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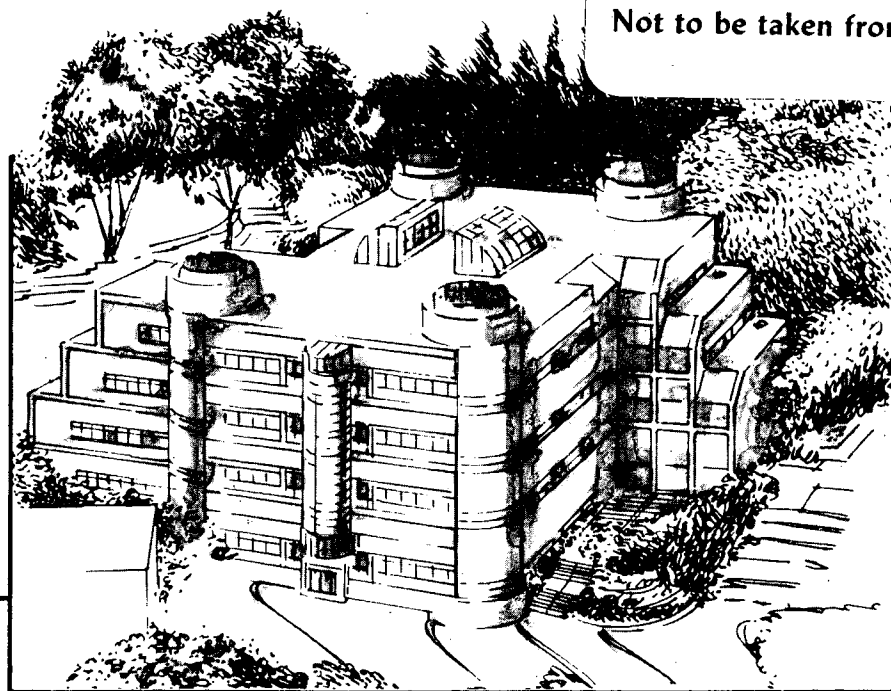
## Observation of the Initial Stages of Growth of Hydrogenated Amorphous Carbon Films by Scanning Tunneling Microscopy

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**For Reference**

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# Observation of the Initial Stages of Growth of Hydrogenated Amorphous Carbon Films by Scanning Tunneling Microscopy

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## Abstract

Scanning Tunneling Microscopy (STM), was used to investigate the initial stages of growth of hydrogenated amorphous carbon (a-C:H) films. The films were deposited on highly oriented pyrolytic graphite (HOPG) and silicon substrates both on the powered (negatively self biased) and on the grounded electrodes from a methane r.f. plasma (13.56 MHz) at 68 to 70 mTorr and room temperature. On graphite substrates, films formed at the powered electrode were observed to nucleate in clusters approximately 50Å in diameter. Cluster density increased with deposition time, while cluster size remained relatively constant. The atomic structure of individual clusters was amorphous. The C-H bonding in these clusters was observed by high resolution electron energy loss spectroscopy. Films formed on graphite substrates placed at the grounded electrode produced very noisy images due to an unstable tunneling gap, indicative of the material's poor electrical conductivity. On silicon substrates placed at the powered electrode, film deposition was uniform and no cluster formation was observed. The films formed were measured to be flat to within 3Å rms.

# 1 INTRODUCTION

Amorphous hydrogenated carbon (a-C:H) films are the subject of many investigations<sup>1)</sup> because of their valuable mechanical properties such as high hardness (30GPa). Good adhesion to the substrate is necessary for their utility as protective coatings. Since the adhesive strength of a coating to its substrate is determined by the interfacial properties, control of these properties, and in particular, a better understanding of the initial stages of growth and of nucleation mechanisms is crucial.

The technique utilized to grow the films was r.f. plasma assisted chemical vapor deposition (PACVD) using methane as the feedgas. In a previous study<sup>2)</sup>, the different roles of the plasma radicals and plasma ions in the process of bulk film growth were elucidated. The essential role of plasma ions in the formation of a silicon carbide interface was also recently investigated<sup>3)</sup>, in the case of films formed on silicon. From these studies we know that due to the energetic ion bombardment on the powered electrode, hard films are formed with a large content of  $sp^2$  type C-C bonds. On the grounded electrode on the other hand, the films are soft and polymeric in nature, as indicated by the large IR absorption band due to  $CH_2$  and  $CH_3$  groups.

In this paper, we present the results of an investigation of the initial stages of growth of a-C:H films on graphite and silicon substrates by scanning tunneling microscopy (STM), and high resolution electron energy loss spectroscopy.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Sample preparation

The carbon films in this study were produced by plasma assisted chemical vapor deposition (PACVD) using methane gas in an r.f. apparatus (frequency 13.56 MHz) with a parallel plate configuration as described previously<sup>2)</sup>. The graphite substrates were received from A. Moore of Union Carbide and cleaved by the scotch tape method immediately before being placed on either electrode in the plasma chamber. Single crystal Si(100) wafers (n type, Boron doped to 15 - 30  $\Omega$  cm) were obtained from the U.C. Berkeley Microfabrication laboratory

and were first etched in an  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$  (7:3) bath, then in a 10% HF bath, and finally, the back sides of the wafers were coated with  $0.5 \mu\text{m}$  of Au to provide a good electrical contact. The wafers were then cleaved into 1cm by 1cm fragments which were then placed on the electrodes and used as substrates. The plasma chamber was mechanically pumped down to a pressure of less than 10 mTorr, then methane was admitted at  $8 \text{ cm}^3/\text{min}$  to reach a preignition pressure of 65mTorr. The plasma was ignited for short (5 - 30 sec.) deposition times to complete the initial stages of growth. The methane flow was then stopped and the chamber pressure increased to atmospheric with Ar gas. The samples were then removed from the electrodes and transferred through air to the STM, where they were finally imaged in air.

