

Epitaxy and scanning tunneling microscopy image contrast of copper-phthalocyanine on graphite and MoS₂

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(Received 9 August 1993; accepted 28 December 1993)

Monolayers of copper-phthalocyanine (Cu-Pc) on highly oriented pyrolytic graphite (HOPG) and MoS₂ prepared by organic molecular beam epitaxy have been investigated by scanning tunneling microscopy. On both substrates there exist well defined preparation conditions leading to ordered two-dimensional arrays of flat lying molecules. On HOPG they form a close-packed structure with a nearly quadratic unit cell, whereas on MoS₂ we found two phases, one close-packed and one rowlike phase. This rowlike phase can be explained by a long range interaction due to an adsorbate induced superstructure of the substrate, which also can be seen in the scanning tunneling microscopy images. In images with submolecular resolution, the molecules appear different on the two substrates. On MoS₂ they look like a four-leaved clover, on graphite they show a more detailed inner structure.

I. INTRODUCTION

For a future realization of molecular electronics it is important to understand the behavior of adsorbates on an interface, especially the mechanisms leading to well ordered overlayers. But whereas the epitaxy of inorganic semiconductors is a wide field of research, little is known about the epitaxial growth of larger organic molecules. As an organic prototype we choose the organic semiconductor Cu-phthalocyanine, which shows a number of interesting properties.^{1,2} It is a thermally very stable dye pigment which allows purification by sublimation technique and deposition by organic molecular beam epitaxy. Due to their structural similarity to biologic molecules like chlorophyll, Pc's are also of interest as electronically active organic molecules. Pc's are the only molecules which have been imaged with all high-resolution techniques, namely field electron microscopy, transmission electron microscopy, and scanning tunneling microscopy (STM) with submolecular resolution.³⁻⁵ Pc's also belong to the first larger molecules which were studied extensively with surface analytical techniques.^{6,7} But there exists no comparative study on a molecular level of the growth and STM image contrast of Pc's on different substrates.

II. EXPERIMENTAL METHODS

The STM investigations were carried out with a specially developed Video-STM able to scan with a scanning speed up to 20 frames/s. A fast frame buffer allows on-line averaging for noise reduction. The STM images were recorded in constant height mode, where the feedback loop has a response frequency lower than the frame rate. So we can exclude artificial corrugations due to a vertical movement of the tip. We used mechanically cut Pt-Ir tips in a nitrogen atmosphere at room temperature. All images presented in this paper represent raw data which were neither analog nor digitally filtered. For organic molecular beam epitaxy the material was evaporated from a graphite effusion cell at a pressure $<10^{-7}$ mbar in a turbo-pumped chamber. Before evaporation the freshly cleaved substrates were heated to 200 °C to desorb

contaminations. Typical evaporation rates were 5 nm/min at an evaporation temperature of 450 °C and a substrate temperature of about 100 °C. To determine the crystallographic structure of the overlayers relative to the substrate, the tunneling resistance was decreased until the tip dragged the molecules away and the underlying substrate became visible. Thus the lattice constants \bar{a} and \bar{b} , the angle Γ , and the relative orientation Φ of the two dimensional unit cells could be directly determined by comparison with the lattice vectors \bar{g}_1 and \bar{g}_2 of the substrates.

III. RESULTS AND DISCUSSION

Figure 1 shows a high-resolution image of a Cu-Pc monolayer on highly oriented pyrolytic graphite (HOPG) recorded in the constant height mode with a scanning speed of 4 frames/s and averaged over four frames. The molecules form a close-packed array with a nearly quadratic unit cell. In lower-resolved scans of a larger area the overlayer shows a superstructure where, in one direction, every third molecular row appears bright. By comparison with the underlying substrate in the way mentioned above, we obtained the structural model shown in Fig. 2(a). To emphasize the registry with the underlying substrate, the molecules are drawn without the central metal ion, so that the substrate shines through. In \bar{a} -direction each molecule of the overlayer is in registry with the substrate lattice, in \bar{b} direction it is every third, corresponding to the observed intensity modulation (see Table I).

