Upper Panel: Line scan of graphite measured in constant current mode showing giant corrugations.
Lower Panel: Grey-scale image of the same data, showing expected hexagonal structure.

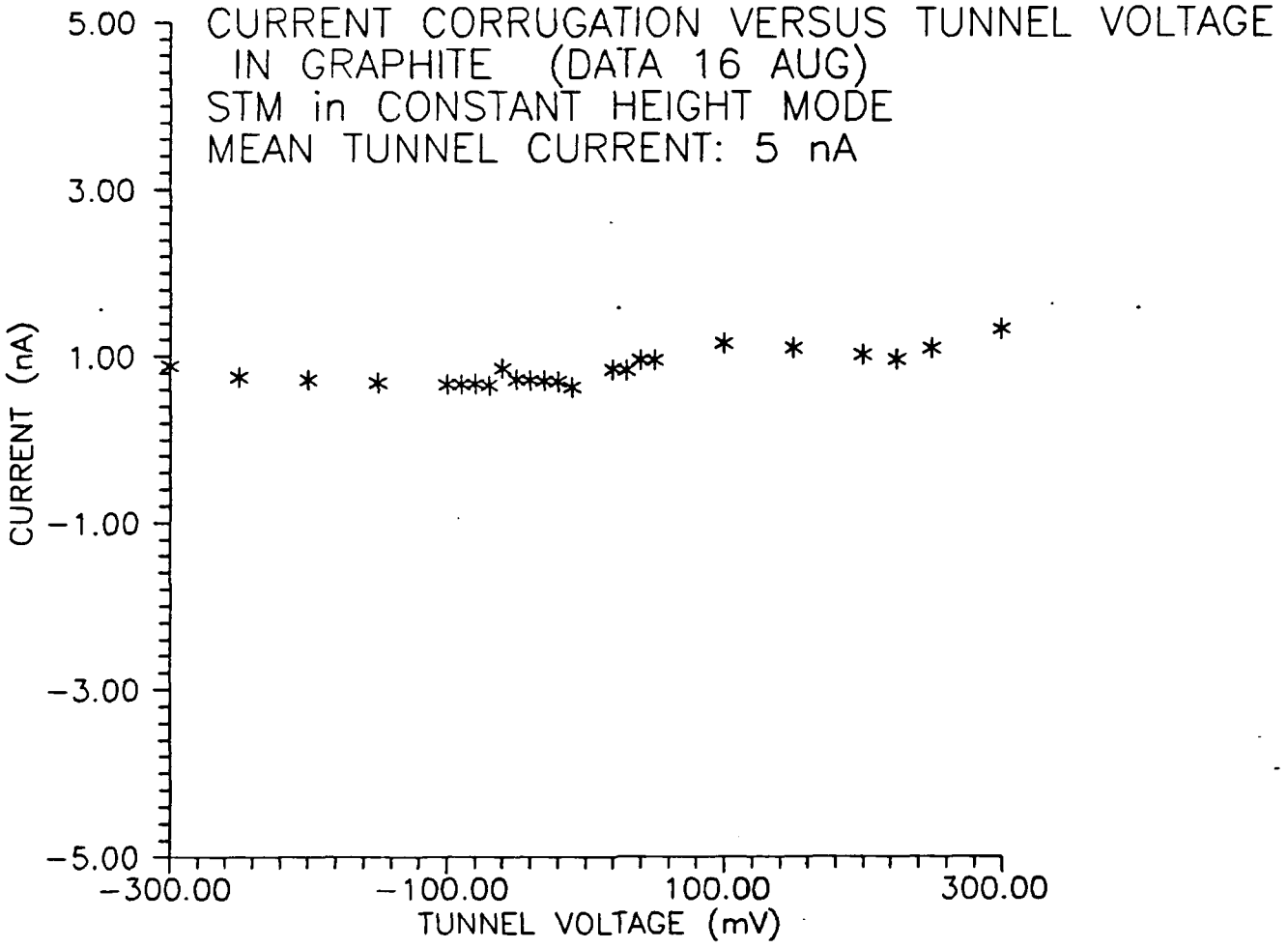


Fig. 4. Corrugation vs Tunneling Voltage measured in constant-height mode.

