Orderly Growth of Copper Phthalocyanine on Highly Oriented Pyrolytic Graphite (HOPG) at High Substrate Temperatures

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The growth of an ordered thin film of copper phthalocyanine (CuPc) on highly oriented pyrolytic graphite at high substrate temperatures was studied. High-resolution electron energy loss spectroscopy investigation revealed that the CuPc molecules remained lying flat on the substrate throughout the growth from monolayer to multilayer. Scanning tunneling microscopy and X-ray diffraction measurements showed the CuPc thin film assumed a dense-packed structure in the horizontal direction and a face-to-face stacking mode in the surface normal direction. The totality of the results presented a clear view of the orderly growth process of CuPc molecules.

Introduction

Organic semiconductors have attracted growing interest, because of their enormous potential for applications in molecular optoelectronic and electronic devices. Structural nature and formation of organic thin films have a great influence on the charge transport and charge injection, as well as on the realization of anisotropic optical and electronic properties in organic devices. Thus, it is important to study the film structure and molecular orientation of organic overlayers on substrates. "Quasi-epitaxial" growth of highly ordered organic thin films on crystalline substrates with lattice coincidence, as illustrated by recent reports, is quite common, even though the interactions between the organic molecules and the substrates are rather weak.[1]

In the present work, we have investigated the adsorption behavior and crystallographic structure of copper phthalocyanine (CuPc) on highly oriented pyrolytic graphite (HOPG) at high substrate temperatures. CuPc is a common organic semiconductor with high chemical stability and outstanding electronic properties. It has been widely applied as gas sensors,[2,3] active layers in organic thin-film transistors,[4,5] and buffer layers in organic light-emitting diodes.[6] Several observations of vacuum-deposited metal phthalocyanine on HOPG, mainly by scanning tunneling microscopy (STM), have been reported,[7,8] which suggests well-ordered adsorption of CuPc molecules with a lying-flat orientation on HOPG. However, detailed description of film growth at high substrate temperatures is absent. To further understand the issue, we have studied the formation and growth features using the combination of several powerful techniques, including high-resolution electron energy loss spectroscopy (HREELS), STM, and X-ray diffraction (XRD).

Experimental Details

The HREELS and STM measurements were conducted in a multifunctional ultrahigh vacuum (UHV) system with base pressures of $<2 \times 10^{-10}$ and $<3 \times 10^{-11}$ Torr in the HREELS

and STM chambers, respectively. The HREELS measurements were performed with a LK Technologies Model 3000 HREELS spectrometer. The spectra were collected in a specular geometry with an incident and exit angle of 62° from the surface normal. The primary electron energy was 6.0 eV, and the energy resolution was set to be ~3 meV. Typical counting rates obtained in the measurements were ~10^6 counts per second. The STM images were taken in constant current mode, using a Park Scientific scanning probe microscope system. The tips were made from electrochemically etched tungsten wires. XRD patterns of the CuPc films were measured in air by a Philips X'Pert-MRD system (Cu Kα, 40 kV, 40 mA).

CuPc films were prepared on freshly cleaved HOPG (NT-M DT, ZYA) by molecular beam deposition in UHV. The base pressure in the deposition chamber and the working pressure during deposition were ~8×10^{-10} and ~6×10^{-9} Torr, respectively. The deposition rate of CuPc was maintained at 0.2 nm per minute, whereas the substrate temperature was kept at 130 °C. The thickness of the deposited layers was monitored by a quartz microbalance. Note that the sample with a 30-nm-thick CuPc film on HOPG successively studied by HREELS and STM in UHV was the same as that measured later by XRD.

Results and Discussion

Figure 1 shows the HREELS spectra taken from CuPc thin films as a function of the film thickness. From submonolayer and monolayer films to multilayer films (curves (ii)−(v) in Figure 1), the HREELS spectra indicate similar vibrational features of the surfaces, with no new features or significant shift of the loss peaks. The assignments of the loss peaks for CuPc and other metal phthalocyanines have been reported previously.[9,10] The dominant feature at 95 meV (peak "c") is assigned to the out-of-plane C−H bending mode, whereas the loss peaks "a" and "d" in Figure 1 are assigned to the Cu−N stretch mode and C=N stretch mode, respectively. The loss peak at 56 meV (peak "b") is related to the ring deformation mode. The loss peak at 192 meV (peak "e") is associated with the ring stretch mode, and peak "f", which is located at an energy of ~382 meV corresponds to the C−H stretch mode.

