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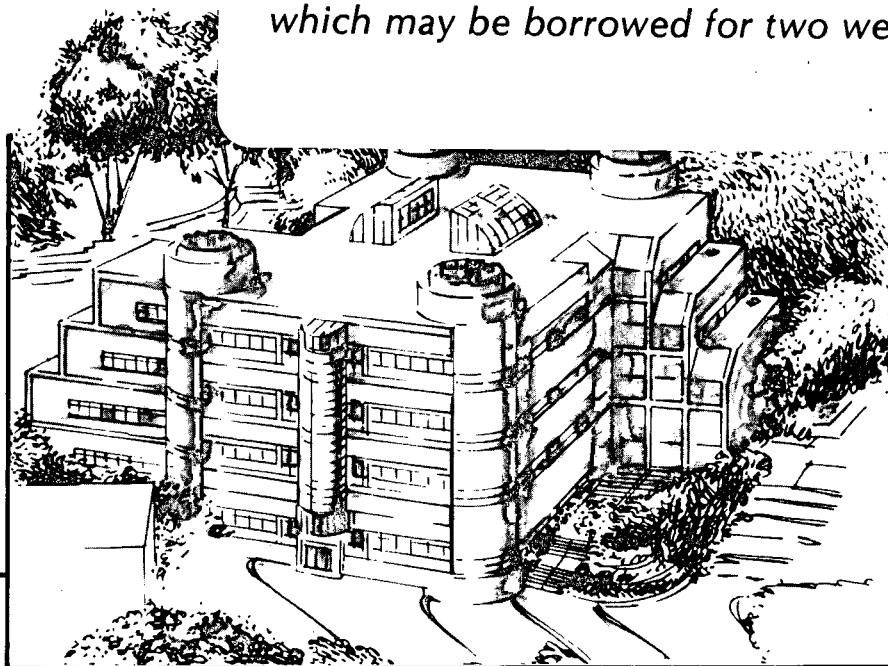
Scanning Tunneling Microscopy of Silver, Gold, and Aluminium Monomers and Small Clusters on Graphite

E. Ganz, K. Sattler, and J. Clarke

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SECOND INTERNATIONAL CONFERENCE ON SCANNING TUNNELING

MICROSCOPY/SPECTROSCOPY

OXNARD, CALIFORNIA

JULY 20-24, 1987

SCANNING TUNNELING MICROSCOPY OF SILVER, GOLD, AND ALUMINIUM

MONOMERS AND SMALL CLUSTERS ON GRAPHITE

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ABSTRACT

We have deposited small numbers of atoms of silver, gold, and aluminum onto cleaved graphite substrates in ultra high vacuum. Using a scanning tunneling microscope, we have observed monomers, groups of monomers, dimers and a trimer. The adsorption sites and atomic spacings are determined by direct observation.

PACS #'s: 61.16.Di, 36.40.+d, 68.35.Bs, 35.20.Dp

In the last ten years, new techniques for the production of clusters in beams have been developed that allow researchers to study free clusters for a wide variety of cluster materials¹. As a result, many interesting differences have been found between the properties of bulk materials and those of free clusters, including dramatic changes in atomic spacing and electronic structure². Studies of clusters are also technologically driven by the need for new and more specific catalysts. But, to use clusters in a catalytic environment, they must be supported on a substrate. The substrate can have a profound effect on the morphology and electronic structure of the ad-cluster, and thus change the catalytic activity of the system^{3,4}. Thus, there is a need for fundamental studies of supported clusters.

Small clusters have been and continue to be extensively studied as tractable model systems for the study of larger clusters, and also as interesting systems in their own right. For example, Ag₄ has recently been shown to be an active catalyst in the formation of the latent image on photographic film⁵. Unfortunately, theoretical calculations on these systems are still very difficult, requiring large amounts of computer time to produce what is often only an approximate result. Thus, it is especially important to obtain reliable and precise experimental information about these systems. In previous work, we demonstrated the potential of the scanning tunneling microscope (STM) as a tool for the study of metal clusters on graphite in air⁶. Here, we extend this work to ultrahigh vacuum (UHV), and demonstrate the capability of the STM to image, atom by atom, isolated monomers and small clusters of Ag, Al, and Au.

We use graphite as a support for three reasons. First of all,

graphite is easily cleaved, providing atomically flat planes over many square microns⁷. Secondly, graphite has been extensively studied with the STM, and can be reliably imaged with atomic resolution. Finally, graphite is both a good conductor, and yet also relatively inert chemically. Thus, the graphite surface is particularly well suited to the study of supported metal clusters with the STM. In the present experiment, we cleaved highly oriented pyrolytic graphite⁸ in a sample introduction chamber at 10^{-8} torr. The sample was then transferred to a UHV chamber at 2×10^{-10} torr without breaking vacuum. To prevent ion contamination, all ion gauges were turned off before the sample was cleaved and left off for the duration of the experiment⁹.

