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STM, SEM and TEM Observations of Lead-phthalocyanine Vacuum-deposited on Graphite

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Lead-phthalocyanine (PbPc) vacuum-deposited on graphite was investigated by STM, TEM and SEM. The selected area electron diffraction pattern of PbPc crystal has proven that the crystal is triclinic and orients its **b**-axis perpendicular to the substrate surface. This means that the PbPc molecules tend to grow making their molecular plane parallel to the substrate surface. Corresponding to this epitaxy, STM image showed a regular arrangement of disk-like images, which are congruent with benzene rings of the phthalocyanine molecules on the **ac**-plane surface of the triclinic PbPc.

KEY WORDS : STM/ TEM/ SEM/ Lead-phthalocyanine

1. INTRODUCTION

There have been many efforts for imaging the crystal structures at atomic or molecular level resolution, because basic information on local regular or irregular structure (distortion of lattices, dislocations, *etc.*) is expected to be obtained in such high resolution images. Transmission electron microscopy (TEM) is a well-established and powerful method for such purpose, but its application is limited in some cases due to unavoidable radiation damage, especially in the studies on organic or biological materials. On the other hand, scanning tunneling microscopy (STM) comes to be widely used even in the field of organic chemistry or biological research,[1] but it still remains unclear what we observe in STM images in such cases. Therefore, at present it is desired to compare a structure image by STM with another structure information by TEM and SEM for reliable interpretation of STM images.

In this work, we investigated a structure of lead-phthalocyanine (PbPc) vacuum-deposited on graphite by STM, SEM and TEM. Three crystal structures have been reported for PbPc; monoclinic form,[2] triclinic form[3] and orthorhombic form.[4] The triclinic form is thermally more stable than the monoclinic form. The orthorhombic form was obtained on KI single crystal surface by vacuum-deposition, and the unit cell dimensions were only reported. Hamann *et al.*[5] and Pester *et al.*[6] have already reported the surface microstructure of PbPc observed with STM, but they did not focus their interest on its molecular imaging and investigated the polycrystalline structure in larger scale. We tried to observe crystal surface of PbPc with STM in finer scale and report here the result, which is discussed together with those obtained by TEM and SEM observations.

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2. EXPERIMENTAL

Thin crystalline film of PbPc was obtained as an epitaxial film on graphite or on KCl by vacuum-deposition. The PbPc was purified beforehand by sublimation method in nitrogen gas flow. The PbPc thus purified was evaporated from a quartz crucible under the vacuum of 1×10^{-5} Pa with the deposition rate of about 1 nm/min. During the deposition, the temperature of graphite substrate was kept at room temperature. For STM observation, in-air cleaved thick HOPG (highly oriented pyrolytic graphite) was used as the substrate. For TEM observation, thin Madagascar graphite flake, which was previously fixed on an electron microscopic grid, was used as the substrate so that the crystallographic correlation between the PbPc and the graphite could be directly determined by electron diffraction. A sample of PbPc was also made on KCl single crystal (001) surface by the vacuum-deposition after degassing by a preheat treatment of the surface at 400°C for 1 hour. In this case the substrate was kept at 200°C during the deposition in order to obtain well-defined crystals, which can make clear the epitaxial relation of PbPc relative to the KCl substrate. The mean thickness of these PbPc films was usually controlled to be about 3–5 nm by monitoring with a quartz microbalance.

STM observation was performed in air with a STM of WA-Technology using gold-tip, and the STM image was obtained under constant current mode with a bias voltage of 200 mV. TEM observation was carried out with JEOL 200CX operated at 200 kV. SEM images were obtained with ASID-4D SEM attachment equipped in JEM-100C electron microscope operated at 100 kV. SEM was used to investigate larger scale surface morphology of the deposited PbPc crystallites.

