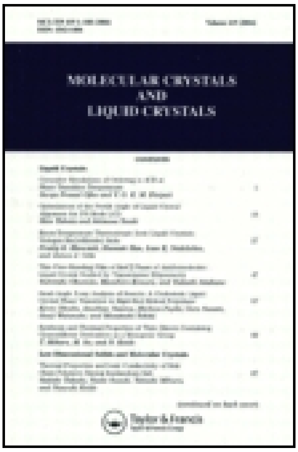

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Enhancement of Photoelectrochemical Properties of Phthalocyanine Thin Films by the Control of Molecular Orientation

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To cite this article: Yasukiyo Ueda, Mayumi Watanabe & Hideyuki Yamaguchi (1995): Enhancement of Photoelectrochemical Properties of Phthalocyanine Thin Films by the Control of Molecular Orientation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 175-180

To link to this article: http://dx.doi.org/10.1080/10587259508033991

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 175–180
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ENHANCEMENT OF PHOTOELECTROCHEMICAL PROPERTIES OF PHTHALOCYANINE THIN FILMS BY THE CONTROL OF MOLECULAR ORIENTATION

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Abstract Orientation-controlled Pc (TiOPc, VOPc and VOPcFx) films were prepared by vapor deposition on a KBr (001) surface. Pc molecules were oriented parallel to the substrate surface. The photoelectrochemical properties of a randomly-oriented and an oriented films were investigated in cells of the configuration ITO / Pc / I_3^-, I^- /Pt. Remarkable enhancement is obtained especially of I_{SC} (short circuit current) and η ' (apparent energy conversion efficiency) by epitaxial orientation.

INTRODUCTION

Thin films of phthalocyanine (Pc) compounds have recently been attracting a good deal of attention as new functional materials. There have been many reports on electronic and photoelectrochemical properties of Pc films deposited on metal electrodes, but few reports on the relationship between these properties and molecular orientation in the films. Application potential of Pc films heavily depends on the controllability of the molecular orientation. We have reported the photovoltaic properties of AlPcCl film were enhanced by the control of molecular orientation (1). Among Pc compounds, TiOPc and VOPc with tetravalent metals at the center have the broad spectral response in the near-infrared region at the longer wavelengths than those with common transition metals such as Fe, Cu and Ni.

In this study, TiOPc, VOPc and polyfluorinated VOPc (VOPcFx) films were prepared on an indium tin oxide (ITO) coated glass and cleavage surfaces of KBr. The molecular arrangements in the films were observed by electron microscopy. The photoelectrochemical properties of films were investigated in cells of the configuration ITO / Pc / I_3^-, I^- / Pt. The effect of molecular orientation on photo-electrochemical properties was discussed.

EXPERIMENTAL

TiOPc, VOPc and VOPcFx were obtained from Konica Co., Aldrich Co. and Nippon Shokubai Co., respectively. These samples were purified twice by vacuum sublimation. The substrates used were an ITO glass and air-cleaved (001) surfaces of KBr. Three Pc compounds were vapor-deposited onto the substrates from a fused silica crucible heated by a tungsten coil. The deposition rate was controlled to be about 2 nm/min in thickness using a quartz crystal microbalance.

The photoelectrochemical measurements of Pc films were performed in a gas-tight 20-mL glass cell using a conventional three-electrode sys-tem. The thickness of Pc films for photoelectrochemical measurement was about 200 nm. The film on the ITO substrates was provided as a working electrode as it was. In the case of the film on KBr, the KBr substrate was dissolved away on a water surface, and the Pc film was transferred onto an ITO glass substrate. The electrolyte contain-ing a redox couple was 5 mM I_2 and 0.1 M KI.