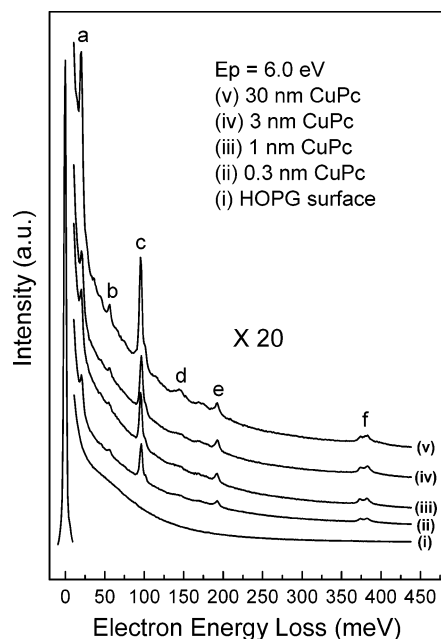* Author to whom correspondence should be addressed. E-mail: apannale@cityu.edu.hk.

Figure 1. HREELS spectra of copper phthalocyanine (CuPc) deposited on highly oriented pyrolytic graphite (HOPG) at 130 °C as a function of film thickness. Curves "(i)−(v)" represent the respective samples of different thicknesses, and peaks "a−f" denote the observable loss peaks. The primary electron energy is 6 eV, and the energy resolution is ∼3 meV.

It is well-known that CuPc molecules have a planar structure and stack easily to form molecular columns. HREELS is a powerful tool to obtain information on the vibrational frequencies of adsorbate, as well as on the surface geometry. Therefore, it is expected that the molecular orientation of CuPc on the HOPG surface in the present case can be understood by HREELS measurements. The HREELS spectra in Figure 1 were collected around the specular direction, in which the vibrational modes perpendicular to the surface are strongly excited by dipole scattering but those parallel to the surface are only weakly excited, because of the screening of image charges.[11] The intensity of the out-of-plane C−H bending mode (peak "c") in Figure 1, the polarization of which orients perpendicularly to the CuPc molecular plane, is much higher than that of the in-plane stretch modes. With increasing CuPc thickness, the out-of-plane C−H bending mode grew in intensity and peak "c" became more dominant. The results suggest that the deposited CuPc molecule was oriented with its molecular plane parallel to the HOPG surface in both low-coverage and high-coverage cases.

Figure 2 shows the comparison of the HREELS spectra of the 30-nm-thick CuPc sample obtained in the specular and off-specular directions. In the latter, the intensity of the in-plane modes, typically the C−H stretch mode (peak "f" of curve vi in Figure 2), is increased much more and becomes comparable with that of the out-of-plane mode (peak "c"). The results are consistent with the inelastic scattering mechanism of HREELS, in which the dipole scattering is strongly localized and dominant around the specular direction, whereas the impact scattering with broad angular distribution is dominant in the off-specular direction.[11] Because the impact scattering is sensitive to vibrational modes of any polarization, the intensity of in-plane vibrational modes will increase, relative to that of out-of-plane modes in the off-specular direction, resulting in alteration of the HREELS spectrum, as mentioned previously. HREELS is an extremely surface sensitive technique; hence, only the topmost layer of the CuPc film contributes to electron scattering.
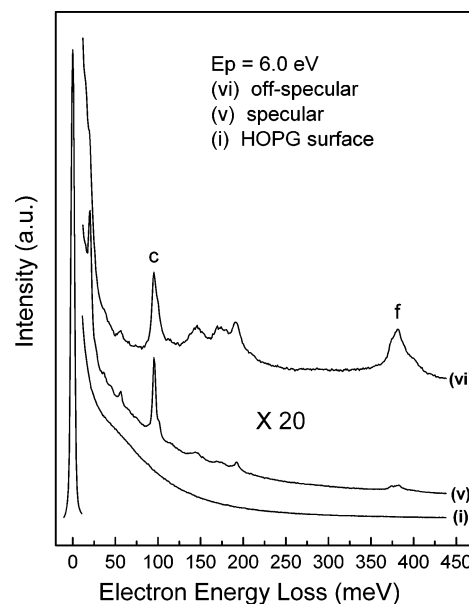

Figure 2. Comparison of HREELS spectra of the 30-nm-thick CuPc sample measured in specular and off-specular geometry. Loss peaks "c" and "f" correspond to the out-of-plane C−H bending mode and the C−H stretch mode, respectively.