In contrast to graphite, we observed on MoS₂ two different phases. A close-packed one with nearly the same unit cell parameters as on graphite (Fig. 3) and a rowlike phase as can be seen in Fig. 4. As expected for the epitaxial growth of molecules having a lower symmetry than the substrate, the films show a multidomain structure on a larger scale (Fig. 5). Small molecular clusters, like the single row in the center of Fig. 5, were only observed in the neighborhood of the rowlike phase. We never observed small quadratic clusters. In the video sequence we were able to observe small molecular aggregates down to only two molecules.



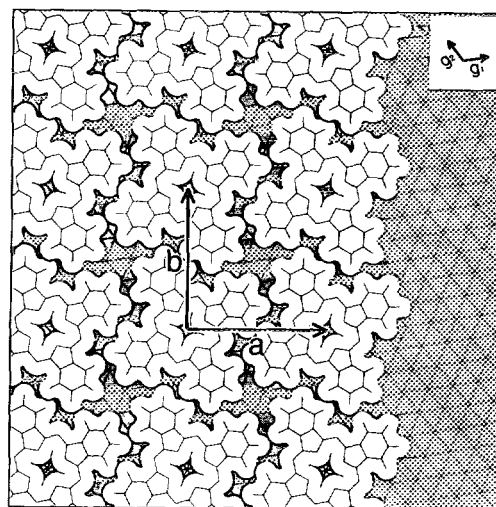
FIG. 1. High-resolution 50 Å × 50 Å image of Cu-Pc on HOPG. The image was recorded in the constant height mode with a scanning speed of 4 frames/s and averaged over 4 frames. ($U = -0.28$ V, $I = 0.4$ nA).

In Fig. 5 one can see at the end of some rows molecules appearing with lower contrast. This is caused by the molecular dynamic. When a molecule stays only a part of the averaging time (about 1 s) at its position, then the frame buffer adds images of the same area with and without a molecule.

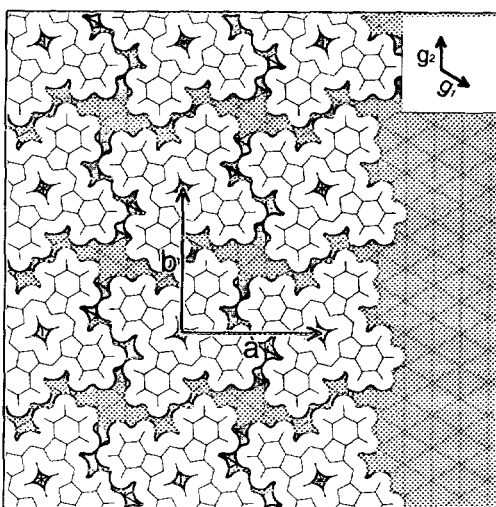
In the uncovered parts of Figs. 4 and 5, the MoS₂ shows stripes, which are always oriented to one of the symmetry-equivalent MoS₂-lattice vectors. The distance between adjacent stripes corresponds to the distance between second next sulfur rows. On the film-substrate boundary one can see on a larger scale that the corrugation of these stripes becomes weaker with a decay length of at least 100 Å. The stripes have not been observed on freshly cleaved MoS₂ substrates or in the surrounding of the close-packed phase and do not depend on the scan direction. This leads us to the conclusion that they represent an adsorbate induced superstructure caused by the rowlike phase. On the other hand, these stripes seem to stabilize the rowlike phase in a self-organizing process because the large distance between the rows cannot be caused by intermolecular interaction. The origin of the stripes may be ascribed in long-range perturbations of the electronic structure of the substrate caused by the adsorbed molecules as it is known from defects on graphite.⁸ Such a mechanism could also explain the observed higher brightness of the stripes compared to the molecules in Fig. 5. But for this discussion further investigations may be necessary.

In Figs. 2(b) and 2(c) the structural models of the two phases on MoS₂ are shown together with the observed stripes. In Table I the crystallographic parameters of the 2D unit cells of Cu-Pc on HOPG and MoS₂ are summarized.

