

Epitaxial Growth and Polymorphism of Phthalocyaninato-Thorium

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Thin films of Th-phthalocyanine made by vacuum deposition on KCl were studied by electron microscopy. The formation of a new polymorph was found and its structure and epitaxial relation to the substrate have been revealed.

KEY WORDS: Epitaxy/Th-phthalocyanine/Crystal structure/Polymorphism

INTRODUCTION

Among many phthalocyanine metal-derivatives, actinoid derivatives, such as uranium- or thorium- di-phthalocyanine (MPC_2 , $\text{M}=\text{U}$ or Th) have firstly been found to form as the sandwich-type molecule¹⁾²⁾³⁾ in which a eight coordinating metal ion is placed between two Pc ligands. During the study of epitaxial growth of various kinds of organic materials, it has become clear that Th-Pc_2 forms a well oriented epitaxial film which is assigned to a new polymorphic crystal. In the present paper the structure of the new polymorph and the epitaxial relationship between the film and the substrate are reported on the basis of the electron diffraction patterns and of the high resolution electron micrographs on which regular molecular arrangements and also many kinds of irregular ones⁴⁾ can be observed.

EXPERIMENTAL

The ThPc_2 was synthesized by heating a stoichiometric mixture of Th metal powder and pure o-phthalodinitrile at about 350°C for several hours. The Th powder was washed with 1.0N HCl before the mixing and the o-phthalodinitrile was purified by sublimation method in air. The crude product was washed with acetone for 12 hours in Soxhlet extractor and then sublimed at 550°C under reduced N_2 gas pressure. The crystalline product thus obtained was evaporated from a quartz crucible in a vacuum of 2×10^{-6} torr and deposited onto a (001) of a substrate KCl single crystal kept at 200°C. The substrate was preheated at 550°C for two hours in the vacuum in order to eliminate surface contaminant. The film thickness was monitored with a quartz microbalance to be 200 Å or less than 100 Å. These thicker and the thinner specimens were used for electron diffraction and for high resolution electron microscopy, respectively.

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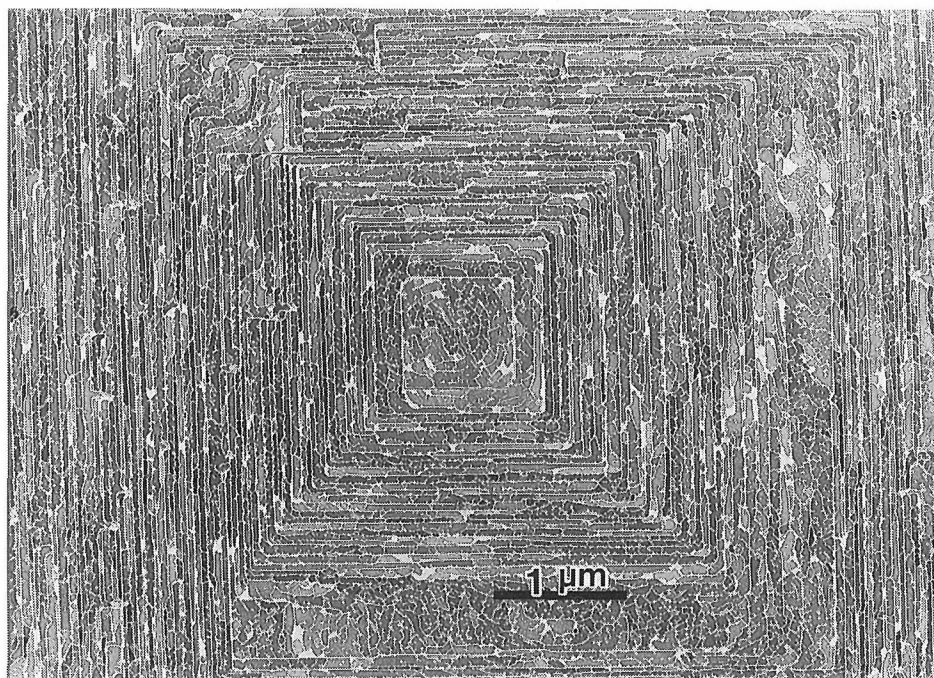


Fig. 1 ThPc₂ grown on KCl (001) plane.