RESULTS AND DISCUSSION

According to the elemental analysis, VOPcFx was found to be $VOPcH_{1.9}F_{13.5}Cl_{0.6}$ (C, 43.40; N,13.04; H, 0.23; F, 30.43; Cl, 2.53; V, 6.05%). Figure 1 shows the electron micrographs and electron diffraction patterns of the TiOPc films deposited on ITO glasses kept at 20 and 200℃. At a substrate temperature of 20℃, the deposited TiOPc formed almost an amorphous thin layer. As the substrate temperature was elevated at 200℃, the crystals grew to form a polycrystalline film. VOPc and VOPcFx films deposited on ITO glasses showed similar morphologies to TiOPc films. Pc films deposited on KBr substrates kept at 20℃ were composed of randomly oriented small granules. When the substrate was kept at 200℃ during the evaporation, Pc films deposited on KBr substrate were composed of rectangular crystallites grown epitaxially, as is shown in Fig.2. In the case of TiOPc and VOPc films, the edges of the crystallites ran along the <110> direction of the substrate crystal. The electron diffraction patterns of both TiOPc and VOPc films showed

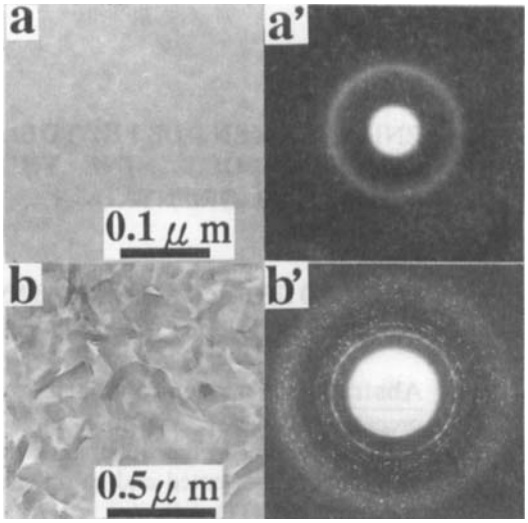

Fig. 1 Electron micrographs and electron diffraction patterns of the TiOPc films deposited on an ITO glass kept at 20℃ (a,a') and 200℃(b, b').

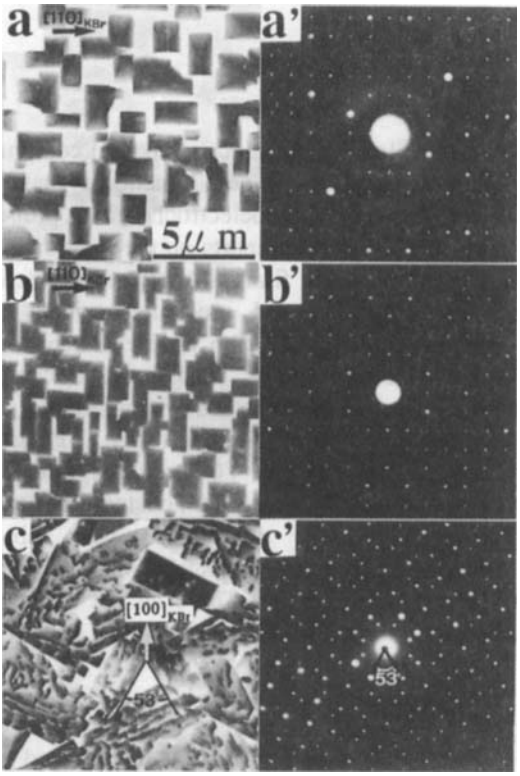

Fig. 2 Electron micrographs and electron diffraction patterns of the TiOPc (a,a'), VOPc (b, b') and VOPcFx (c, c') films deposited on a KBr (001) surface kept at 200℃.