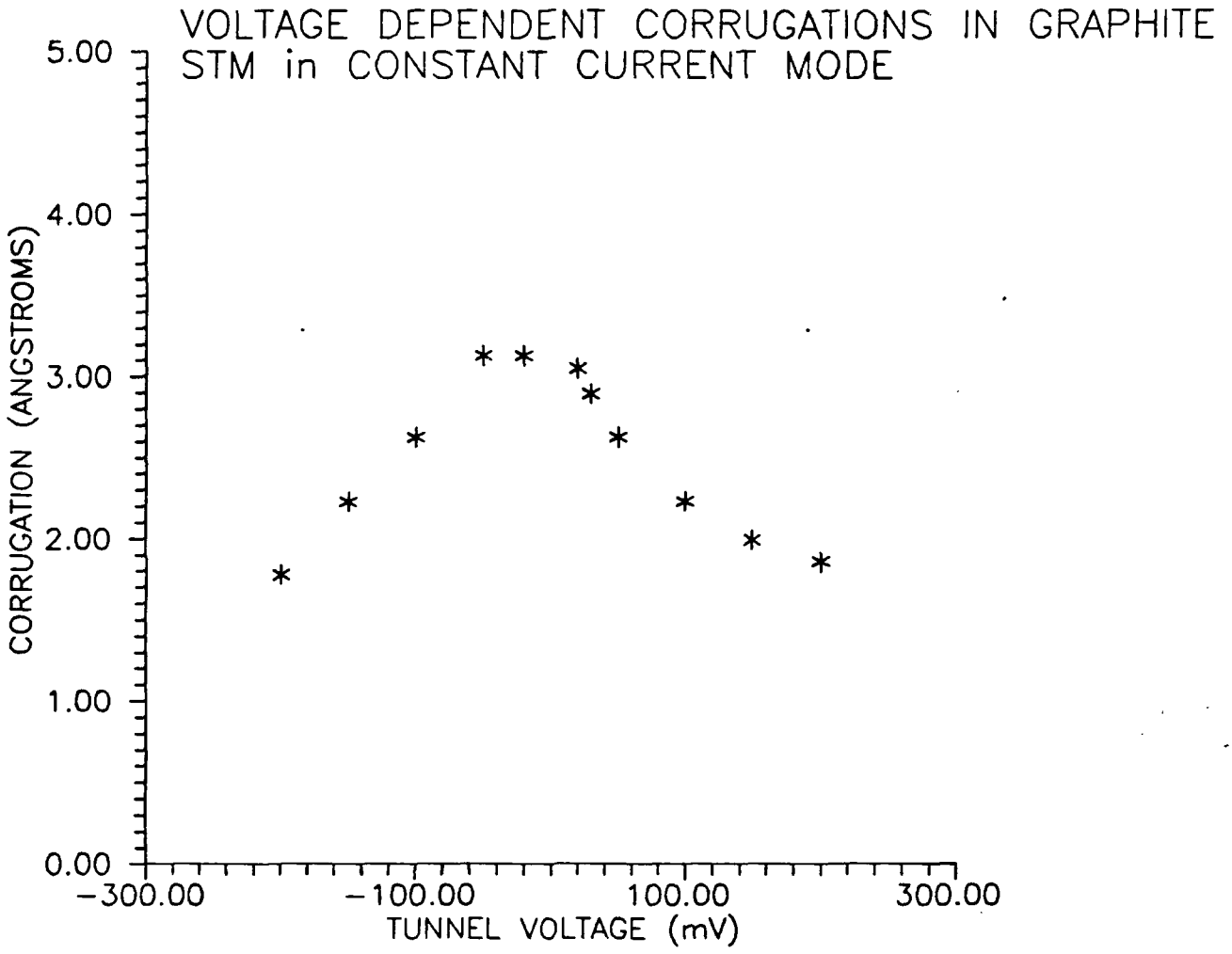


Fig. 5. Corrugation vs Tunneling Voltage measured in constant-current mode.