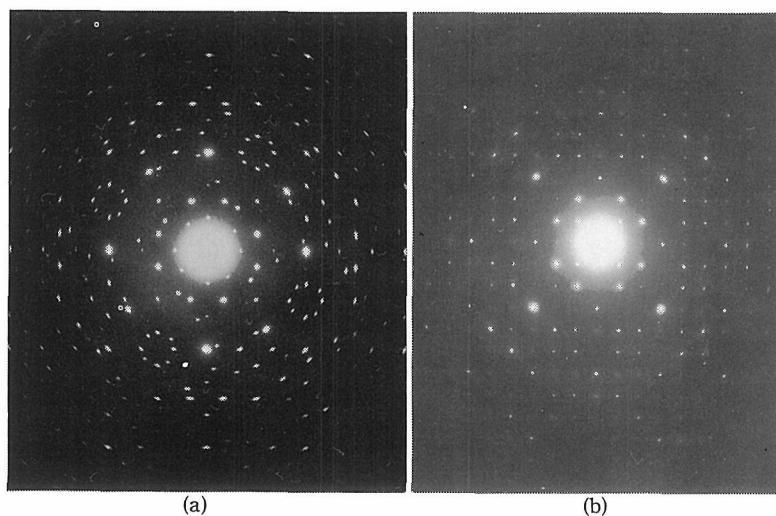


Fig. 2 Selected area electron diffraction patterns of ThPc₂ grown on KCl from relatively wide area showing a double orientation (a) and from a small area exhibiting a single orientation (b).

RESULTS AND DISCUSSION

An electron micrograph of a film of ThPc₂ grown on KCl is reproduced in Fig. 1. As is evident from this micrograph, the film is composed of many small crystallites whose mean size is about several hundred angstrom or less in length. Their growth

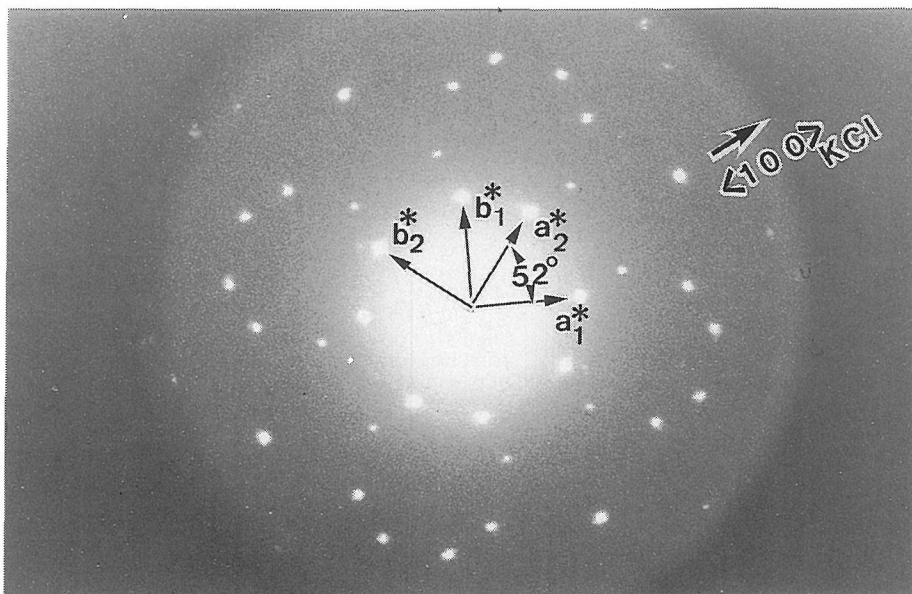


Fig. 3 Orientational relationship between two tetragonal lattices of ThPc₂ and the substrate.