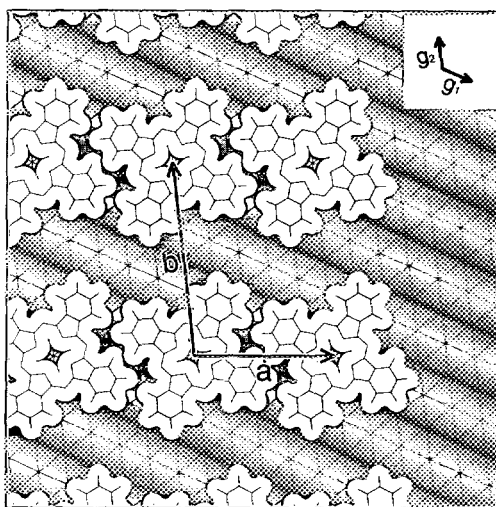
As can be seen from the images, the Cu-Pc molecules appear different on the two substrates. On graphite the molecules show a detailed structure with a fourfold symmetry, similar to the images on Cu(100).⁵ On MoS₂ they are less distinct and look more like a four-leaved clover with a dark spot in the middle of the molecule. On graphite we were able



(a)



(b)



(c)

FIG. 2. Structural model of the ordering of Cu-Pc on HOPG and MoS₂. To emphasize the registry with the substrate, the molecules are drawn without the central metal ion. (a) CuPc on HOPG, (b) CuPc on MoS₂, close-packed phase, and (c) CuPc on MoS₂, rowlike phase.

TABLE I. Crystallographic parameters of Cu-Pc on MoS₂ and HOPG.

Cu-Pc on	HOPG	MoS ₂	MoS ₂
	$ g_1^- =2.46\text{ \AA}$	$ g_1^- =3.16\text{ \AA}$ close-packed	$ g_1^- =3.16\text{ \AA}$ rowlike
$ \vec{a} $	13.7 \AA	13.7 \AA	13.8 \AA
$ \vec{b} $	13.6 \AA	14.2 \AA	19.0 \AA
$ \vec{a}\times\vec{b} $	187 \AA^2	195 \AA^2	259 \AA^2
$\Gamma=\angle(\vec{a},\vec{b})$	90.3°	90.0°	96.6°
$\Phi=\angle(\vec{a},\vec{g}_1^-)$	8.9°	-30.0°	-23.4°
Superstructure	$\begin{pmatrix} 5 & -1 \\ 4 & 6\frac{1}{3} \end{pmatrix}$	$\begin{pmatrix} 5 & 2\frac{1}{2} \\ 0 & 4\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 5 & 2 \\ 0 & 6 \end{pmatrix}$

to record images with both polarities showing the same image contrast, the better resolution we got always with negative sample bias. On MoS₂ we got only images with positive polarity because of the rectifying behavior of the substrate. All high-resolution images were recorded with a tunneling distance close to the critical value where the tip destroys the film. Because of the high reproducibility of our images, we believe that the influence of the tip geometry and other uncontrollable parameters on the image contrast can be neglected.

On MoS₂, the observed tunneling current distribution is broader than on HOPG. An analysis of the Fourier-transformed images shows that on graphite the highest Fourier component observed is the space frequency of the substrate lattice, whereas on MoS₂ only space frequencies lower than half the lattice frequency were found. That the tunneling current distribution of molecules shows more details on HOPG than on MoS₂ has been observed from different authors.⁹ The origin of this is not the lower resolution of the STM but a specific property of the total electronic system of MoS₂ and the molecules, as has been showed by Fisher and