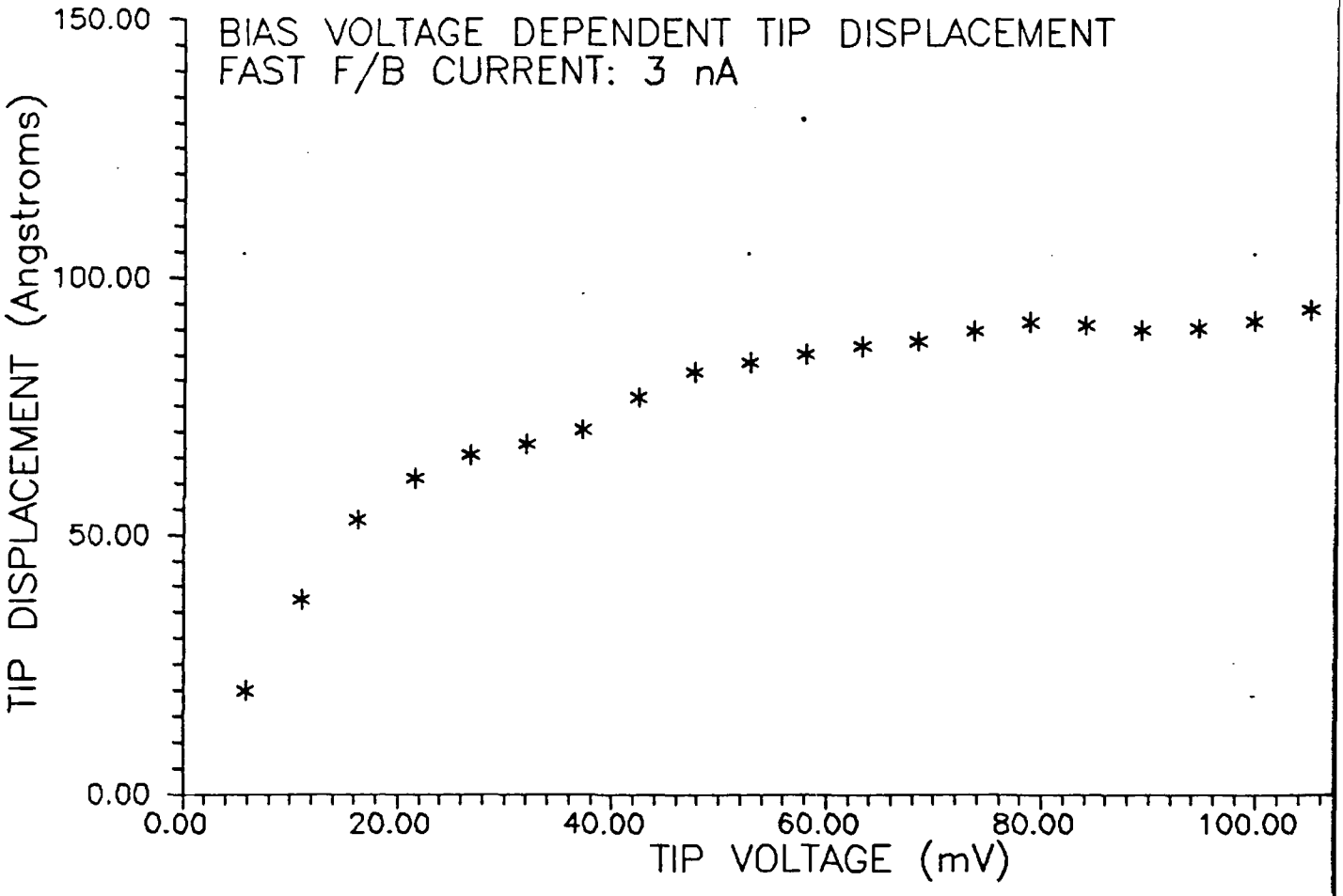