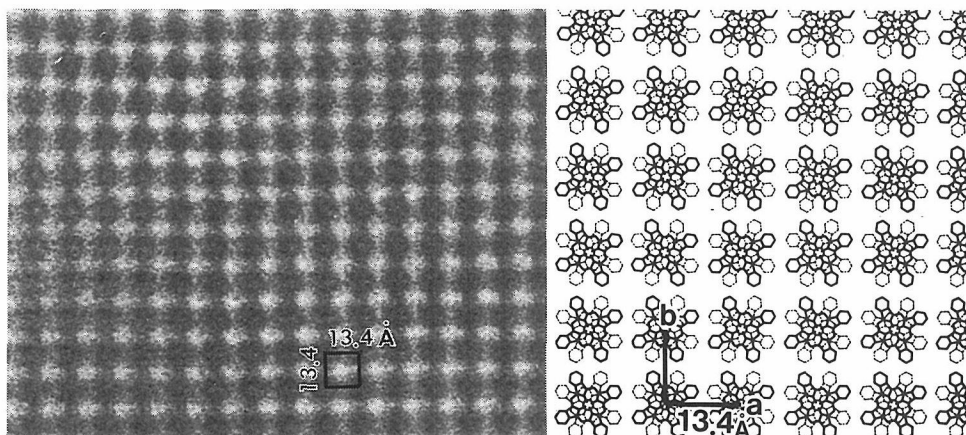


Fig. 4 High resolution electron micrograph of ThPc₂ shown in Fig. 1 and its model.

seems to be controlled by a surface structure of the substrate. The square frames along which the crystallites are arranged correspond to the surface steps of KCl produced by thermal etching caused by the preheat treatment of the KCl in vacuum. A selected area electron diffraction pattern from this epitaxial film is shown in Fig. 2(a), in which two single crystal patterns are superimposed with mutual positions rotated by 52° or 38° to each other. This relationship is illustrated in Fig. 3 where only the inner part of the pattern is reproduced for the simple interpretation. The direction of the crystal axis of KCl is also indicated by an arrow. When the smaller area of the specimen was selected, the individual patterns were isolated, clearly exhibiting a tetragonal symmetry with a

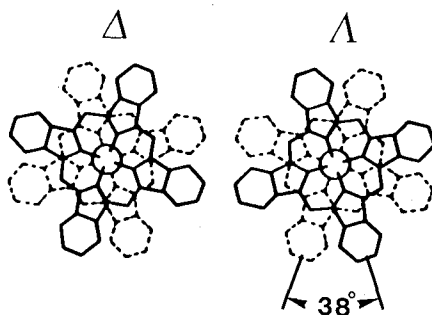


Fig. 5 Molecular structure showing the two isomers of ThPc_2 .

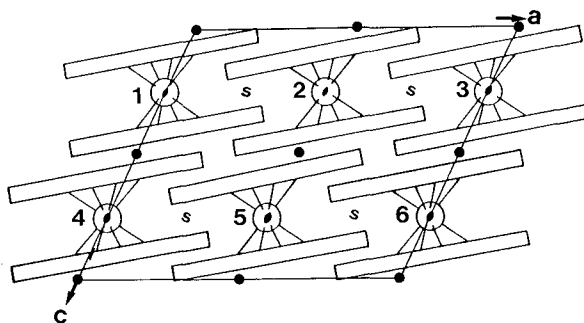


Fig. 6 A projection of ThPc_2 crystal in the monoclinic form along the b -axis and symmetry elements in the unit cell.