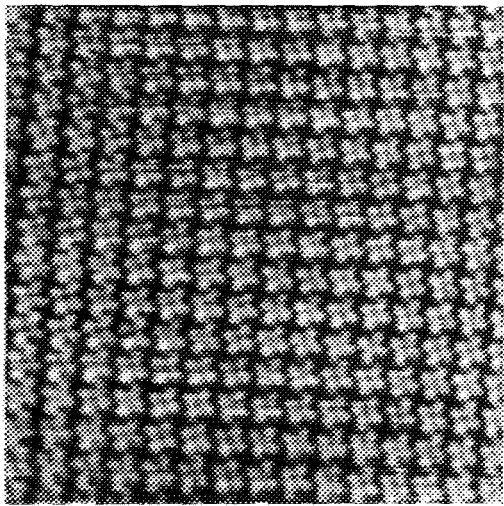


FIG. 3. Constant height image of the closed-packed phase of Cu-Pc on MoS₂. The unit cell parameters are nearly the same as on graphite. (200 $\text{\AA}\times 200\text{ \AA}$, 4 frames/s, 8 frames averaged, $U=1\text{ V}$, $I=0.15\text{ nA}$.)

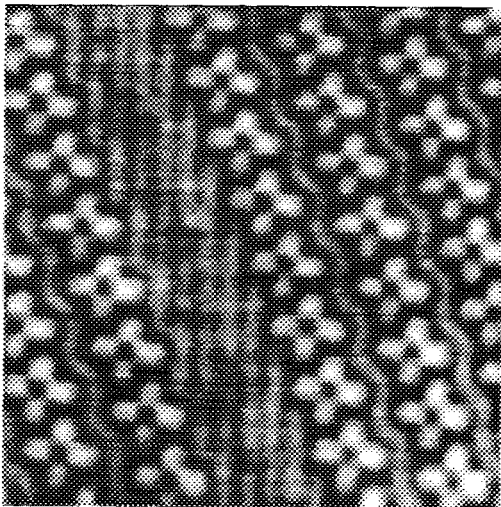


FIG. 4. Image of the rowlike phase of Cu-Pc on MoS₂ (constant height). The adsorbate-induced superstructure of the substrate can clearly be seen in the area where one row is missing. (100 $\text{\AA}\times 100\text{ \AA}$, 4 frames/s, 8 frames averaged, $U=1.1\text{ V}$, $I=0.3\text{ nA}$.)

Blöchl.¹⁰ Adsorbate-substrate complexes which show a tunneling current distribution independent of the substrate also exist.¹¹

In summary, there exist well defined preparation conditions leading to highly ordered monolayers of flat lying Cu-Pc molecules on MoS₂ and HOPG. On HOPG they form a close-packed array with a nearly quadratic unit cell; whereas on MoS₂ we found two phases, one close-packed and one rowlike. The rowlike phase can be explained by an adsorbate induced superstructure of the substrate which, on the other hand, seems to stabilize this phase in a self-

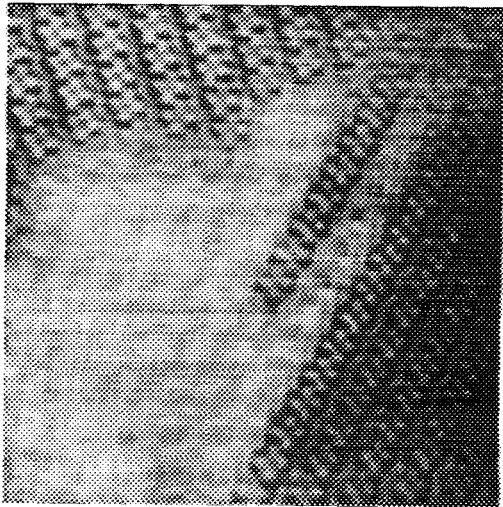


FIG. 5. Boundary between two different domains of the rowlike phase (constant height image). In the video sequence we were able to observe small molecular rows, like that in the center of the image, down to only two molecules. (200 $\text{\AA}\times 200\text{ \AA}$, 4 frames/s, 8 frames averaged, $U=1.2\text{ V}$, $I=0.4\text{ nA}$.)

organizing process. In the images with submolecular resolution, the Cu-Pc molecules appear different on the two substrates.

ACKNOWLEDGMENT

The authors would like to thank the Deutsche Forschungsgemeinschaft for financial support under SFB 329.

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