## 2.2 STM imaging

The imaging was done in air at room temperature using a "double-tube" type STM similar to that built by Lyding et al.<sup>4)</sup>, and Zeglinski et al.<sup>5)</sup>. The STM was controlled using electronics developed at Lawrence Berkeley Laboratory, and the data were acquired using a PC compatible computer with a 12-bit 150 kHz analog to digital converter. All the images were obtained with the STM in the topographic (constant current) mode using tips mechanically cut from 1mm diameter Pt-40%Rh alloy wire. The images of films on graphite substrates were obtained using a sample bias of -100mV and tunneling current of 1.0 nA. These images showed very little bias dependence between -200mV and +200mV. Images of films formed on the Si(100) substrates were obtained using a bias of -3.0V and tunneling current of 20 - 50 pA. The tunneling gap was unstable at higher tunneling currents, with positive sample biasing, or with negative sample biasing of less than 2.7 V. Scan velocities from 200 to 5000 Å/sec were used and images were recorded with 256 points per line and 128 lines per image.

## 2.3 HREELS

High resolution electron energy loss spectroscopy was carried out with a view towards chemically distinguishing the low coverage a-C:H film from the graphite

blank and perhaps gaining information concerning the character of the C-H bonding present in the films. The sample of a-C:H on graphite was prepared identically to those prepared for use in the STM studies, with a deposition time of 10 seconds. The graphite blank received identical treatment excluding plasma ignition. The samples were then transferred through air to an ion pumped UHV chamber which attained a base pressure of  $7.5 \times 10^{-11}$  Torr. A HREELS spectrometer similar to that of Froitzheim et al <sup>6)</sup> was used with an incident electron energy of 5 eV. The energy resolution (FWHM) for the graphite blank was  $75 \text{ cm}^{-1}$  and  $90 \text{ cm}^{-1}$  for the a-C:H film.

### 3 RESULTS

#### 3.1 a-C:H on graphite

Graphite substrates exposed to the methane plasma for deposition times between 5 and 20 seconds showed distinct cluster formation, as is demonstrated by the  $(1000\text{\AA})^2$  grey scale image in figure 1. This image was taken of a graphite substrate which had been exposed to the plasma for 15 seconds. The cluster diameter was seen to be typically about  $50\text{\AA}$ . Cluster size remained roughly constant with deposition time, while cluster density increased with deposition time. For deposition times greater than about 20 seconds, the clusters completely covered the graphite surface, leaving no exposed graphite where atomic resolution images of the graphite substrate could be obtained. An example of such a high coverage is shown in figure 2. Actual cluster density varied considerably from area to area on the same sample, as well as from sample to sample. Apparently the plasma conditions were not very homogeneous spatially during the initial stages of growth. The trend of increased cluster density as a function of time was clear, however, because of the noted lack of uniformity, it was not possible to quantify the cluster density behaviour as a function of time. Deposition times of 5 seconds always gave images showing a low cluster density and times greater than 25 seconds always showed a complete coverage, but for times in between 5 and 25 seconds, images showed considerable fluctuation between these two extremes of cluster density from area to area and from sample to sample. Since thick a-C:H films are quite insulating, the tunneling



conditions became quite unstable for deposition times greater than 30 seconds, as the conducting substrate becomes completely covered by the insulating film.

The atomic structure of the individual clusters is of great interest. Marchon et al <sup>7)</sup> succeeded in resolving atomic structure by STM at the surface of amorphous carbon films (non-hydrogenated) prepared by dc magnetron sputtering. These authors observed small graphitic domains of approximately 15Å as well as numerous five membered rings. In our study the cluster structure, consisted of disordered bright and dark spots. It is clear that these clusters have an amorphous structure, lacking in any apparent local order even down to an atomic scale. Figure 3 shows how the the regularly ordered atomic structure of the graphite substrate is observable between the a-C:H clusters, while the clusters themselves have an amorphous appearance. Figure 4 shows a closeup image of a cluster, where bright spots are visible, separated by distances consistent with C-C bond lengths.

The presence of hydrogen at the surface of these films is demonstrated in the HREELS spectra shown in figure 5. HREELS has been widely used as a surface vibrational technique in recent years, largely due to its high surface sensitivity ( $10^{-2}$  -  $10^{-3}$  of a monolayer) and its wide spectral range (100 to  $5000 \text{ cm}^{-1}$ )<sup>10-12</sup>). Displayed in figure 5 are the HREELS spectra for an a-C:H film deposited for 10 seconds onto graphite at the self biased electrode, as well as that for a graphite blank substrate. The broad band at  $1200 - 1400 \text{ cm}^{-1}$  corresponds to C-H bending vibrations, and the loss at  $2935 \text{ cm}^{-1}$  is associated with the C-H stretch mode. In contrast, the graphite blank substrates shows no such modes. Thus we observe the presence of C-H bonding that terminates the surface of the a-C:H films. As expected, this bonding is not present at the surface of the graphite blank, which received the identical treatment as did the a-C:H film, including exposure to the methane flow, and air transfer, but excluding only plasma ignition. Similar features to those in the a-C:H spectra were observed for a semiconducting diamond (111) surface<sup>13</sup>). The width of the observed modes is quite large, even though the width of the elastic peaks ( $75 - 90 \text{ cm}^{-1}$ ) is considerably less. This result is perhaps not surprising, considering the fact that we have a very disordered, amorphous surface. Unfortunately, this fact prevents us from making any unambiguous assignments of the bands

observed to more specific vibrational modes. We can clearly see, however, the presence of hydrogen at the surface of the a-C:H film, and the absence of the same at the surface of the graphite blank.

It is interesting to compare the initial stages of growth in the case of films formed at the self biased electrode, where high energy ion bombardment takes place, to the growth of films formed at the grounded electrode, where this high energy bombardment is absent. Figures 6a and 6b display this comparison. The images taken on the powered electrode are always stable and show distinct cluster formation after the initial stages of growth as shown in figure 6a. Notice the vertical scale of the figure indicating that the average corrugation of the cluster covered surface is about 5 to 10 Å. In contrast, images taken at the grounded electrode were always unstable and poorly reproducible, with large excursions of the tip in the vertical direction. In the example shown in figure 6b the range of vertical tip displacement is nearly 50 Å. This instability is a consequence we believe, of the polymeric nature of the film formed at this electrode, with lower conductivity than the hard films formed at the powered electrode and poorly bonded to the graphite surface. The poor bonding is due to the lack of ion bombardment that creates active sites in the powered electrode.

### 3.2 a-C:H on Si(100)

In order to facilitate the observation of features due to the initial stages of growth of a-C:H on silicon, it is first necessary to prepare a relatively featureless substrate. Using the techniques described in the experimental section we were able to produce silicon substrates which were quite flat (figure 7a). The STM images gave a standard deviation of tip positions around the mean of less than 3 Å. The silicon surface is probably smoother than this, as the measured smoothness was limited by noise, not on actual observable topographic structure. Substrate smoothness was stable for more than 24 hours.