3. RESULTS AND DISCUSSION

3.1. TEM observation of PbPc

Figure 1(a) shows a low-magnified image of PbPc deposited on thin graphite flake at room temperature, where the PbPc is crystallized on graphite and also directly on the thin amorphous carbon film supporting the graphite flakes. The crystal size of PbPc on graphite is somewhat larger than that on carbon film. Fig. 1(b) shows a selected area electron diffraction pattern obtained from an area of the PbPc on the graphite. The basic diffraction spots of graphite are indicated with the capital letter "G" in the figure. The other diffraction spots showing longer lattice dimensions can be assigned to those from PbPc crystallites. The unit cell of PbPc shows that the crystallites are triclinic among the three polymorphs. The diffraction pattern can be interpreted as the **b**-axis projection, so that it can be indexed with the $\mathbf{a}^*\mathbf{c}^*$-net pattern of the triclinic structure. The same orientation of PbPc was also observed clearly in the case of PbPc grown on KCl at a higher substrate temperature.

Figure 2 shows such an example of singly oriented diffraction pattern obtained from a larger PbPc crystal grown on KCl at 200°C. The $\mathbf{a}^*\mathbf{c}^*$-plane is also on the Ewald sphere as the case on graphite. Though the crystal size of PbPc deposited on graphite at room temperature is smaller than that on KCl at 200°C, their basic orientations and crystal structures are the same; i.e., the vacuum-deposited PbPc takes the triclinic form both on graphite and KCl, and the **b**-axis of the crystal orients in perpendicular to the substrate surface. In such

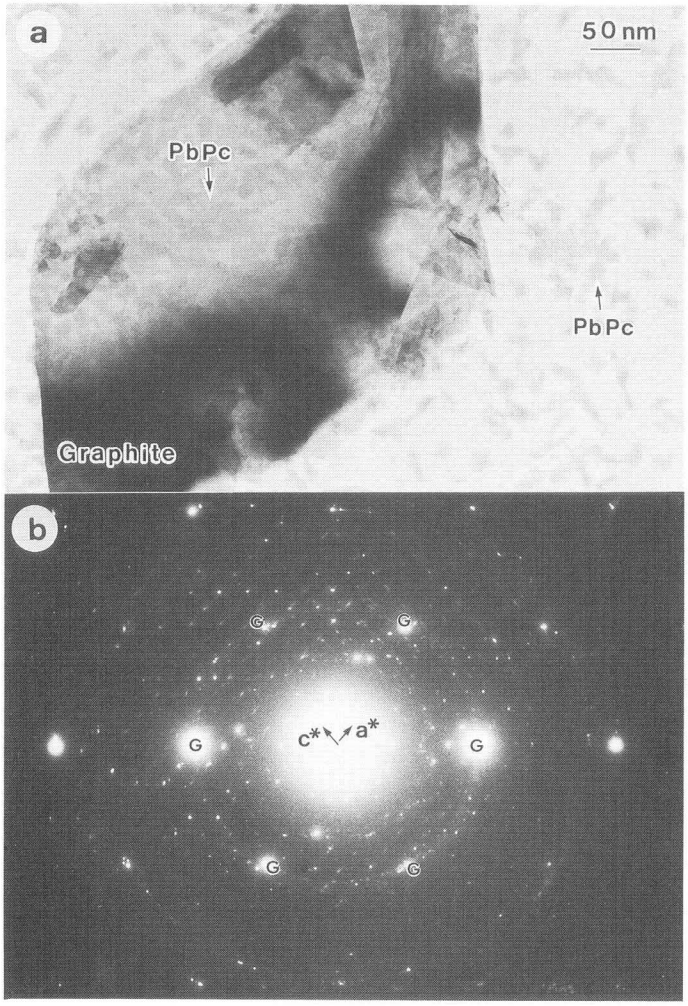


Fig. 1. (a)Low-magnified TEM image of PbPc grown on thin graphite flake supported on thin carbon film. The PbPc crystallizes as small crystallites both on the graphite and on the amorphous carbon film. (b)Selected area electron diffraction pattern taken from PbPc on graphite, where basic reflections from the graphite are indicated with "G", on which the **a***$\mathbf{c}^*$-net pattern from PbPc is superimposed. The pattern from PbPc can be indexed with the triclinic form assuming that the electron beam is nearly parallel to the **b**-axis.

orientation, half of PbPc molecules orient their molecular plane almost parallel to the substrate surface (see the molecules 3 and 4 in Fig. 4(a)), which means that the molecules are deposited to form a growing nucleus in the most energetically favored manner.