To prevent the STM from contaminating the surface, we found it necessary to clean the W tip *in situ* before scanning the sample. The tip was cleaned by field emission to a clean Si surface with a bias voltage of 900V and a current of $100 \mu\text{A}$. For each run, after cleaning the tip and cleaving the sample, we searched $1 \mu\text{m}^2$ with the STM. The STM images showed a perfect graphite lattice over the entire region, with no observable contamination. Furthermore, no grain boundaries, defects or steps were observed on the cleaved substrate. These two facts ensure that all features observed after deposition of the metal were due to adsorbed metal atoms. We used a new tip for each metal, and a freshly cleaved substrate for each run. Since the metal evaporation was done *in situ* in UHV, it is unlikely that contamination played any role in the imaging process.

The Ag and Au atoms were evaporated from a resistively heated Ta boat 0.1m from the sample, while the Al was evaporated from a W coil. Both the Au and the Al eventually alloyed with the boat and coil,

respectively, preventing further evaporation, but only after several evaporation cycles. A quartz crystal microbalance was used to monitor the deposition rate, and a shutter was used to determine the exposure time. We deposited approximately 1% of a monolayer of Ag, as measured by the crystal monitor, in 0.5 sec. The work of Arthur and Cho¹⁰ suggests that the sticking coefficient of Ag on graphite might be less than 0.1 for clean graphite, so we would expect to find no more than 0.1% of a monolayer of Ag on the surface. This corresponds roughly to what we observed in a survey performed with the STM: A survey of 10^8 \AA^2 found $1.2 \times 10^5 \text{ \AA}^2$ covered with Ag adatoms distributed in small groups and islands. Comparable amounts of Au were deposited in the same manner, but we were unable to measure the Al deposition rate accurately because of thermal drift in the crystal monitor. We chose this low coverage so that we could find isolated metal atoms surrounded by clean graphite. We then were able to image the graphite lattice and the metal adatoms simultaneously. Thus, the image of the graphite lattice provides an internal calibration for each image and allows us to determine adsorption sites by direct observation.

The STM was operated in the current imaging mode where the tip is scanned at a constant height over the surface and variations in tunneling current are observed.¹¹ This technique is limited to relatively flat surfaces, but provides rapid image production and high image quality. A bias voltage of 5mV and a tunneling current of 10nA were typical and were chosen to optimize image quality and stability. When we brought the tip closer to the surface (higher current) the tip-sample interaction was increased, rendering the tip less stable and breaking up the metal islands. When we retracted the tip (lower

current) the image resolution was reduced and the system noise was increased. The computer can digitize and display an image of 256x256 points every 4 seconds, or an image of 128X128 points every 1 second. The images are viewed on a graphics monitor and stored in real time on videotape; individual frames can be stored on hard disk for post-processing. The gray scale images are displayed in top view with lighter areas corresponding to higher tunneling current. The large dark shadows cast to the left of bright areas are an artifact due to high pass filtering of the current signal.

In the figures that follow, we have used a computer to generate a model showing the observed position of the adatoms. The computer calculates a linear transformation which corrects the observed distortion in the graphite lattice. This distortion is caused by coupling between the different axes of the scanner and by thermal drift. To produce a model, we first digitize the observed positions of the graphite atoms along each of the three lattice directions. The computer then fits directions and spacings for each of the three lines. Two of these lines are used to generate the transformation, and the third is maintained as a consistency check. We digitize the outline of the observed adatoms, and the computer rescales the image and produces the model. Thus we can use the model to make accurate determinations of adsorption sites and spacings, since the graphite surface has an accurately known honeycomb lattice spacing¹² of 2.46Å.

During the metal deposition, individual atoms arrive at the surface, where they are mobile until they re-evaporate or are captured into an island. Surveys of large areas showed most of the substrate to be clean, with small areas containing groups of metal islands and

clusters. By extensive searching, we were able to find several examples of stable isolated monomers, but always within 10\AA of a large island or cluster. In this paper we will give representative examples of a few of the many monomers and small clusters that we have observed.

Figures 1(a) and (b) show single Ag adatoms on a clean graphite substrate. The Ag atoms are clearly visible as sites of enhanced current. The gray scale ranges from 5nA in black regions to 10nA in white areas. These isolated Ag monomers are observed on or near the bright spots of the graphite lattice which correspond to the carbon β -sites of the graphite honeycomb lattice¹³: A β -site has no atom directly below in the next layer. The adatom in Fig. 1(a) was imaged stably for several seconds, while that in Fig. 1(b) was imaged only for a single scan before moving away.

Figure 2 shows an isolated Al monomer at a β -site. This image of a single isolated adatom is clearly resolved to better than 2\AA , and provides a rigorous test of the resolution of the STM. Without detailed knowledge of the tip geometry and from this a prediction for the current modulation, one cannot use an image of clean graphite to test the resolution: Because the substrate is periodic, the amplitude of the modulation will drop with decreasing resolution, but the signal will always show the same periodicity independent of resolution.