The surface topography of a-C:H films grown on silicon substrates at the self biased electrode (figure 7b) was also exceedingly smooth. In fact the topography of the film surface was practically indistinguishable from the topography

of the substrate surface ( $<3\text{\AA}$  standard deviation from mean position) for all deposition times from 5 to 20 seconds. Some topographic features are barely visible in figure 7b, but the height of these features is comparable to the noise level. It is clear that the clusters observed in the case of a-C:H formation on graphite are not observed in the case of silicon substrates. Tunneling gap stability degraded with increasing thickness, as was the case on graphite substrates.

As with graphite, films formed on silicon at the grounded electrode produced noisy images due to instability in the tunneling gap. Since, in both cases, we expect to have an insulating material poorly bonded to a semiconductor, this result is not surprising.

## 4 DISCUSSION

### 4.1 a-C:H on graphite

From previous studies <sup>2)</sup>, we know that the plasma growth conditions are very different for films grown on substrates placed at the negatively self biased electrode, as compared with those grown at the grounded electrode. The most significant difference is the higher kinetic energy of ions striking the growing surface at the self biased electrode (approx. 350eV), as compared to the kinetic energy of ions striking the film surface at the grounded electrode (approx. 15eV). The ion flux is probably also significantly higher at the self biased electrode <sup>2)</sup>. In contrast, the flux of low energy neutral radical species (predominantly  $\text{CH}_3\cdot$ ), is about the same at both electrodes. Evidence suggests that the growth mechanism for these films is one where the radicals react and bond to the growing film surface to provide the bulk mass of these films by polymerization <sup>2)</sup>. Without high energy ion bombardment, as is the case at the grounded electrode, the films grown are soft and polymerlike. In contrast, films grown on silicon at the self biased electrode, where high energy ion bombardment is present, exhibit much different properties, such as a high hardness, and lower hydrogen content. Films formed at the self biased electrode also exhibit better adhesion onto silicon than do films formed at the grounded electrode. The high energy ions impinging on the substrate at the self biased electrode, contribute to the formation of a silicon carbide interface, not present in the case of soft

films grown on silicon at the grounded electrode <sup>3</sup>).

In figures 6a and 6b, a difference is observable between the initial stages of growth at the self biased electrode, as compared to the grounded electrode, for a-C:H films on graphite substrates. There is distinct cluster formation evident at the self biased electrode, with a corrugation of about 10 Å (see Fig. 6a). In contrast, unstable images were observed at the grounded electrode giving rise to an apparent corrugation about 4 times larger.

Our proposed explanation for these observations is as follows. The ideal graphite surface has no dangling bonds and is quite unreactive <sup>14</sup>). The sticking coefficient of CH<sub>n</sub> radicals to an ideal graphite surface is probably extremely small. Estimates of methyl radical sticking coefficients with the reactive film surface are near 0.03 <sup>2,15,16</sup>). An ideal graphite surface would likely give sticking probabilities even smaller than these. As a result, a rapid and strong homogeneous chemical attachment of radicals to the graphite surface is unlikely. Additional support for this statement is the markedly small initial deposition rate of a-C:H on graphite. The average bulk deposition rate of these films on silicon is about 2Å/sec <sup>2</sup>). The initial deposition rate is smaller, as complete coverage does not occur over the stable graphite surface until a deposition time of more than about 20 seconds, instead of about 4 seconds, as calculated using the bulk deposition rate.

We believe that a disruption of the graphite surface is necessary before plasma radicals can chemically bond to the surface. Such a disruption is provided by the high energy ions impinging on the surface at the self biased electrode. The observed clusters are formed as a result of the more rapid and irreversible bonding of reactive plasma species at the site of the ion induced defects. The clusters grow rapidly until they reach a critical size which might be determined by the size of the area perturbed by the ion collision event. Further cluster formation would stop then because the surface has become depleted in active sites, or dangling bonds, and hence it would remain relatively inactive until a new disruption is formed by means of another ion bombardment event. This would explain why cluster size is relatively constant, as the density increases. At the grounded electrode, in contrast, there are comparatively few active sites where radicals can bind to the substrate due to the absence of en-

ergetic ion impacts. Deposition is still observed, however, as seen in figure 6b. The material deposited here is more polymerlike, and only weakly bonded to the surface, as revealed in our previous work <sup>2)</sup>. The fact that the tunneling gap is unstable at this surface, is due to two different effects. One is the polymerlike nature of the material deposited and the abundance of -CH<sub>2</sub>- and -CH<sub>3</sub> groups<sup>2)</sup> which implies a less conductive film. The other is the weaker bonding of the species at the surface. Weakly bonded polymeric material might also be formed at the powered electrode. The fact that it is not observed between the clusters seems to imply that energetic ion bombardment is causing the desorption of this material from the regions between the clusters at the powered electrode.

## 4.2 a-C:H on silicon

Cluster formation during the growth of a-C:H on silicon substrates at the self biased electrode was not observed, as shown in figure 7b. From previous angle resolved x-ray photoelectron spectroscopy studies <sup>3)</sup>, we know that a silicon carbide interface is formed completely in less than 10 seconds of deposition time. We expect that, even at our shortest deposition time of 5 seconds, most of the silicon substrate has been covered up by a-C:H. Since we cannot control deposition time accurately for intervals less than 5 seconds (the time required to ignite and stabilize the plasma), we are not able to study coverages of less than about one half monolayer. If the initial deposition rate were equal to the average bulk deposition rate of about 2Å/sec, we would certainly have passed the point of complete coverage in less than 5 seconds. The initial deposition rate in the case of the graphite substrates, is clearly much less than the bulk deposition rate of these films, as complete substrate coverage does not occur until after about 20 seconds. We have no information on the initial deposition rate of a-C:H films on silicon substrates, as the substrate surface and the film surface are indistinguishable by our current STM capabilities. We can not rule out an initial cluster formation, before our shortest 5 second deposition time. The present STM results however, clearly indicate that the films formed on Si are indeed atomically smooth, as assumed in our growth models that

explained the formation of a SiC interface between the a-C:H film and the silicon interface<sup>3</sup>.