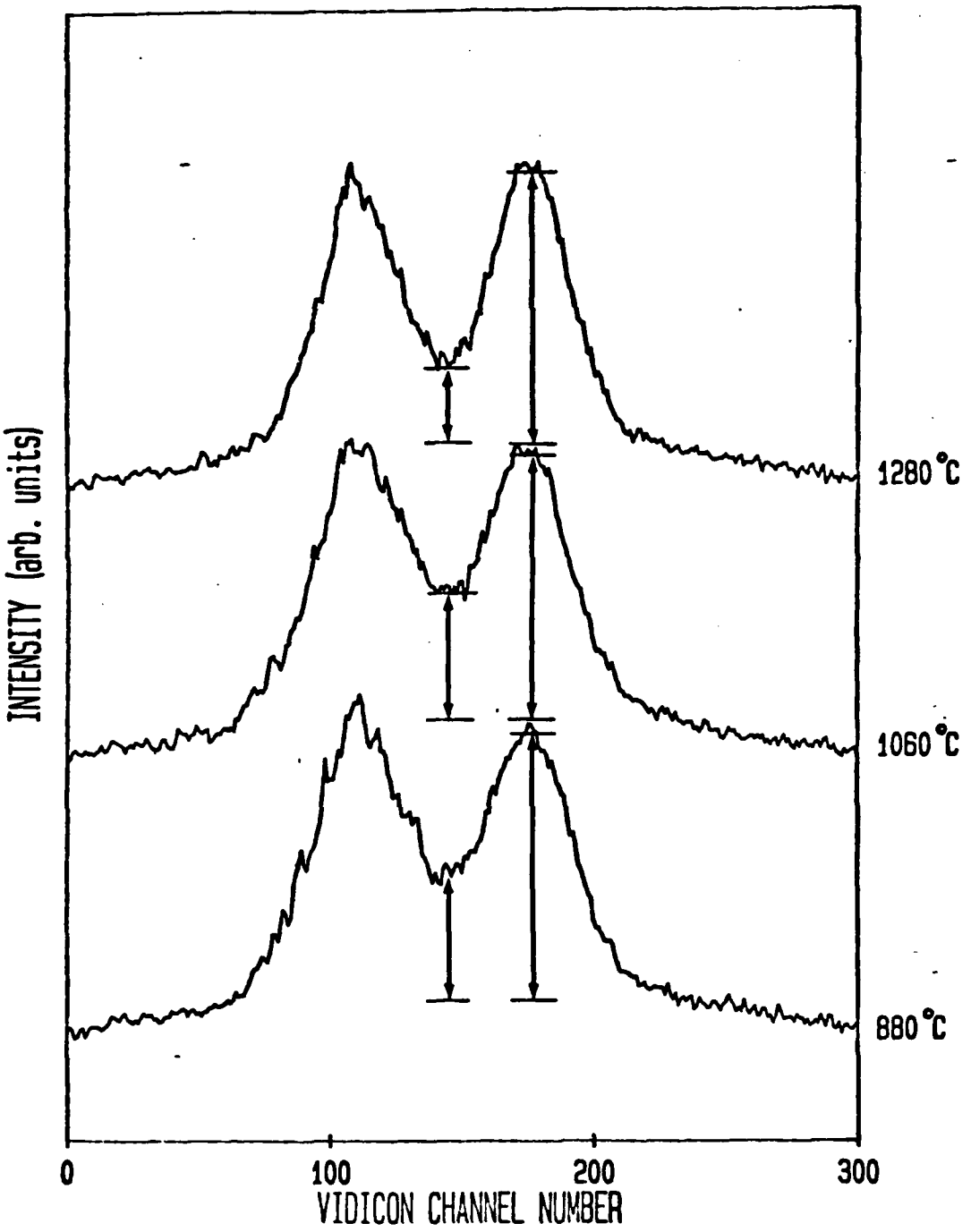