periodicity of $1/13.40 \text{ \AA}$ as shown in Fig. 2(b). This periodicity is tentatively taken as the unit length of the a^* - and b^* -axes for the tetragonal crystal. A high resolution electron micrograph of the same film is shown in Fig. 4(a) with its model (b) which also exhibits the molecular arrangement of the tetragonal symmetry. On the other hand, the molecular and single crystal structures of ThPc_2 obtained by sublimation method were revealed by x-ray diffraction analysis. The crystal belongs to a space group of a monoclinic form (space group $C2/c$) which is isomorphic with those of Uranium (IV) di-phthalocyanine and has the following lattice constants, $a=18.92$, $b=18.81$, $c=15.92 \text{ \AA}$ and $\beta=116^\circ$. Therefore, the epitaxial film can be concluded to be composed of crystallites of a different polymorph of ThPc_2 . The molecule in the monoclinic form revealed by x-ray diffraction method is composed of an eight-coordinating Th-atom sandwiched with two phthalocyanine macrorings which, being separated by a distance of about $3.5 \text{ \AA}$, mutually rotate by 38° around the normal axis as illustrated in Fig. 5. This molecule has no mirror symmetry or no inversion center as a whole, as is evident from the figure. On the contrary, the crystal lattice belonging to the space group of monoclinic $C2/c$ has the symmetry elements of glide plane or inversion center. The molecular stacking of ThPc_2 in the monoclinic crystal is schematically drawn as a b -axis projection in Fig. 6, the molecules 1 and 4 are, for example, related by a glide plane $c(x \ 0 \ z)$ or $c(x \ 0.5 \ z)$. This means that two pairs of sandwich type molecules

related by mirror symmetry co-exist in the crystal. Two molecular configurations are shown in Fig. 5 which are the molecular isomers designated as Λ - and Δ -forms. If the molecular site 1 is occupied by the Λ -form, the sites 2 and 3 also should be occupied by the Λ -form and the 4,5 and 6 are by the Δ -form. In the case where the rotation angle of one ligand relative to the other is 45° , no such isomers exist and the molecule has mirror symmetries on planes through the Th(IV) vertical to the molecular plane. The molecular structure itself in the tetragonal polymorph is reasonably considered to be identical to that in the monoclinic form expecting easily from the structural characteristics of many other phthalocyanine derivatives. Therefore, the same stacking situation is expected where the Λ - and the Δ -forms are stacked alternately in the tetragonal form. In order to achieve such a stacking the size of the tetragonal unit lattice should be twice or more as large as $13.4 \times 13.4 \text{ \AA}^2$ if one restricts the discussion to two dimensional lattice packing. For example, a face-centred lattice of $2a \times 2b$ can contain two sandwich type molecules in the unit cell. When one take the third dimension, i.e. the c-axis length, into consideration, the unit cell of $a=b=13.4 \text{ \AA}$ is permissible making the c-dimension of about $7 \text{ \AA}$ which is the size of the sandwich type molecule in the perpendicular direction to the molecular plane longer than $14 \text{ \AA}$ which is twice the size of the sandwich type molecule. In the former case the molecular images on the ab-plane are identical. In the latter case the images of the projection along the c-axis become the superimposed one of the Λ - and Δ -forms. However, the discriminating the superimposed or the respective molecular images is impossible at the present resolution of $2.0 \text{ \AA}$. Three dimensional electron diffraction study may decide the real structure of such thin small crystalline specimen as the present case.

The crystal a- or b-axis of the new polymorph takes a rigid orientation relative to the surface lattice of the substrate KCl. That is, the a-axis of the ThPc_2 in the epitaxial film makes an angle of 26° toward clockwise or anticlockwise direction from the a- or b-axis of KCl as shown in Fig. 3. This axial correlation between a deposited organic crystalline film and a substrate alkali halide is often observed for tetragonal crystallite of other di-phthalocyanines or poly-phthalocyanines. For example, germanium oxy-phthalocyanine polymer crystal⁵⁾, various lanthanoid phthalocyanine derivatives^{6),7)} or also some porphyrine derivatives⁸⁾ grown on KCl or NaCl show the same orientational relationship with the crystal axis of the alkali halide substrate. There is an argument⁹⁾ as to whether these orientational relationships between these phthalocyanines and the substrates are regulated by lattice misfit or by molecular registry of the first fixed molecule on the substrate surface. The conclusion for this argument is not drawn yet and will be reported in future. We can present an example of epitaxy¹⁰⁾ to strengthen a general rule for tetragonal phthalocyanines to crystallize epitaxially on alkali halides with an angle of 26° to the a-axis of the substrates.

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