Our proposed explanation for the apparent lack of clustering on silicon is as follows. The silicon substrate surface, before deposition, is hydrogen terminated<sup>17-19</sup>), and presumably is much more reactive towards plasma radicals than is the very stable graphite surface. The low initial deposition rate on graphite was justified by the small sticking coefficient of radicals onto the graphite surface. This condition does not exist on the silicon surface, and the initial growth rate is much greater. The effect of the high energy ion bombardment on the hardness and other bulk properties of a-C:H films on silicon is quite clear<sup>2)</sup>, however its affect on the topology of the a-C:H film surface is not noticeable in the STM images.

## 5 SUMMARY

Scanning tunneling microscopy was used to study the initial stages of growth of a-C:H films on graphite and silicon substrates. On graphite, at the self biased electrode, where high energy ion bombardment occurs, the films were observed to nucleate in clusters, possibly at ion induced damage sites. Cluster size remained constant, at approximately 50Å in diameter, and cluster density increased with deposition time. On graphite at the grounded electrode, where high energy ion bombardment is absent, no imaging of the true topography was possible, due to high gap instabilities. a-C:H films grown on silicon substrates at the self biased electrode, were observed to have a very smooth topology ( $<3\text{\AA}$  roughness) and no cluster formation was observed. This more homogeneous growth is likely a consequence of the greater reactivity of the silicon surface with plasma species, as compared with that of the graphite surface.

## 6 ACKNOWLEDGEMENTS

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## 8 List of Figures

1. 1000 by 1000 ( $\text{\AA}$ )<sup>2</sup> STM topographic image of a-C:H clusters formed on a crystalline graphite substrate. This image is of an area of relatively low cluster density in the initial stages of growth. The graphite lattice can be seen in smaller images as in Fig. 3.

2. 1000 by 1000 ( $\text{\AA}$ )<sup>2</sup> STM topographic image of a-C:H formation on graphite. High cluster density area.

3. 200 by 200 ( $\text{\AA}$ )<sup>2</sup> STM topographic image of clusters of a-C:H on a graphite surface. The regular periodicity of the graphite substrate is visible between the amorphous clusters.

4. 25 by 25 ( $\text{\AA}$ )<sup>2</sup> STM topographic image of a cluster of a-C:H as formed on a graphite substrate. The distances between bright spots is consistent with C-C bond lengths. No long range periodicity is observed inside the cluster.

5. High resolution electron energy loss spectra of a graphite blank, and of a film of a-C:H grown on graphite. The broad peaks at 1200 - 1400  $\text{cm}^{-1}$  and around 2935  $\text{cm}^{-1}$  correspond to C-H bending and stretching vibrations, respectively. The signal from the graphite sample was multiplied by a factor of 1000, and that of the a-C:H sample by a factor of 100, with respect to the height of the elastic peak also shown in the figure.

6. Comparison between film structure formed at powered a) and grounded b) electrodes.

a) 600 by 600 ( $\text{\AA}$ )<sup>2</sup> three dimensional view of a topographic STM image taken of the initial stages of a-C:H growth at the powered electrode. Cluster formation during the initial stages of growth is observable. Notice the corrugation of about 10  $\text{\AA}$ .

b) 600 by 600 ( $\text{\AA}$ )<sup>2</sup> three dimensional view of topographic STM image taken of the initial stages of growth at the grounded electrode. The roughness observed in this case is due to the instability of the STM when trying to image weakly bonded, nonconductive, polymerlike material. It gives rise to a corrugation that is 4 times larger than at the powered electrode.

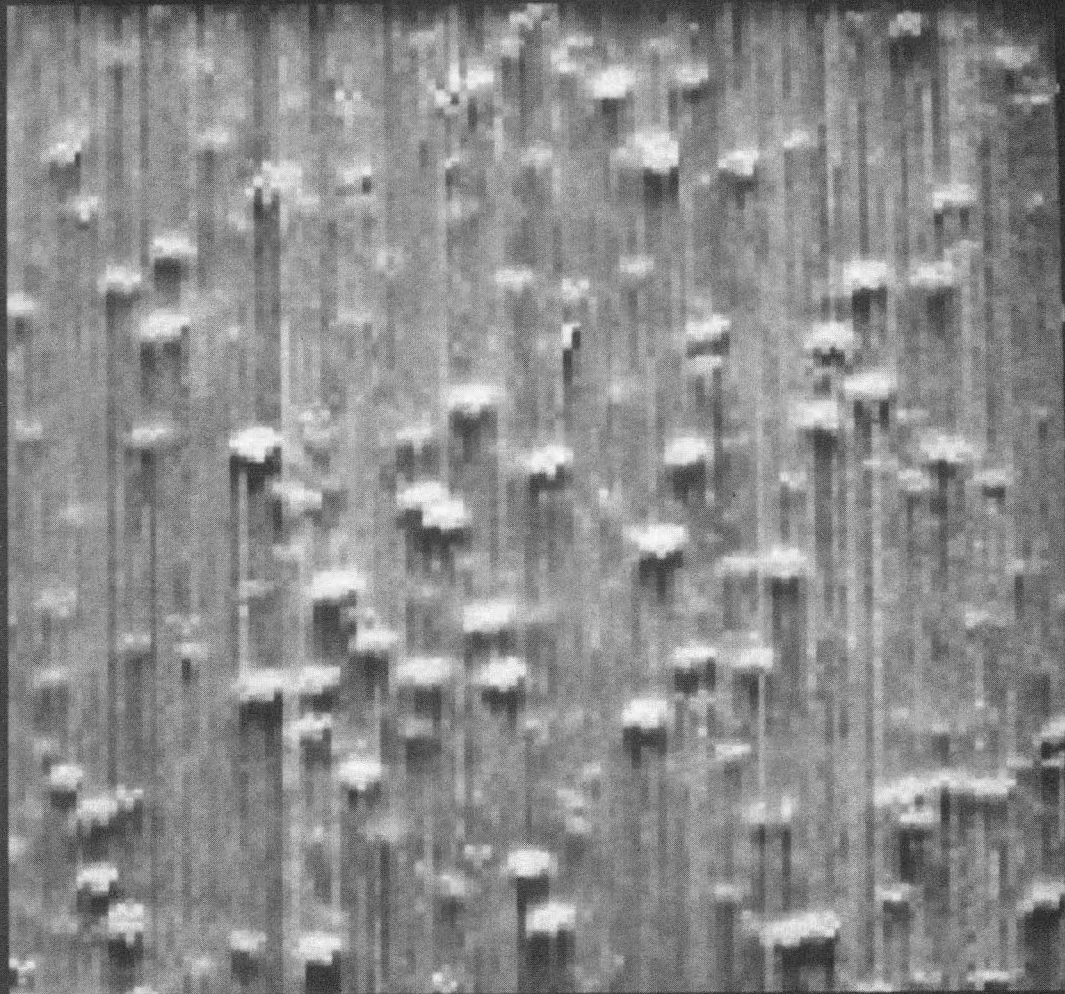
7. Comparison between an image of a blank silicon substrate, and the surface of an a-C:H film formed on such a substrate.