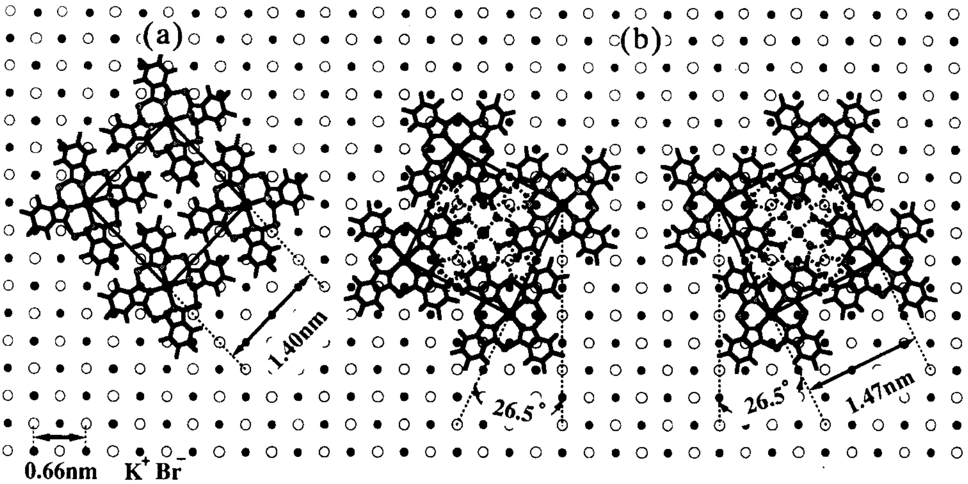

Fig.3 Possible arrangement of TiOPc (a) and VOPcFx(b) molecules on a KBr (001) surface.VOPcFx molecules form two equvalent square lattices($\sqrt{10}$x$\sqrt{10}$-R±26.5°).

the tetragonal net patterns with same periodicity of 1.40nm^{-1} . In the case of VOPcFx film, on the other hand, the edges of the crystallites ran along the <120> direction of the substrate crystal. The electron diffraction pattern of the film showed the supperposition of two single tetragonal net patterns with the periodicities of 1.47nm^{-1} crossing at 52° , in which all reflections observed satisfy the relation $h+k = 2n$. In bulk crystals of TiOPc and VOPcFx, some phases are known (2,3), but the tetragonal phase has not been identified yet. The essential nature of the epitaxial growth was discussed by the interaction between the substrate and admolecule. In the case of Pc molecule deposited on alkali halide surfaces, it has been suggested that the most likely form of interaction is one between the electron attracting alkali-metal ions of the substrate and the electron-rich aza-bridging nitrogen atoms of the Pc ring system. On comparison of lattice matching between the periodicities of the substrate crystal and those of deposited Pc crystals, it is concluded that TiOPc and VOPcFx molecules are arranged on a KBr (001) face as represented schematically in Fig.3. TiOPc and VOPcFx molecules were oriented parallel to the substrate surface and formed a unique square lattice (3x3-R45°) and two equivalent square lattices ($\sqrt{10}$x$\sqrt{10}$-R±26.5°), respectively. These commensurate square lattices have been observed in other Pc films with pyramidal molecular structures deposited on various

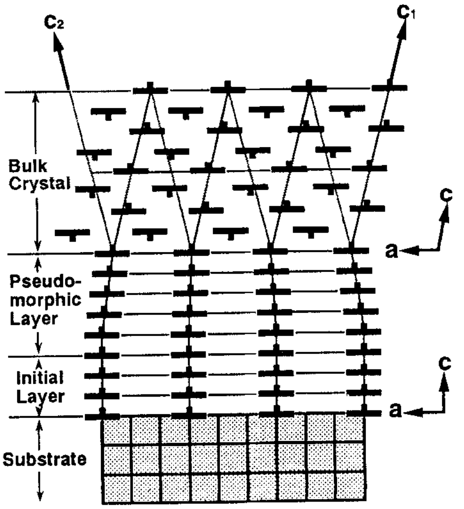

Fig. 4 A schematic model of pseudo-morphic layer.

alkali halides (4 , 5). The $\sqrt{10}\times\sqrt{10}$ epitaxial structure in VOPcFx film was maintained regardless of film thickness. In TiOPc film, however, com-mensurate square lattices were formed at the adsorbed initial layer and the structures came close to bulk ones through pseudo-morphic layers with an increase in film thickness, as shown in Fig.4 (4).