3.2 TM image of PbPc

Figure 3 shows an example of a bird-eye view STM image of freshly deposited PbPc on HOPG. Disk-like molecular images, whose sizes and mutual distances correspond to the ben-

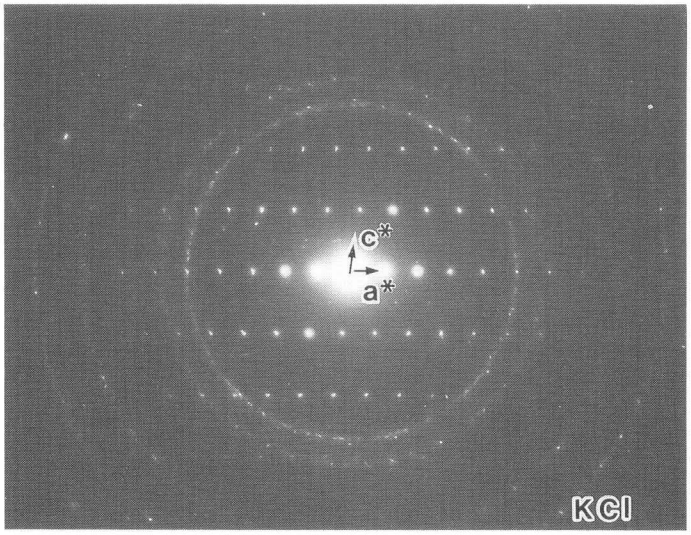


Fig. 2. Electron diffraction pattern taken from PbPc grown on KCl at 200°C. The diffraction pattern corresponds also to the $\mathbf{a}^*\mathbf{c}^*$-net pattern of the triclinic form. The ring patterns come from gold crystallites deposited on a microgrid frame.

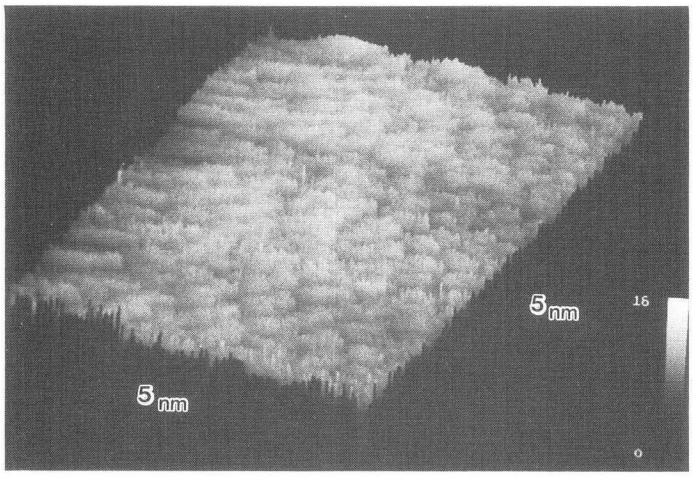


Fig. 3. A bird-eye view STM image obtained with PbPc crystallites on HOPG under the constant current mode with a gold-tip. Here the surface inclination was already corrected.

zene rings of PbPc, are observed to arrange regularly. At some places, however, the images are distorted, probably due to instability of STM or crystal defects of PbPc surface. The interpretation of such an image is a common problem in STM for organic materials, because sometimes artifact images are observed especially in observation in air. In the present case,