a) 1800 by 1800 ( $\text{\AA}$ )<sup>2</sup> topographic STM image of a typical surface of a silicon



blank substrate. Blanks were prepared with a surface roughness of less than 3 - 5 Å rms roughness, and the smoothness of the images was limited by the noise of the STM.

b) 1800 by 1800 (Å)<sup>2</sup> topographic STM image of a typical surface of a-C:H on silicon. The silicon substrate, in this case, was exposed to the methane plasma for 10 seconds at the powered electrode, a sufficiently long deposition time to completely cover the substrate. The images obtained indicated that, for these films also, the topography was smoother than the limits of the microscope, 3 - 5 Å rms.



1000 Å

$\delta z = 74.1 \text{ \AA}$

Offsets -96, 48 Å

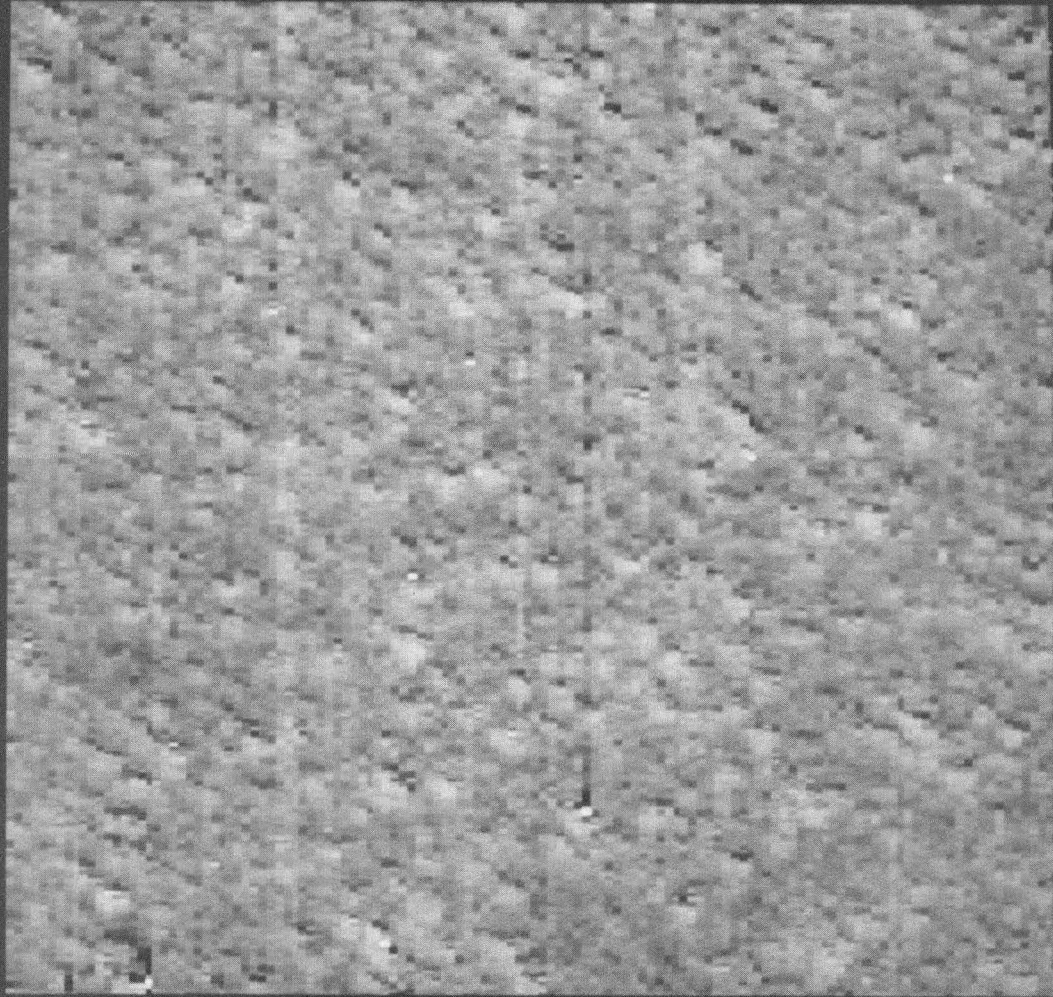
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Gap 95.2 MR, sample bias -0.100, tip velocity 4063 Å/sec

Carbon film on graphite 15sec deposition at 50W, 75mT Gil's chamber

3/11/89

Fig. 1



$\delta z = 111.1 \text{ \AA}$

Offsets -2245, 1781  $\text{\AA}$  999  $\text{\AA}$   
A:\CGP15S21.SM2 Topographic Mode page 1 of 2, 03/30/89 01:38:01  
Gap 98.0 M $\Omega$ , sample bias -0.099, tip velocity 2440  $\text{\AA}/\text{sec}$

Fig. 2

XBB 905-3947





200 Å

$\delta z = 43.1 \text{ \AA}$

Offsets -115, 43 Å      200 Å  
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Fig. 3