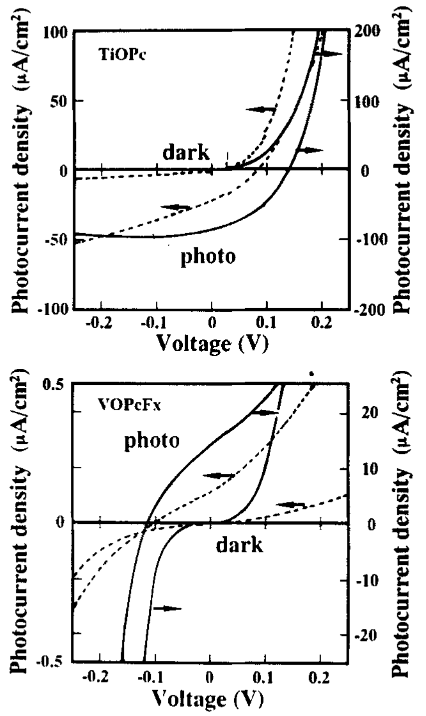

Fig.5 I-V curves for TiOPc/ITO and VOPcFx/ITO electrodes prepared by deposition on an ITO glass kept at 20℃(dotted line) and a KBr (001) surface kept at 200℃(solid line) in the dark and under illumination.

After separating the film from the KBr substrate in water, Pc films were trans-ferred on ITO glasses as an electrode. It was confirmed that the bare ITO glass used as substrate for the Pc working electrode exhibits no prominent redox peak in the potential range related to the present measurements in the redox couple of 5 mM I_2 and 0.1 M KI. Figure 5 shows the current-voltage (I-V) curves of the TiOPc and VOPcFx films deposited on ITO glass and on KBr substrate in the dark and under illumination. The voltage 0 was referred to the rest potential (an equilibrium potential of the I_3^-/I^- redox couple; Eeq) of the cell in the dark. The illumination was carried out with white light of 100 mWcm^{-2} from the Pc front side. The I-V curves of TiOPc film in the dark are characterized by a typical rectification for the blocking contact between the redox couple solution and the p-type semiconducting TiOPc. Under illumi-nation, cathodic photocurrents were observed for TiOPc/ITO electrodes. The electrochemical behaviors of VOPc film in the dark and under illumination were similar to those of TiOPc film. In contrast, anodic photocurrents were observed for VOPcFx/ITO electrode under illumination. This finding suggests that VOPcFx film acts as an n-type semiconductor. In general, Pc compounds indicate a p-type semiconducting behavior. It is also well-known that the semiconducting behavior of Pc compounds changes from p-type to n-type by the substitution of electron-withdrawing groups such as nitrile groups and chlorine atoms for pheripheral hydrogen atoms(7,8). In VOPcFx molecule, the strong electron-withdrawing effect of peripheral fluorine atoms is considered as a reason of n-type behavior.

In Figure 6, the spectral dependence of I_{SC} (photo-current action spectra) of TiOPc/ITO electrodes is compared with the electronic absorption spectra. The monochromatic light was irradiated from both TiOPc/solution (●) and ITO/TiOPc (○) sides. Photocurrents were normalized for an incident intensity of 1mW/cm^2 . The TiOPc electrode deposited on ITO glass at 20℃ had absorption bands in the wavelength region from 500 to 900 nm attributed to the π - π * Q-band transition and showed a maximum peak at 710 nm. When the light was irradiated from the TiOPc/solution side, the photocurrent action spectrum in the region above 500 nm was in good agreement with the absorption spectrum of TiOPc film. No intensities of the photocurrents in the region below 500 nm are due to the absorption of the light with solution. When irradiated from ITO/TiOPc side, the action spectrum had a maximum I_{SC} at about 800 nm corresponding to the foot of the absorption spectrum of TiOPc, and had a minimum at about 700 nm coinciding with the top of band. This optical filtering effect of TiOPc suggests that the photoactive region is the TiOPc/solution interface. In the case of the oriented TiOPc film/ITO electrode prepared by deposition on KBr at 200℃, it had a broad absorption band in the wavelength of 600-850 nm. It is known that the Q-band region is very sensitive to the enviroment of the molecule and to changes in numbers and orientation of nearest neighbor Pc's in the solid(9). The difference in the electronic absorption spectra of the films deposited on an ITO glass and a KBr substrate indicates the different molecular orientation in the films. The photocurrent action spectra for the cell consisting of the oriented TiOPc film/ITO electrode roughly matched the absorption apectrum. However, it is noteworty that the photocurrents for illumination from the ITO/TiOPc side is about 3 times larger than those from the TiOPc/solution side. As shown before, the TiOPc film deposited directly on ITO glass at 20℃ was composed of a continuous thin layer. The solution can not penetrate into the film because of the hydrophobility of TiOPc. Therefore, the photogeneration of charge carriers takes place at the interface between TiOPc and solution, as shown in Fig.7(a). In the case of the oriented TiOPc film, on the other hand, the film was composed of the discrete rectangular crystallites. The solution seems to penetrate to the ITO surface through the cracks in the film. The photocarriers seem to be generated not only at the film surface but also at the lateral planes of