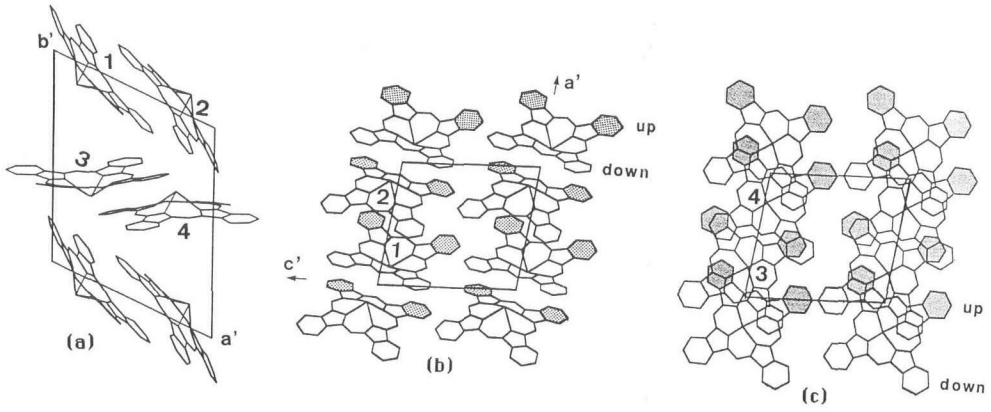


Fig. 4. (a)The **c**-axis projection of triclinic PbPc. (b)The **b**-axis projection of the 1- and 2-molecules in triclinic PbPc. Extruded benzene rings are indicated with screen tones. (c)The **b**-axis projection of the 3- and 4-molecules.

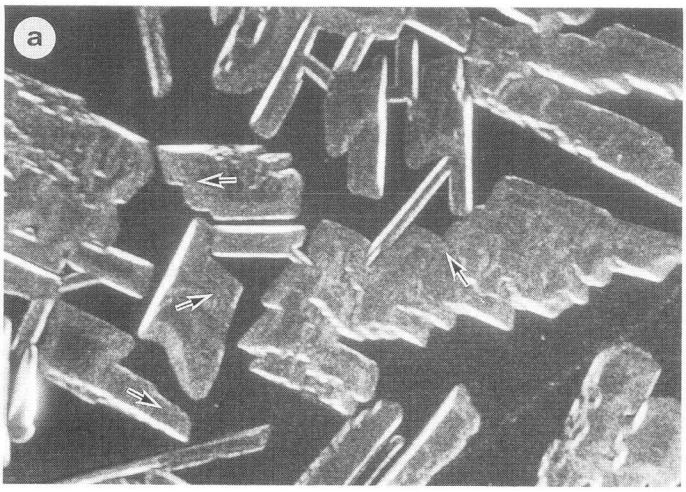
it is not easy to assign these images to some crystallographic plane of PbPc crystal without any other evidences. Accordingly the PbPc samples vacuum-deposited on the thin graphite flakes were examined with TEM in order to reveal the structure and its orientation correlation with the graphite substrate as mentioned above.

3.3. Interpretation of STM image

From the orientation of PbPc described in section 3.1, it is considered that the STM image shown in Fig. 3 corresponds to a plane nearly perpendicular to the **b**-axis of the triclinic PbPc crystal, that is, molecular arrangement on a surface of the triclinic crystal. The **ac**-plane of the triclinic PbPc is the most plausible, but it is inclined to the normal to the substrate surface. The inclination angle is 25° as calculated from the crystal data, but the inclination was corrected with a computer in the STM image in Fig. 3 and, therefore, the STM image obtained corresponds to the image of the surface viewed along the **b**-axis. The **b**-axis projection of the triclinic PbPc, corresponding to a surface structure observed by STM, is shown in Figs. 4(b) and (c) together with the **c**-axis projection in Fig. 4(a). If the exact **b**-axis projection of the surface is realized, the two kinds of molecular images are expected as STM image; a projected surface being formed with the 1- and 2-molecules (Fig. 4(b)) and the other with the 3- and 4-molecules (Fig. 4(c)). However, the benzene rings, which might be detected with bright contrast in STM, are arranged roughly in the same manner as in (b) and (c), and the difference could not be resolved at present.

Figure 5(a) shows a SEM image of well-developed PbPc, where every surface of crystallites is observed to be not parallel, but to incline to the substrate surface, though the inclination direction is different from crystallite to crystallite owing to multi-orientation of the crystallites. In Fig. 5(b), the geometrical relation between STM scanning direction and the **ac**-plane surface of the deposited PbPc is explained schematically. This corresponds to the actual STM images shown in Fig. 3.