The fact that a single metal adatom can be reproducibly imaged for several seconds in one spot demonstrates that it is relatively strongly bound to the substrate. Metois and Heyraud estimated a binding energy of 0.26eV/atom for large Au islands on graphite¹⁴. This energy is too small to explain the lifetimes that we observe. However, this value is actually a lower bound for the binding of a single adatom: As groups of

adatoms bind to each other, they bind less well to the substrate. This rebonding effect has been discussed by Feibelman¹⁵. A relatively strong adatom-substrate interaction is also supported by the observation of pinning at the edges of the metal islands¹⁶. The strong binding may be due to the presence of defects on the surface, but we note that no defects were imaged by the STM before deposition of the metal. An alternative explanation is that the proximity of the metal islands may perturb the structure of the graphite sufficiently to enhance the binding of monomers.

Figure 3 shows a single isolated Au adatom on a clean graphite background. This Au monomer was quite stable, and was observed at the same spot for ten minutes. In contrast to the Ag atoms, the Au monomer is not located above a β -site. Unfortunately, we only have this one example of a single isolated Au monomer, and the background lattice is quite distorted in these images due to nonlinearities in the STM scanner. Thus, we cannot draw firm conclusions about the positions of isolated Au atoms on graphite.

Figure 4 shows an array of four silver atoms on bridge sites. This array was only visible for a single image, and thus any identification must be tentative. Figure 5 shows a pair of Au atoms which are clearly on β -sites. It is interesting that these atoms are clearly resolved, since they are only 2.46\AA apart. This separation is smaller than the bulk nearest neighbor spacing of 2.88\AA in both Ag and Au¹⁷, but quite close to the dimer bond lengths of 2.50\AA for Ag¹⁸ and 2.47\AA for Au¹⁹. Perhaps charge transfer to the substrate (or some more subtle Au-C interaction), weakens the Au-Au and Ag-Ag bond and localizes the electrons, thus allowing the STM to resolve the individual atoms. We

do observe atomic resolution of monolayer islands of Au and Ag on graphite¹⁶, which we attribute in part to the effect of the substrate. We note that the four Ag atoms are clearly not in the compact equilibrium form of a free cluster. Thus, in this case, the substrate has a profound effect on the morphology of these small clusters.

However, on occasion we see groups of several adatoms in which the individual atoms are not resolved. Figure 6 shows a complex structure which we interpret as two Ag clusters (of two to five atoms each) with several monomers or dimers grouped nearby. This identification is still tentative because of our limited theoretical understanding of the STM imaging process for metal on graphite. This group was very stable, and we were able to study it for 20 minutes without any change in morphology. The two large clusters produced an unusually large tunneling current, 120 nA, much larger than the 5nA produced by the background lattice. This high current is presumably due to the large size of these clusters, approximately $2.7\text{\AA} \times 4.5\text{\AA}$, which we can compare to the Ag atomic radius of 2.88\AA , and the dimer bond length of 2.50\AA . It is also conceivable that one or two atoms form a second layer on the clusters.

As a final example, in Fig. 7 we show images of an Al trimer with several monomers grouped around it. We obtained 10 images of this group over a period of 10 seconds before the tip changed. The relative positions of the adatoms remained constant during the period of observation. The monomers are above β -sites. The three-lobed trimer has one corner above a β -site, and is slightly rotated relative to the graphite substrate. The measured spacings from the center of each lobe to the others is roughly 2.5\AA , somewhat shorter than the recent

theoretical result of Upton²⁰, who found spacings of 2.61Å and 2.63Å for the Al trimer and 2.51Å for the dimer, respectively. Of course, the apparent size in the STM image depends on the details of the tunneling process and also on the gray scale used for presentation. It is also possible that the presence of the graphite substrate has compressed the adsorbed trimer.

A fact common to all of our images is that we have never observed isolated metal atoms above hole sites. This result is very different from the adsorption of noble gas atoms. For low coverages, noble gases physisorbed on graphite at low temperatures form registered patterns, with atoms located above the hole sites. These results for noble gases have been modelled with Lennard-Jones potentials, which encourage the adatoms to sink down into the graphite hole sites²¹. The stability and location of metal adatoms atop β -sites or bridge-sites suggests that the details of the graphite-metal bonding are more complex than a simple Lennard-Jones model.

In summary, we have observed metal monomers, groups of monomers, a dimer, and a trimer adsorbed onto the basal plane of graphite substrates in UHV. These adatoms and small clusters were stable enough to be imaged reproducibly for periods of several seconds to many minutes. Single adatoms were only observed within 10Å of an island: The fact that these single adatoms were stable is surprising, perhaps indicating bonding to defect sites or the stabilizing influence of the nearby island. The Ag and Al monomers were more usually observed at graphite β -sites, while the one Au monomer we observed was not. We observed clusters that were resolved into individual atoms usually above β -sites as well as compact clusters which were not atomically

resolved. We conclude that for monomers and very small clusters, the effects of substrate-adsorbate interaction are important even for the relatively inert graphite substrate.

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FIGURE CAPTIONS

FIGURE 1 (a) $14\text{\AA} \times 16\text{\AA}$ and (b) $31\text{\AA} \times 32\text{\AA}$ images showing isolated Ag monomers on graphite. To the right of each image is a computer generated model showing lattice positions. The Ag atoms are at or near graphite β -sites.