Fig. 6. Displacement of the tip as a function of Tunneling Voltage, in the constant current mode.

V. Clean Surface Studies with STM

Installation of the STM in a UHV chamber greatly increases the difficulty of the experiment. The major new problems are 1) lack of access to the tip for changes following bumps or (unexplained) poor resolution, and 2) the need for rigorous heat cleaning prior to measurement resulting in thermal drift. Some interesting LEED measurements [10] regarding the faceting of Si(111) led us to investigate this surface using the STM. As a first step in this investigation we, compared the efficacy of LEED [11] and STM in monitoring the cleaning of the surface.

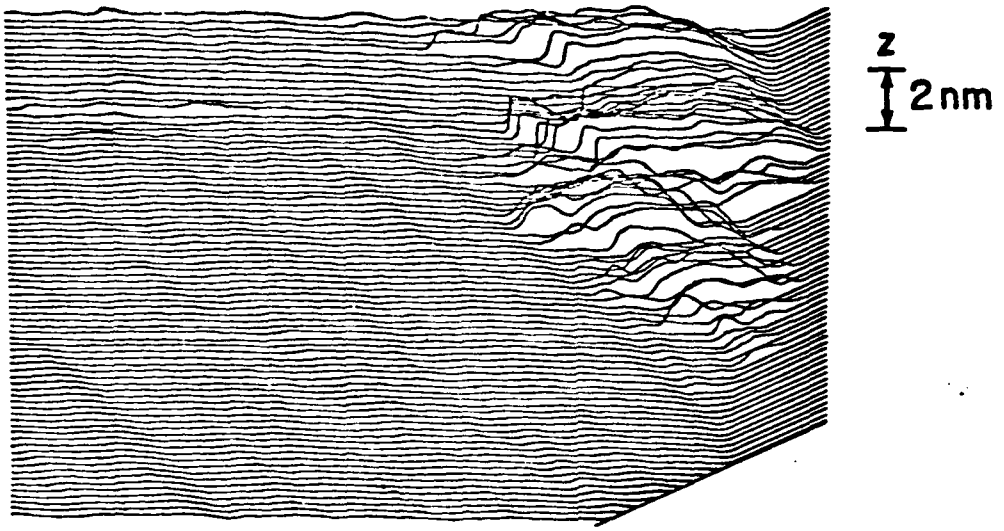
The preparation and cleaning of Si surface is the subject of a vast and often contradictory literature. Most difficult to assess has been the effect of various cleaning procedures on surface smoothness or morphology. In this work we have investigated the cleaning of a surface vicinal to Si(111). Ordinarily, one might expect the structure of a vicinal surface to contain an ordered staircase of steps whose separation is determined by the angle of misorientation. Si(111) vicinal surfaces show this behavior only above $\sim 850^{\circ}C$ [12] (where its 7x7 reconstruction disorders). Below this temperature, surfaces misoriented toward the $[\bar{1}10]$ or the $[\bar{2}11]$ directions phase separate into (111) facets and regions of high step density [10]. Using LEED we have found that initial heating at 850-900°C, a common cleaning procedure for Si(111), gives measurably less well ordered step structures on both the uniform and phase separated surfaces compared to heating at 1250°C. The data are shown in Fig. 7. The characteristic beam splitting for the uniform array of steps becomes sharper and better resolved upon cleaning at higher temperatures. The reason for this effect is illustrated in the STM images of Fig. 8. Heating at low-T leaves patchy disordered regions on the



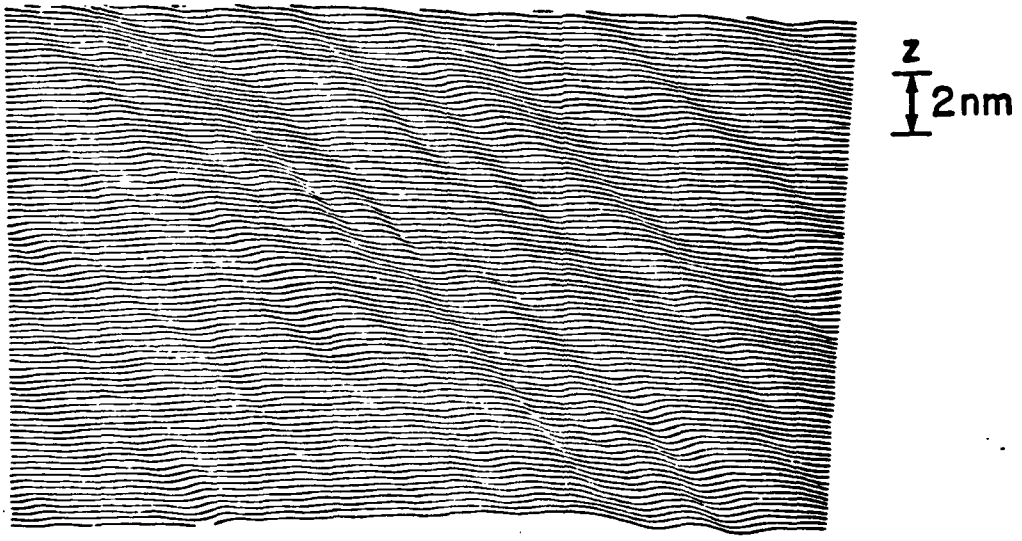
Angular profiles through the specular beam as a function of cleaning temperature. Profiles are measured at 880°C. Incident electron energy is 48eV. Incident angle is 8°.