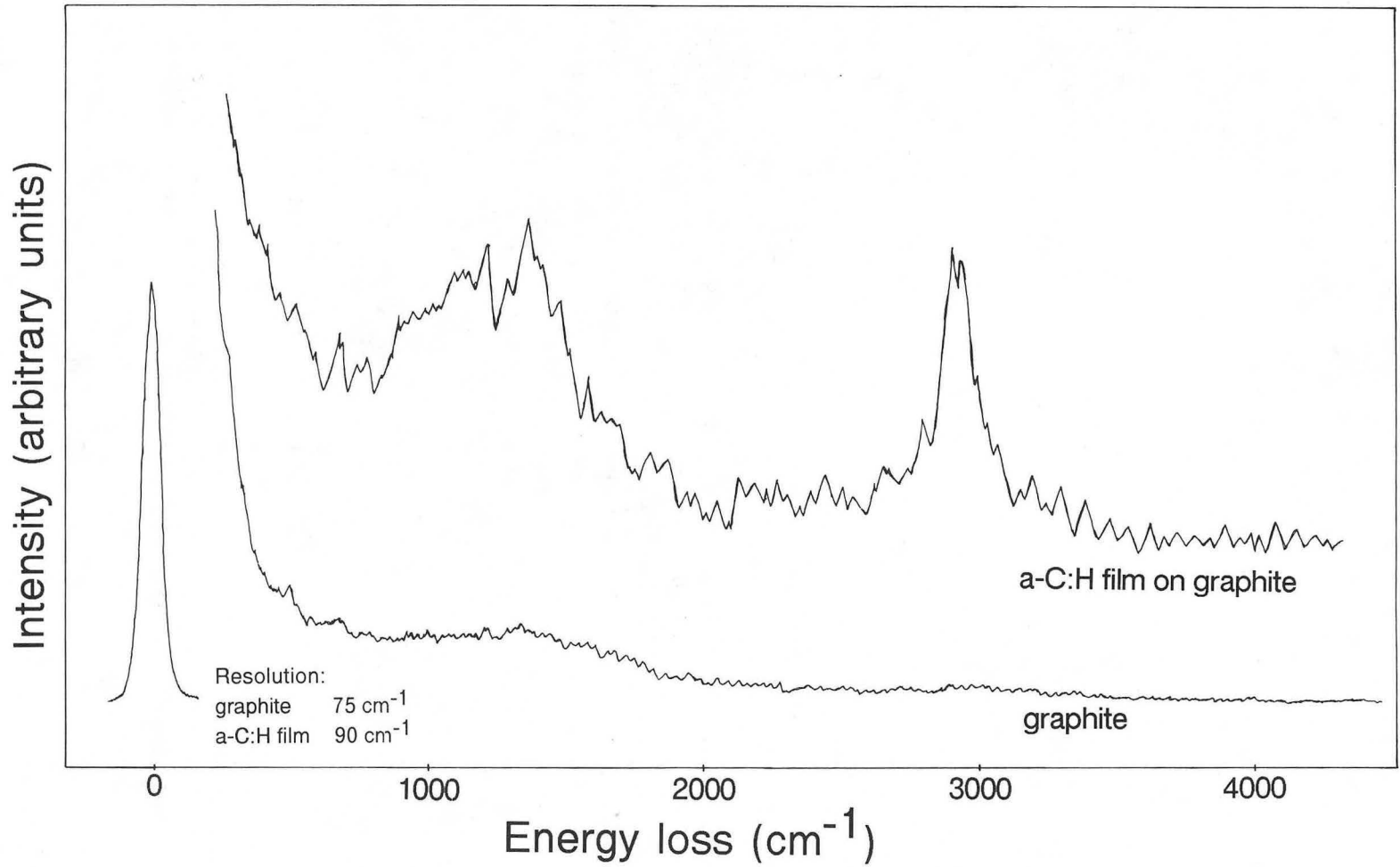


25 Å

$\delta z = 29.3 \text{ \AA}$

Offsets -1974, 976 Å  
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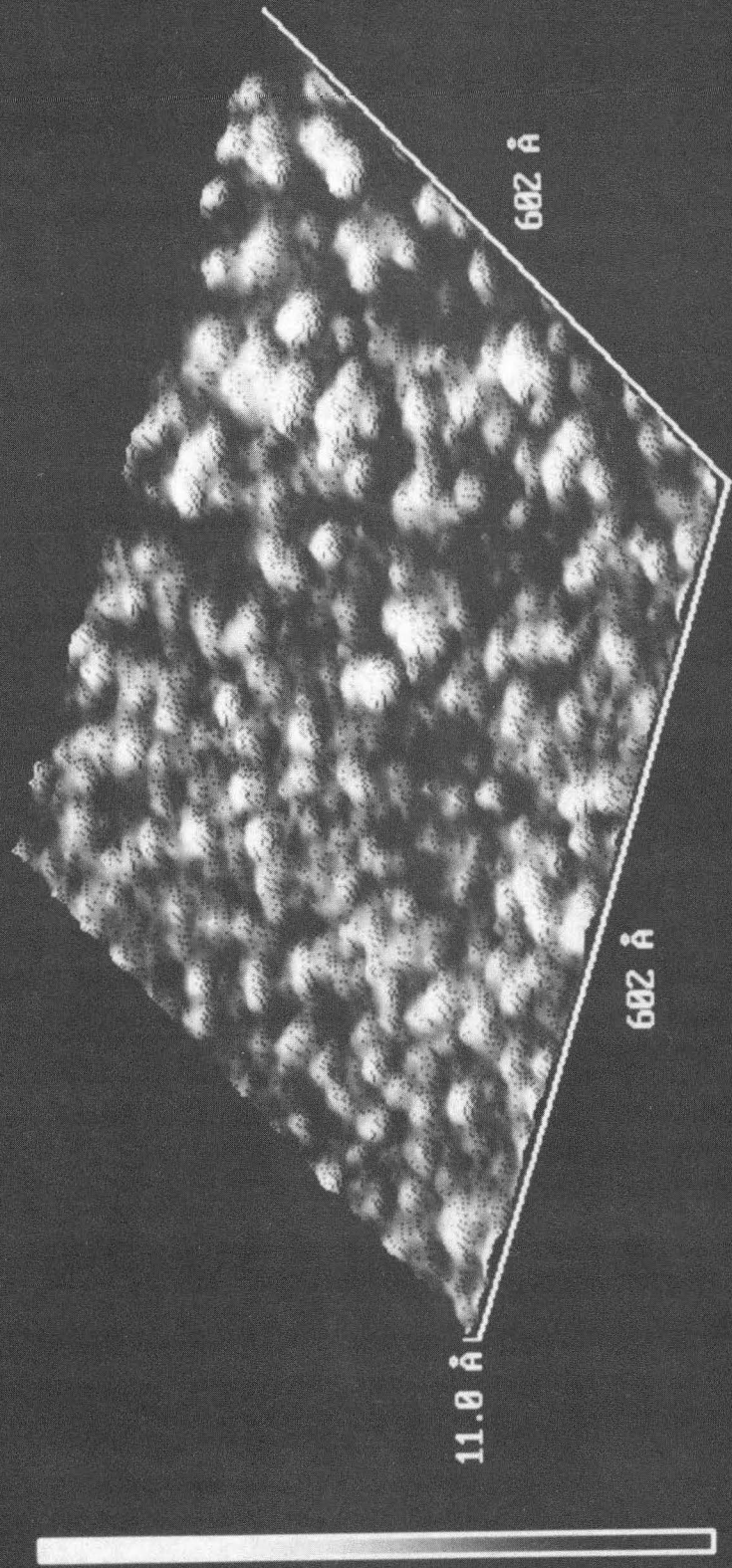
Fig. 4