FIGURE 2 $33\text{\AA} \times 37\text{\AA}$ image of an Al monomer near an Al island. The Al monomer is above a β -site.

FIGURE 3 (a) and (b) show two $37\text{\AA} \times 39\text{\AA}$ images of an isolated Au monomer taken one minute apart. The atom appears to be at a bridge-site.

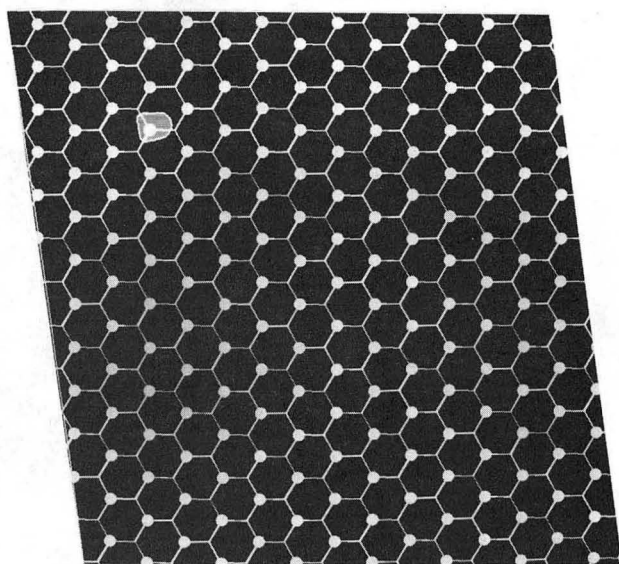
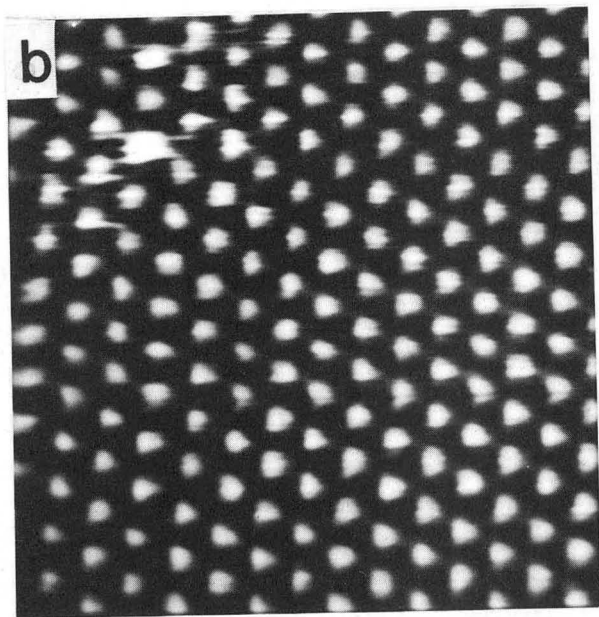
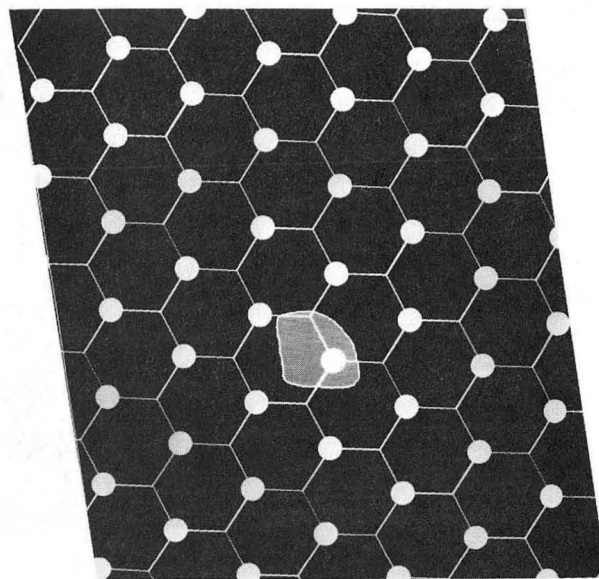
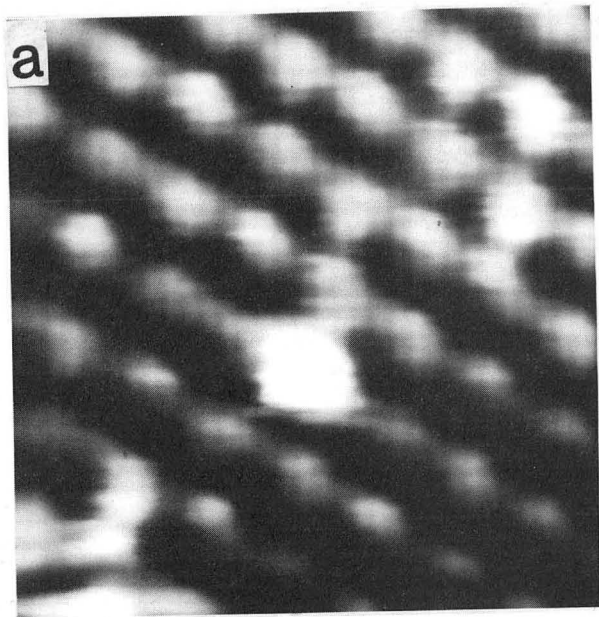
FIGURE 4 $31\text{\AA} \times 34\text{\AA}$ image showing a group of four Ag atoms at bridge-sites.