The HREELS results thus confirm that the CuPc molecules prefer the lying-flat orientation on a HOPG surface at high substrate temperatures and maintain the same orientation during subsequent film growth.

The surface morphology of the 30-nm-thick CuPc film on HOPG is revealed by scanning electron microscopy (SEM), as shown in Figure 3. Isolated striplike islands of CuPc with grain sizes in excess of 1 µm were evident. The crystalline structure of the islands in the horizontal and vertical directions was investigated by STM and XRD, respectively.

The surface configuration of the CuPc islands is illustrated by the STM image shown in Figure 4. A two-dimensional ordered structure with 4-fold symmetry was observed, and no other phases were observed on the sample. The high-resolution image (Figure 5a) in a smaller area reveals more structural information in detail, showing that the two sides of the unit cell are almost perpendicular to each other and exhibit almost the same length value of 1.38 nm. The lattice parameters suggest that the CuPc molecules form a dense-packed configuration with a quadratic unit cell on HOPG at high substrate temperatures. To form the minimized or close-packed structure, the phenyl groups of one CuPc molecule must fit into the hollow sites of the neighboring molecules, as illustrated by the model of CuPc molecules shown in Figure 5b. The array formation leads to an interspace among four adjacent CuPc molecules, which corresponds to the dark cores in the lattice in Figure 5b. The absence of intramolecular resolution in the image is probably due to the imperfect shape of the STM tip. Our STM results are consistent with those of previous reports on a CuPc monolayer prepared under similar conditions on HOPG and Cu(100).[8,12] Recent molecular mechanics simulations indicated that CuPc molecules prefer a close-packed structure that results from energy minimization,[13] and the calculated distance of the neighboring CuPc molecules was ∼1.40 nm, which is in agreement with the parameters that we previously mentioned.

The XRD pattern for the 30-nm-thick CuPc sample is shown in Figure 6. Comparison to the pattern of the clean HOPG substrate (Figure 6a) shows that no other new diffraction features were observed from the 30-nm-thick CuPc film (Figure 6b),
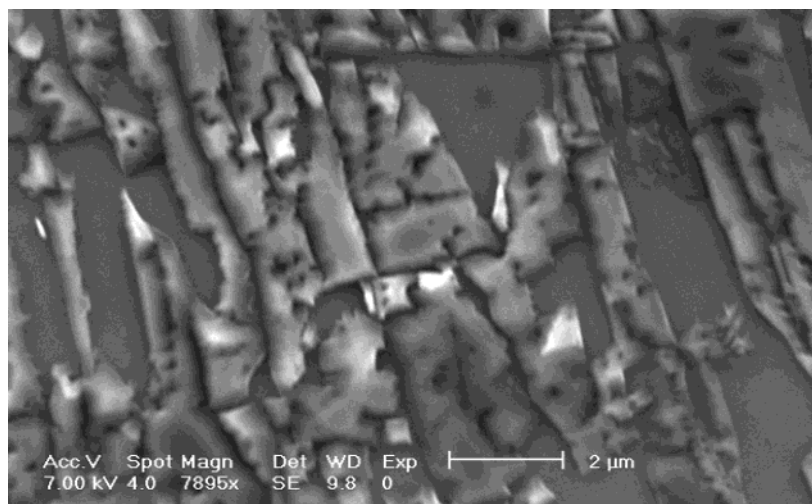
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Figure 3. SEM image of the 30-nm-thick CuPc sample deposited on HOPG at 130 °C.
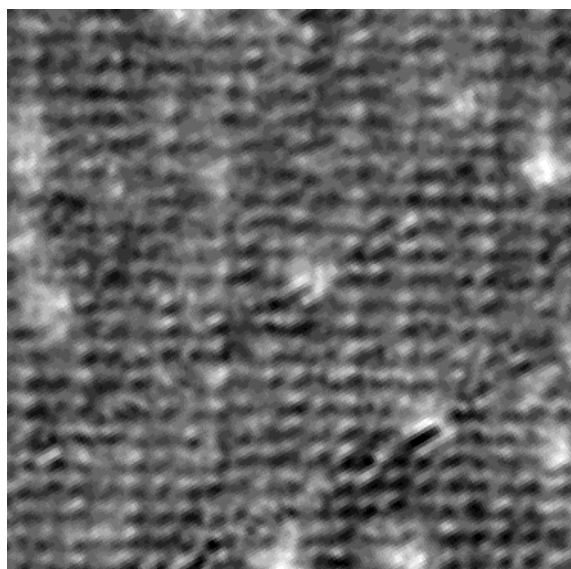