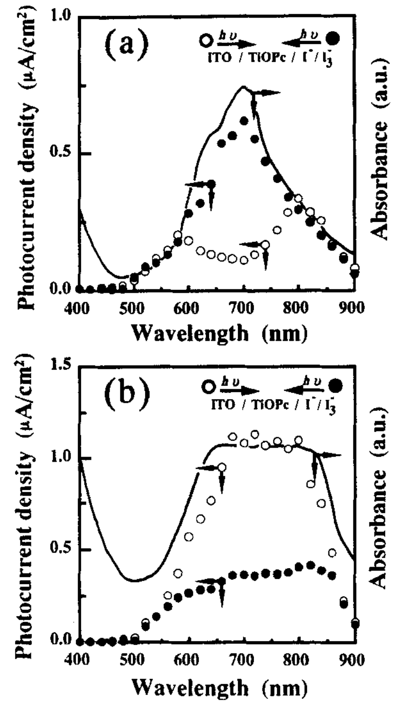

Fig.6 Absorption spectra (solid line) and photocurrent action spectra for TiOPc/ITO electrodes prepared by deposition on an ITO glass kept at 20℃(a) and a KBr (001) surface kept at 200℃ (b).

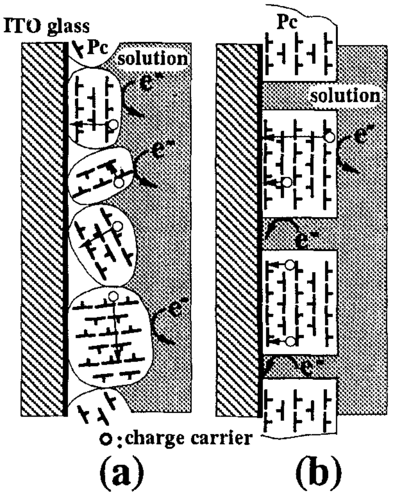

Fig.7 Schematic diagram for crystal morphology, molecular orientation and generation of photocarriers in polycrystalline (a) and epitaxial (b) Pc Films.

Tab. 1 Photoelectrochemical properties for Pc films deposited on an ITO glass and a KBr (001) surface.

Sample	Substrate	Substrate temp. °C	Isc μA/cm^2	Voc mV	FF	η'%
TiOPc	ITO	20	21.6	91.5	0.30	0.60×10^{-3}
		200	32.0	101.5	0.28	0.90×10^{-3}
	KBr	200	83.9	141.6	0.46	5.13×10^{-3}
VOPc	ITO	20	9.34	52.3	0.31	1.49×10^{-4}
		200	8.38	34.5	0.29	8.45×10^{-5}
	KBr	200	9.80	77.5	0.34	1.93×10^{-4}
VOPcF$_X$	ITO	20	0.12	101.5	0.25	3.01×10^{-6}
		200	0.26	108.8	0.29	8.36×10^{-6}
	KBr	200	13.7	226.5	0.29	9.66×10^{-4}

the crystallites, as shown in Fig.7(b). The photocarriers generated near the ITO electrode seem to contribute effectively to the increase of the photocurrents.

The photovoltaic parameters of the various Pc/ITO electrodes are summarized in Table1, where the abbreviations indicate ; I_{SC}: short circuit current, V_{OC}: open circuit voltage, FF: fill factor and η ': apparent energy conversion efficiency.

The photovoltaic parameters of the epitaxial films deposited on KBr substrate are improved in comparison to those of the polycrystalline films deposited on ITO glass at the same substrate temperature. Remarkable enhancement is obtained especially of I_{SC} and η ' by epitaxial orientation. Therefore, charge-carrier mobility is probably much larger through the molecular columns in the epitaxial film, which results in a higher photocurrent, I_{SC}.

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