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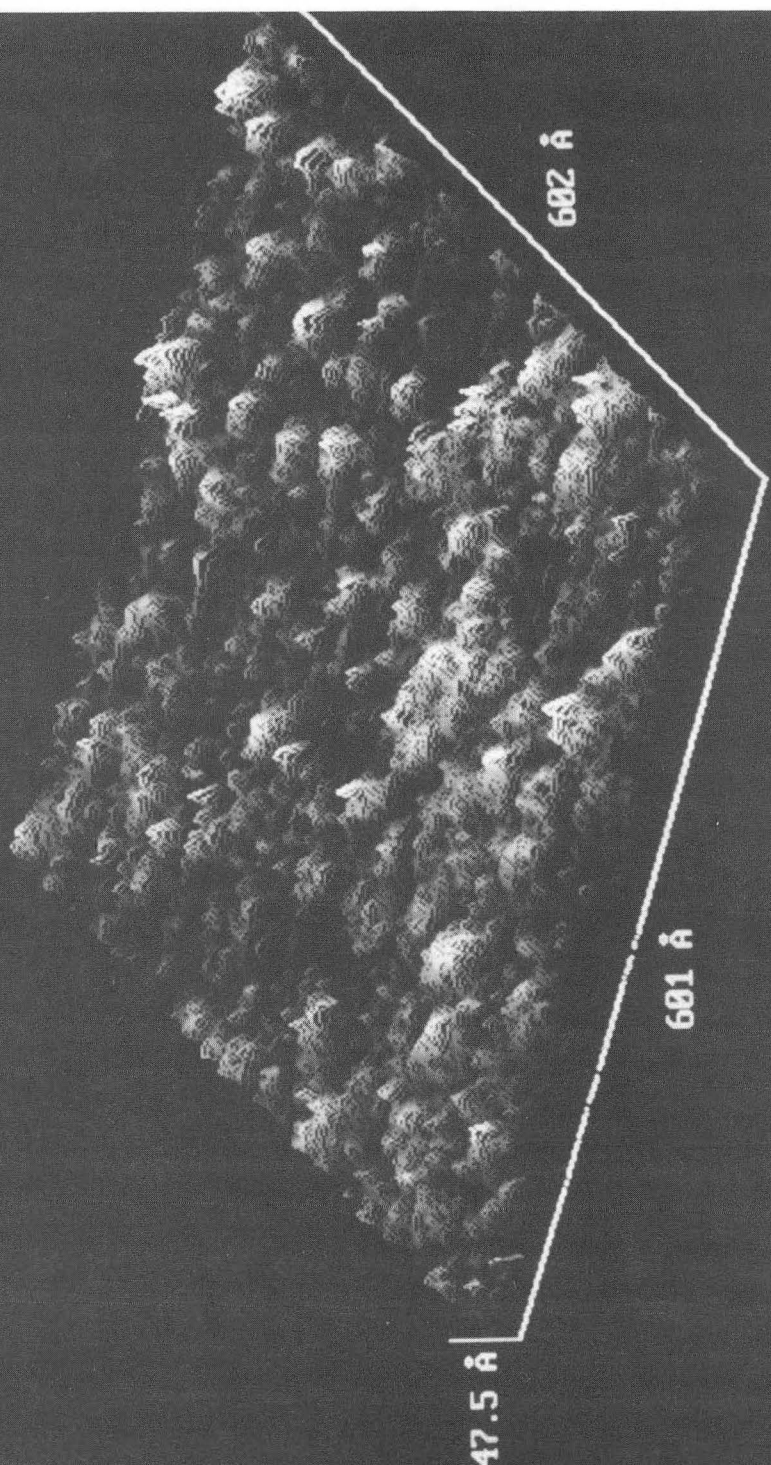
Fig. 5





Offsets 700, 1720 Å  
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 Gap 315.1 MÅ, sample bias -0.334, tip velocity 2440 Å/sec  
 a-C:H film on HCPG 10 sec dep PE ue 50W 75mT made GV 7/12/89 1pm