Figure 4. STM image (300 Å × 300 Å) of the 30-nm-thick CuPc sample at $V_T = -0.2$ V, $I = 1$ nA.

except for the emergence of a shoulder peak on the large 2θ side of the HOPG(002) peak. Considering that the lattice constants of most CuPc crystal forms are relatively large and usually result in the XRD pattern being located in the small 2θ region,[14−16] the only new peak at 27.3° in Figure 6b, which corresponds to a very small spacing of 0.32 nm, illustrates that the CuPc molecules are lying flat on the substrate and are stacked face-to-face, with the short *b*-axis parallel to the surface normal. The similar stacking mode of CuPc was observed on an H-terminated Si(111) surface at elevated temperatures,[17] where the authors reported a structure of CuPc crystals with a 0.322-nm spacing in the vertical direction and {1.5×,1.5×,99°} lattice parameters in the horizontal direction. The latter parameters are slightly different from those in the present case, and the difference is probably due to the dissimilar registry of the molecules on the disparate substrates. Altogether, the structural information derived from the STM image and XRD pattern is in accord with the vibrational results from the HREELS spectra.

According to the adsorption energy calculation,[13] the lateral corrugation barrier for CuPc on a HOPG surface is very small and the interaction between the stacking CuPc molecules is much weaker than the CuPc-to-surface attraction. At high
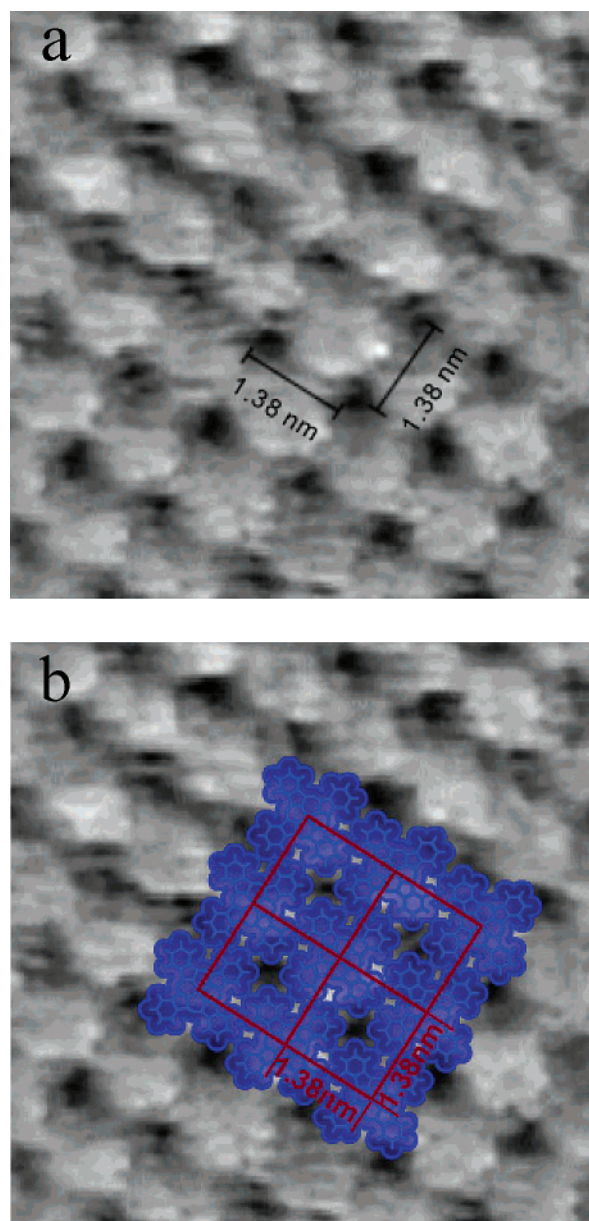
Figure 5. (a) STM image (80 Å × 80 Å) of the 30-nm-thick CuPc sample at $V_T = -0.2$ V, $I = 1.5$ nA. (b) The assembly of CuPc molecules is illustrated by the model.
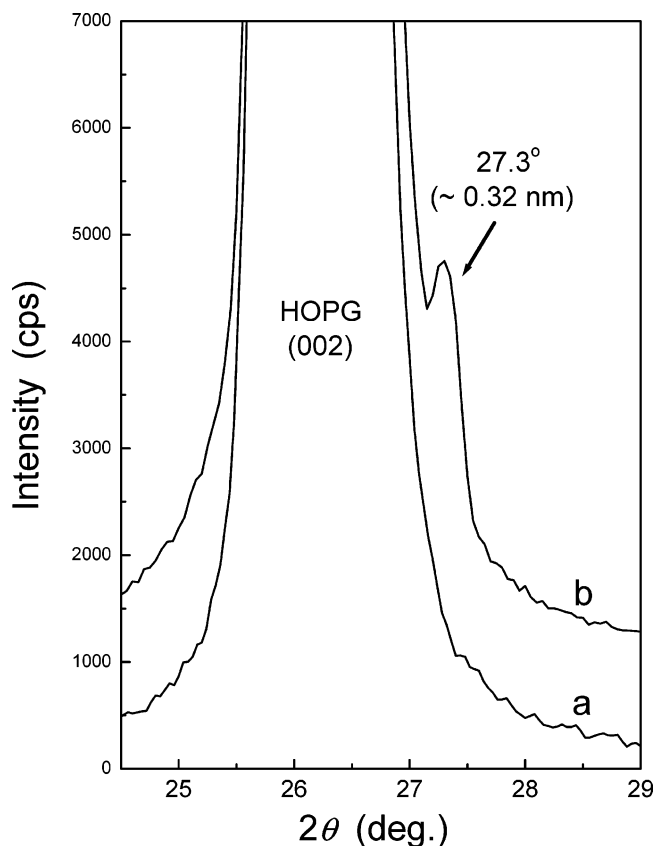
Figure 6. XRD patterns of (a) the HOPG substrate and (b) the 30-nm-thick CuPc sample; the peak at 27.3° corresponds to the 0.32-nm spacing of the CuPc ordered layers along the surface normal.

