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Epitaxial Growth of 5,10,15,20-Tetraphenylporphyrin Metal Complexes and Their Photovoltaic Properties

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EPITAXIAL GROWTH OF 5,10,15,20-TETRAPHENYLPORPHYRIN METAL COMPLEXES AND THEIR PHOTOVOLTAIC PROPERTIES

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ABSTRACT 5,10,15,20-Epitaxial growth tetraphenylporphyrin metal complexes (MTPP; M = Zn, Mg, properties Co, VO) and their photoelectrochemical investigated. MTPP crystals grew epitaxially (001) surface by a physical vapor deposition method. The (100)the crystals belong to the tetragonal system. plane of MTPP crystals is parallel to the KC1 (001)plane, and the [100] axis is parallel to the KC1 <120> axis. Photoelectrochemical properties were the indium-tin oxide(ITO)/MTPP/I3-,I-/Pt system.

INTRODUCTION

Porphyrin films attract interests as a functional material in solar energy conversion.1 Many porphyrin derivertives various central metals and substituents were prepared in order the photovoltaic properties.2 Most improve photoelectrochemical investigations using organic semiconductors have been made for amorphous or polycrystalline Ha TPP orientation-controlled thin films. film exhibited Α photocurrent three times that οf its polycrystalline film. The results suggensts that a molecular and a crystal orientation in important role in photovoltaic properties of organic cell.

In this paper, MTPP films were prepared on a KCl cleavage surface and the molecular arrangement in the film was observed by electron microscopy. The photoelectrochemical properties of films were investigated in wet cells.

RESULTS AND DISCUSSION

Figure 1 shows electron micrographs and selected area electron diffraction patterns of the ZnTPP films deposited on a KCl and ITO substrates. The film deposited on a KCl substrate (a) was

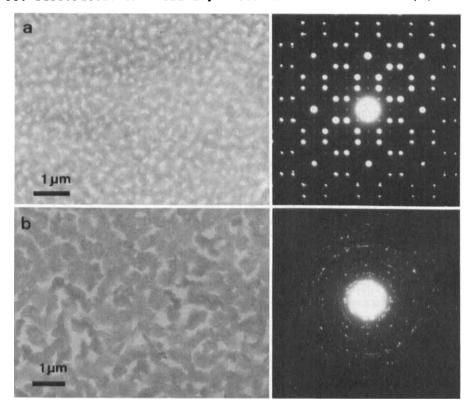


FIGURE 1 Electron micrographs and electron diffraction patterns of the ZnTPP films deposited on KCl (a) and ITO glass (b).

composed of crystals which grew epitaxially on the substrate. The electron diffraction pattern consisted of superposition of two tetragonal single pattrens, and the angle between the two patterns was 37°. On the other hand, the film deposited on an ITO substrate (b) was composed of crystallites, so that the electron diffraction showed a ring pattern. The crystal belonged to a tetragonal system, and the lattice constants

were as follows: a = 1.34, c = 0.97 nm, which agreed well with those of ZnTPP·H₂O crystal.⁴ The c-axis of the crystal was perpendicular to the KCl (001) plane, and the a-axis was parallel to the KCl $\langle 210 \rangle$ direction.

Figure 2 shows $2\theta/\theta$ X-ray diffraction patterns from the original powder of ZnTPP (a), the film deposited on the KCl (b), and the film on the ITO glass (c). The pattern from

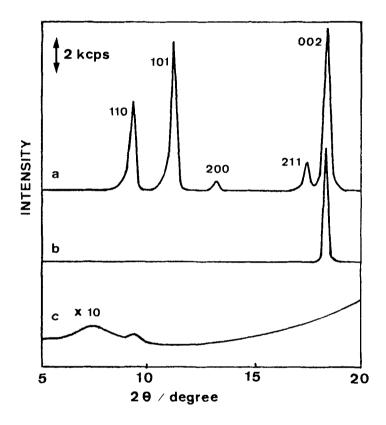
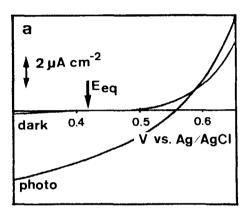


FIGURE 2 X-ray diffraction of the original powder (a), the film deposited on KCl (b), and the film on ITO glass (c).

powder showed diffraction peaks of the tetragonal crystal. The film deposited on the KCl showed only one reflection from the (002) plane. This indicates that the ZnTPP crystals grew epitaxially all over the substrate taking its (001) plane

paralell to the substrate. No clear peak was observed for the film deposited on the ITO glass, which was caused by crystallines with random orientation.

After separating the epitaxial film from the KCl substrate in water, the MTPP film was mounted on an ITO glass as an electrode. Figures 3 (a) and (b) show current-voltage characteristics in the dark and under illumination of the polycrystalline and oriented ZnTPP electrodes, respectively.



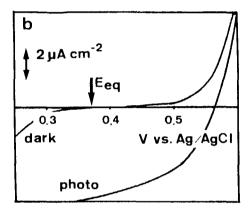


FIGURE 3 Current-voltage curves in the dark and under illumination of the polycrystalline (a) and oriented (b) ZnTPP electrodes, respectively.

The thickness of the ZnTPP films were about 200 nm for cases. The illumination was carried out with white light 100 mW cm⁻² from the side of electrolyte solution ZnTPP films. The current-voltage curves in the dark indicate a rectifying behavior due to a p-type semiconduction of The cathodic photocurrent observed under illumination to a band-bending of ZnTPP downward at the inteface the ZnTPP and the I_{3}^{-}/I^{-} solution. The photoelectrochemical data are listed in Table I. The fill factor for the film was an extremely high value of about 0.46. This caused by orientation effect of the ZnTPP crystal.

			Polycrystalline fil	lm Oriented film
Isc	/μA	cm-2	3.88	7.19
Voc	/mV		140.0	197.5
Imax	/μA	cm-2	2.13	5.06
Vmax	/ m V		82.5	130.0
f f			0.323	0.463
n'			1.8x10-4 %	6.6x10-4 %

TABLE I Photoelectrochemical data for the ZnTPP films.

The molecular arrangements and the molecular packing in the epitaxial film are shown schematically in Fig. 4. The

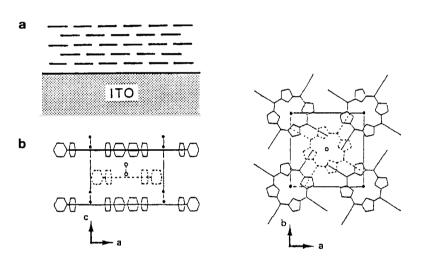


FIGURE 4 Schematic diagrams of the molecular arrangement (a) and the molecular packing (b) in the epitaxial film electrode.

planar MTPP molecules stack with its molecular plane paralell to the substrate surface. In this film, a carrier mobility seems to be larger than that of the polycrystalline film because of the high orientation.

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