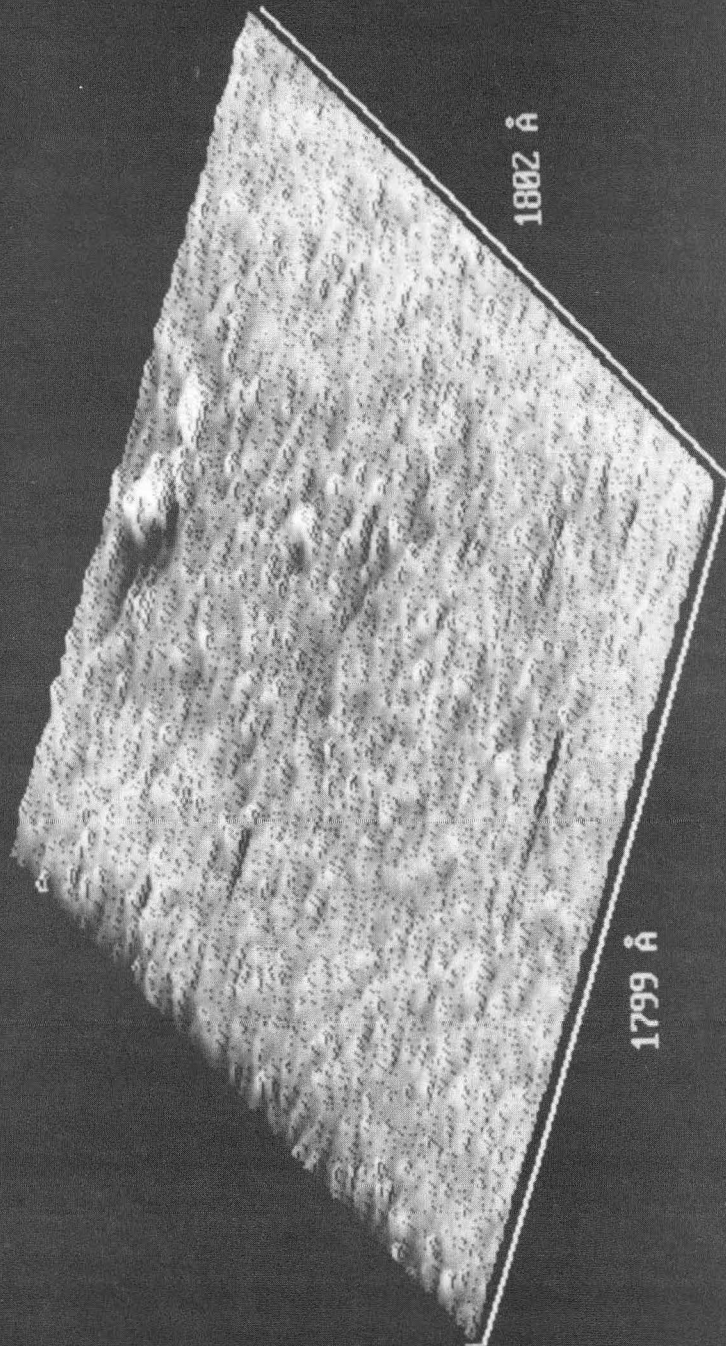
Fig. 6a



Offsets -43, -947 Å  
A:\CGM10S03.SM2 Topographic Mode page 1 of 2, 04/18/89 20:20:29  
Gap 98.9 MR, sample bias -0.094, tip velocity 1220 Å/sec

Fig. 6b

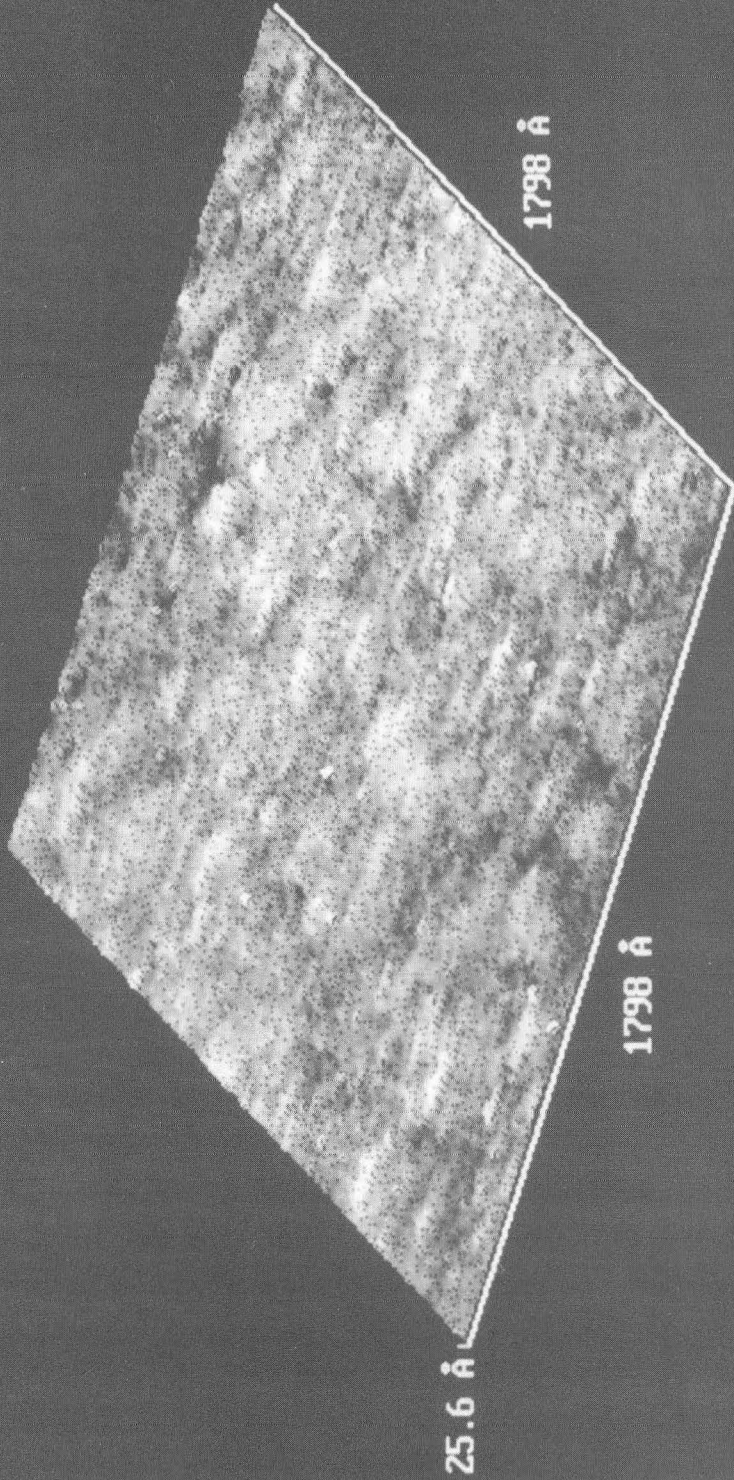




1799 Å

Offsets 212, 213 Å  
A:\BSI0VH03.SM2 Topographic Image page 1 of 2, 12/29/89 12:23:44  
Gap 300.5 GÅ, sample bias -3.005, tip velocity 2445 Å/sec  
Si(100) blank Troy's fab12/21bf wafer

Fig. 7a



Offsets 323, 251 Å  
A:\BCPSUJ06.SM2 Topographic Data page 1 of 2, 02/26/90 12:07:57  
Gap 99.6 GÅ, sample bias -2.988, tip velocity 2443 Å/sec  
10sec PE a-C:H on Si(100) ulab2/24/90tw made 2/25/90 3pm  
inset

Fig. 7b

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