FIGURE 5 $36\text{\AA} \times 40\text{\AA}$ image of a Au dimer. The atoms are at β -sites.

FIGURE 6 $16\text{\AA} \times 16\text{\AA}$ image of a group of Ag clusters.

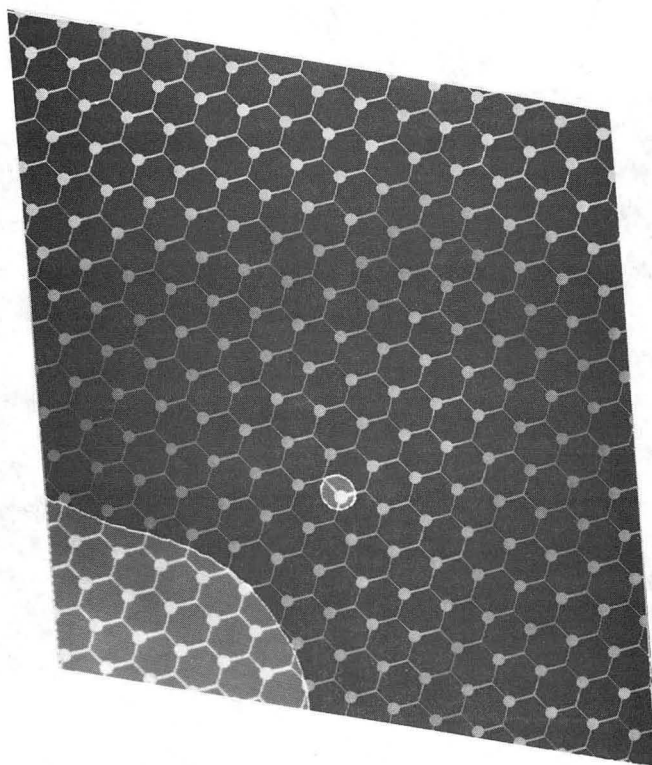
FIGURE 7 (a) and (b) show sequential $34\text{\AA} \times 30\text{\AA}$ images one second apart of an Al trimer, with several monomers nearby.

FIGURE 1



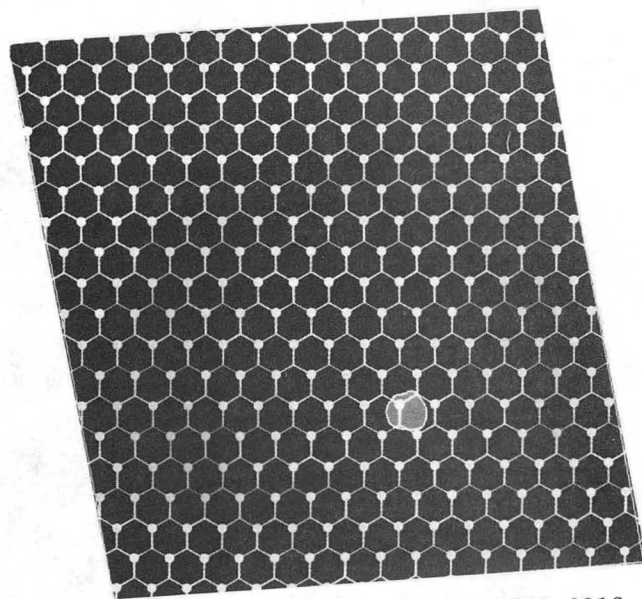
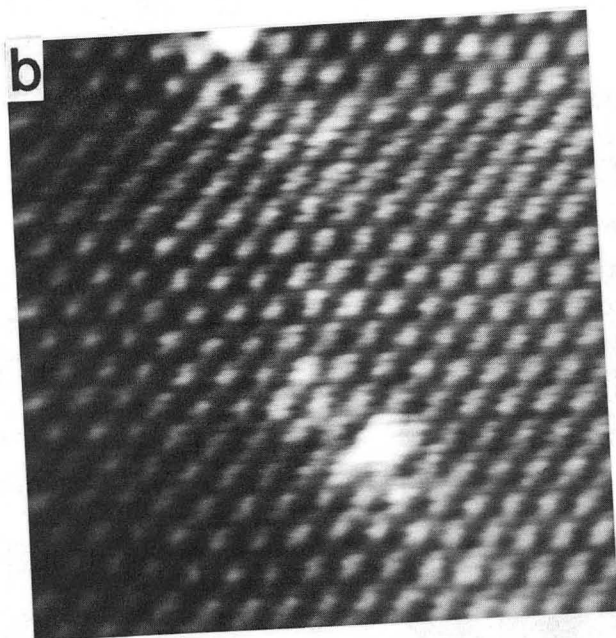
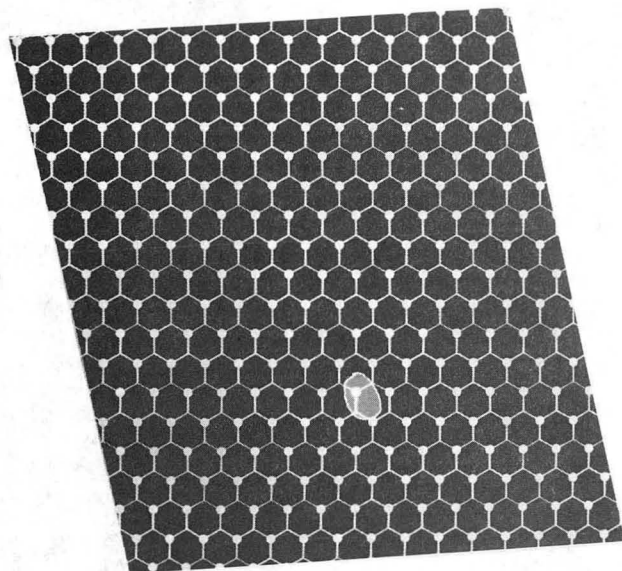
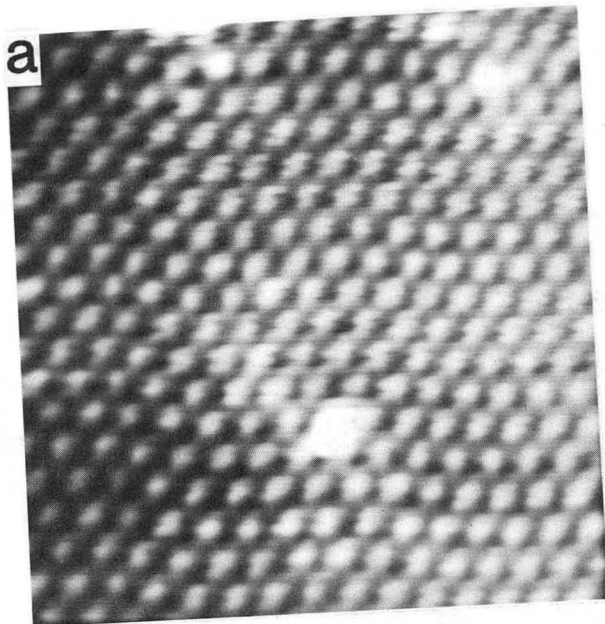
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FIGURE 2