Fig. 7

(a)



(b)



Sections from large area scans of vicinal Si(111) surfaces cleaned in vacuum at two different temperatures.

a) 350Å x 100Å area scans, cleaning temperature 850°C.

b) 300Å x 250Å area scan, cleaning temperature 1250°C.

Fig. 8

surface which may be associated with residual carbon on the surface. Only following heating at 1250°C do large smooth regions with well-ordered step-structure appear.

LEED also shows that the formation of a well-ordered surface is sensitive to the rate of cooling; to maintain equilibrium the cooling rate must be less than about 0.2°C/s. A natural explanation of the thermal sensitivity is simply kinetics; low cleaning temperatures do not allow enough surface diffusion for the steps to move so that they can achieve an equilibrium ordered structure. However, the STM images rule out such a straightforward explanation. The quenched surface contains large scale corrugations of width 5-10nm. The rms vertical amplitude of the surface is approximately 2nm, as compared with 0.4nm for the slowly cooled surface (Fig. 8b).

LEED beam profile measurements show that vicinal Si(111) surfaces prepared by two methods, low temperature cleaning or rapid cooling from above the structural transition both contain poorly ordered step structure. However, STM measurements reveal that the nature of the disorder is quite different in the two cases. Low-temperature cleaning leaves regions of crystalline disorder which are possibly correlated with the presence of carbon. These disordered regions apparently restrict the ordering of the steps. Rapid cooling results in a wave-like surface structure quite different from simple expectations of kinetically limited step motion. These results confirm the general observation that extraction of detailed atomic information from LEED profiles is fraught with problems of uniqueness. Clearly, the use of STM imaging can immediately provide qualitative information to guide interpretation of the LEED results. In the future more

detailed STM measurements will allow the direct determination of step-step correlation functions for comparison with statistical mechanical models of step-wandering.

VI. Conclusions

Scanning Tunneling Microscopy has proven to be remarkably powerful [3]. However, it is still a difficult technique to use and places severe demands on the scientists performing the experiment and analyzing the results. In particular, because of the ephemeral nature of the tip and the small field of view, any one STM scan may not present a true representation of the overall surface character. Repeated scans over the surface and comparison with the results of other measurements are needed before a confident interpretation can be made. Because of these constraints, STM has been used primarily as a qualitative probe. This is exemplified in its role in structure determination: STM has been used to locate unit cells of the symmetry known from LEED. The location of the adatoms in these cells has been imaged, ruling out all but a few possible models for the structure. Diffraction or scattering techniques then have been used to quantify the structure. In this sequence the role of STM has been invaluable, but strictly qualitative.

This leaves the question of what sorts of quantitative measurements are possible with STM. One type of quantitative measurement has been elegantly demonstrated in the CITS studies of Si(111) performed by Demuth and co-workers [13]. The registry of the spectroscopic and structural measurements in this technique is accomplished by excellent experimental design. Similar quantitative results with respect to the kinetic and thermodynamic properties of surfaces will be possible with equivalent care in experiment and analysis. In particular, Jaklevic has recently presented the prototype experiment for measuring surface kinetics using STM [14]. The type

of care required in quantitative analysis is illustrated in our graphite study. To prevent unconscious biasing of the results, a fixed reference criterion such as the Fourier transform must be used in selecting the data to be analyzed. Thus, out of hundreds of experimental scans, those which can be reasonably compared can be selected.

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IIX. Publications and Presentations

a. Publications

1. R.D. Gomez and E.D. Williams, "Appearance Potential Study of Ba-Activated Oxidation of Ni", Surface Sci., in press.

2. X.-S. Wang, R.J. Phaneuf and E.D. Williams, "Comparison of LEED and STM Measurements of Vicinal Si(111) Surfaces", J. Microsc., in press.

3. R.D. Gomez and E.D. Williams, "STM-Measurements of the Corrugation of the Surface of Graphite", in preparation.

b. Presentations

E.D. Williams, X.-S. Wang and R.J. Phaneuf, "Facet Structure of Vicinal Si(111)", Third International Conference on STM, Oxford, July 1988.

R.D. Gomez and E.D. Williams, "Measurements of the Corrugation of the Graphite Surface Using STM", 35th National Symposium of the AVS, Atlanta, October 1988.