From these results, the plan-view STM image can be interpreted with the surface struc-



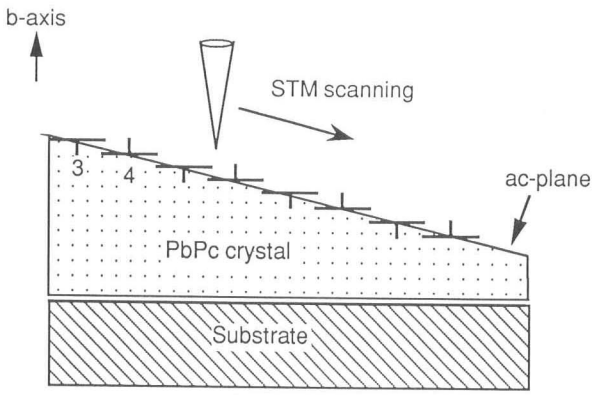
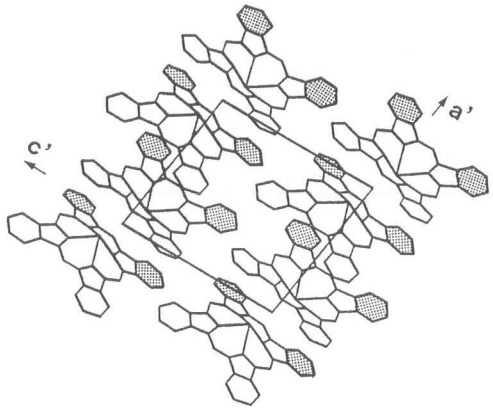


Fig. 5. (a)SEM image of deposited PbPc on KCl at 200°C. The arrows indicate the inclination of crystal surface. (b)Schematic drawing of inclined surface of PbPc crystal and STM tip scanning.

ture as shown in Fig. 6, where a part of the STM image is enlarged. As considered previously, the disk-like images can be assigned to the extruded benzene rings of PbPc, which are arranged periodically. Though it is hard to discuss structures of organic materials only from STM images, the combination of STM, TEM and SEM observations will give more reliable information for the interpretation.



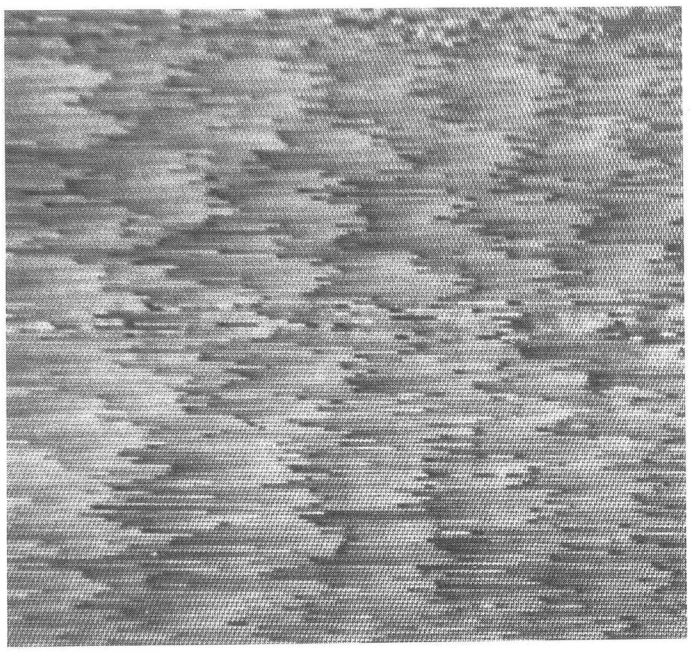


Fig. 6. The enlarged STM image can be interpreted with a regularly arranged benzene rings on the ac-plane as shown above in a schematic drawing of the **b**-axis projection of the triclinic PbPc.

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