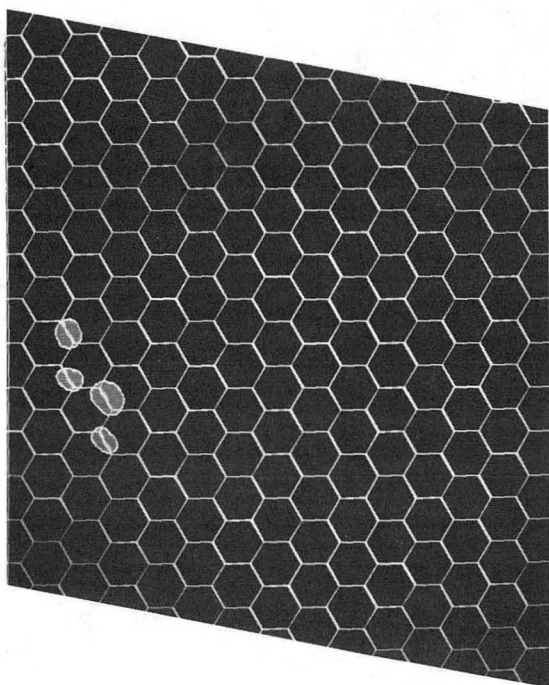
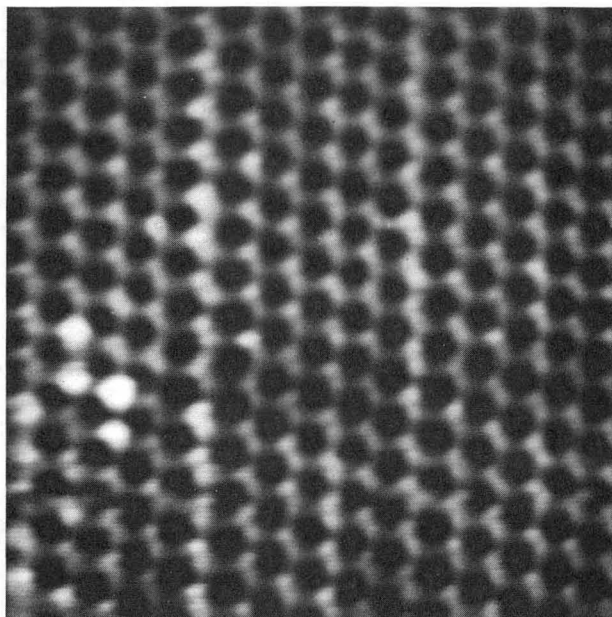
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FIGURE 3