of CuPc on HOPG prepared at room temperature in UHV and found that CuPc molecules were oriented parallel to the substrate in a similar fashion, but the well-ordered structure was difficult to observe by STM and XRD in this case. The difference between the high-temperature and room-temperature results implies that thermal activation facilitates the crystalline structure formation of CuPc on HOPG, which leads to CuPc films with fewer defects.

Conclusion

Orderly growth of copper phthalocyanine (CuPc) was observed on highly oriented pyrolytic graphite (HOPG) at high substrate temperatures. Scanning electron microscopy showed that the thin films of CuPc on HOPG had a morphology of striplike crystals with micrometer-scale sizes. Vibrational and structural results suggested that CuPc molecules formed a close-packed structure on the substrate with a face-to-face columnar growth that maintained the lying-flat orientation throughout the growth process.

References and Notes

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substrate temperatures, the thermal motion of the deposited molecules is drastic; thus, the resultant large-scale surface migration of the molecules and the small lateral corrugation barrier (lower than the thermal energy) will cause a preference of the island growth. It is understandable that van der Waals forces dominate the interaction between the molecules themselves and that between the molecules and the substrate. To minimize the intralayer van der Waals potential, the CuPc molecules favor a close-packed configuration in the horizontal direction.[13] At the same time, the face-to-face π-stacking of the molecules leads to the formation of molecular columns and the unaltered molecular orientation parallel to the substrate during growth. The mechanism that prevents the molecular columns from falling down may have three origins. The first one is the strong interaction between the molecules and the substrate. Second, the force between the neighboring molecular columns is large. Lastly, the force between the edge of molecular columns and the substrate is weak. We also investigated the same system