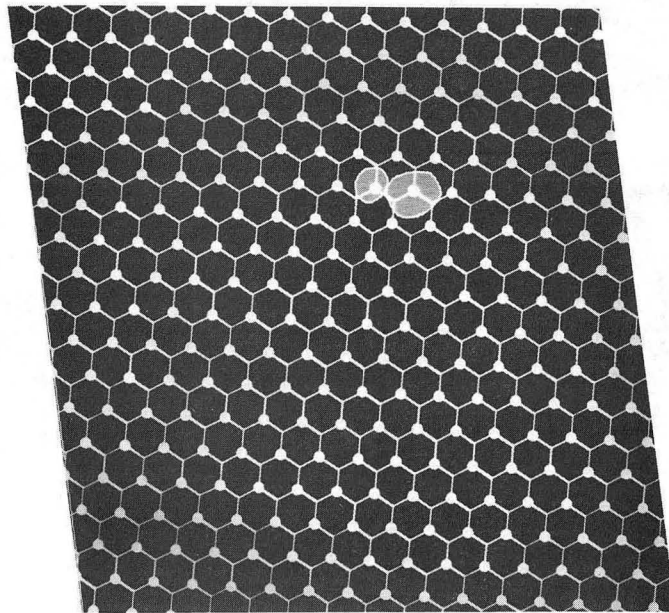
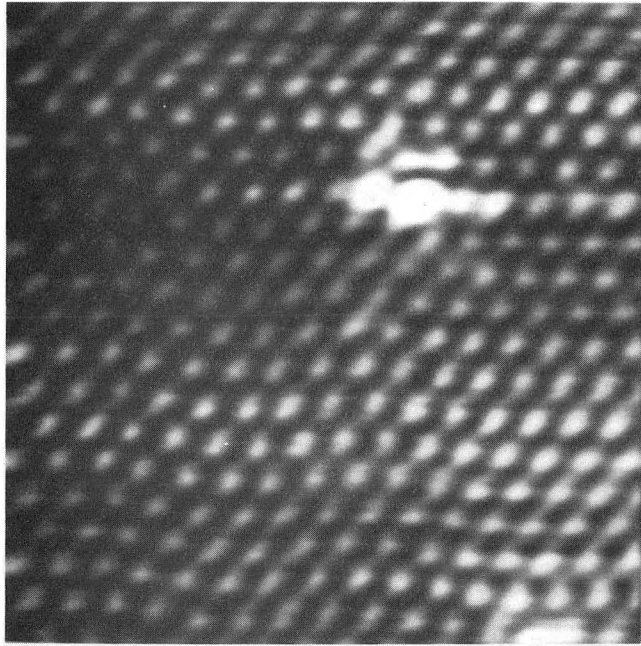
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FIGURE 4



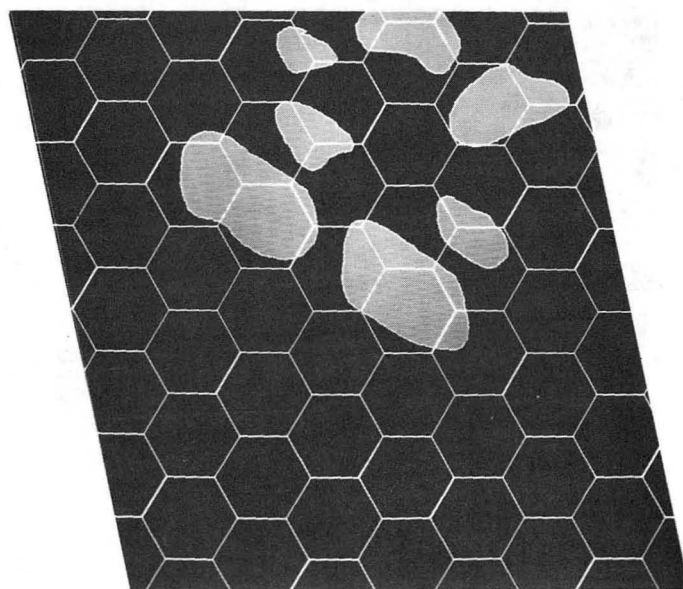
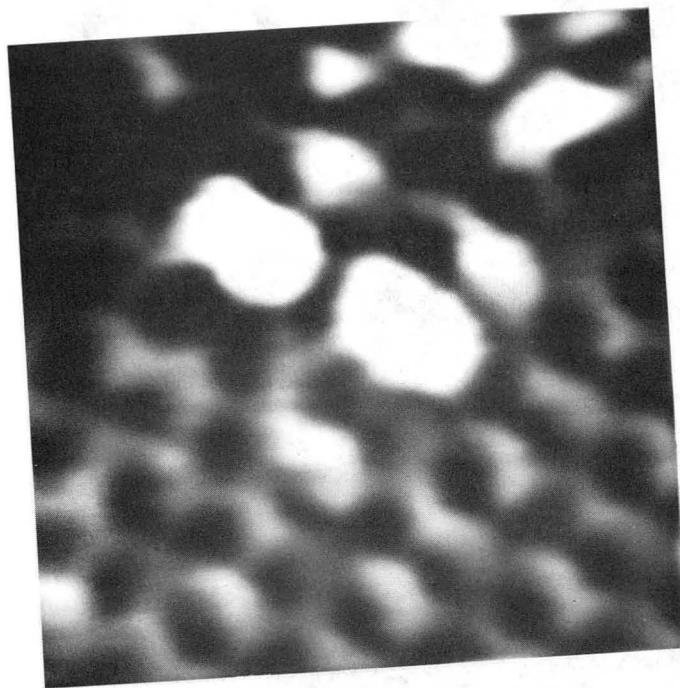
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FIGURE 5



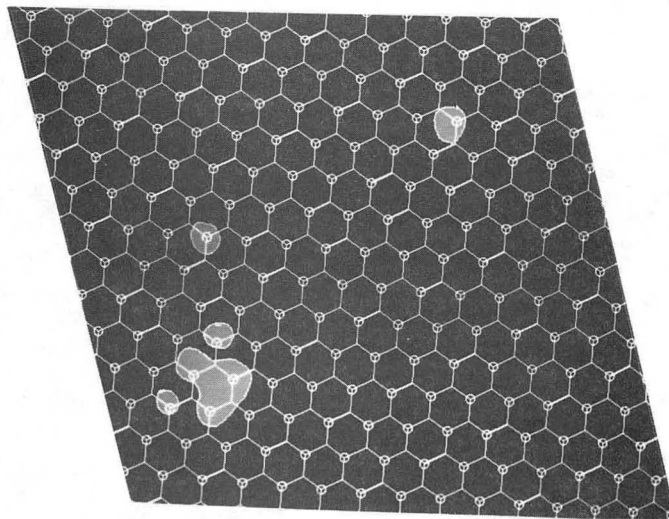
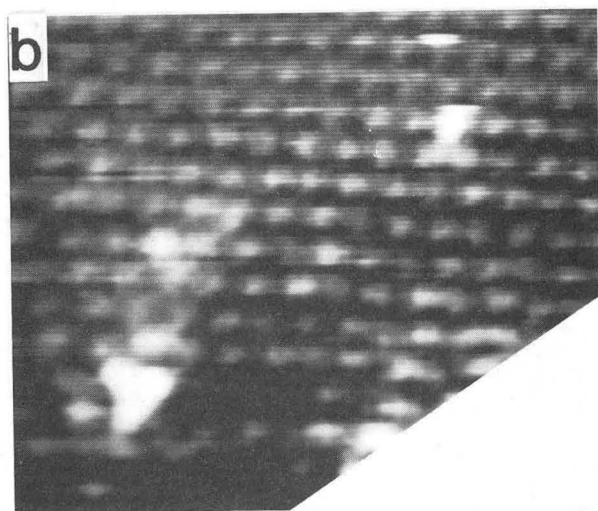
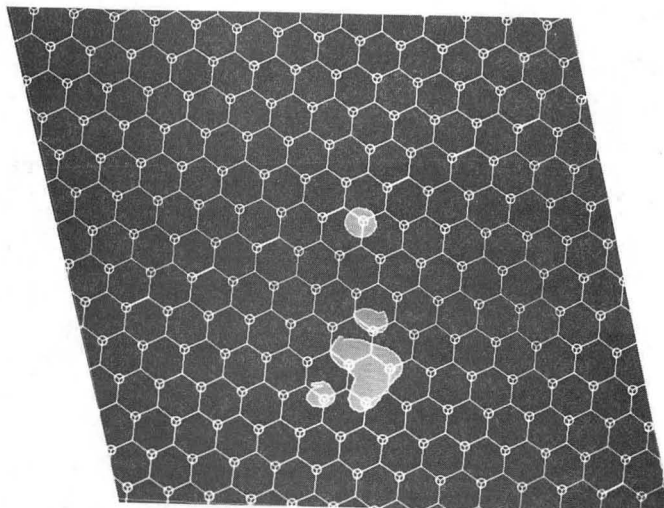
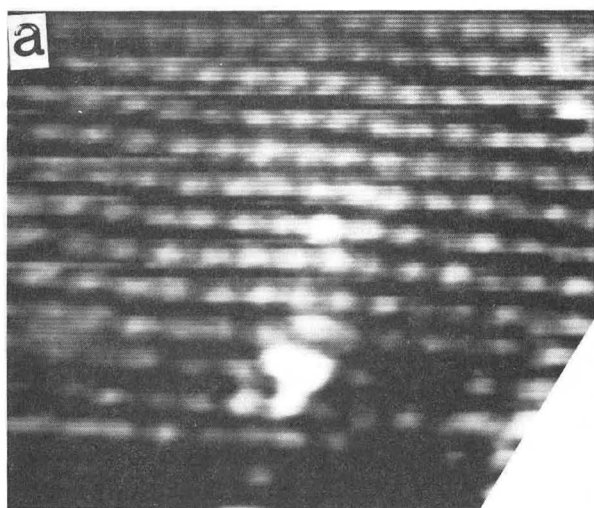
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FIGURE 6



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FIGURE 7



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