

Effect of solvent vapor annealing on TiOPc thin films and the application on hybrid solar cells

Rongbin Ye, Koji Ohta, Mamoru Baba

Abstract— This article reports on effect of solvent vapor annealing on TiOPc thin films and the application on hybrid solar cells based on ZnO/TiOPc with DH-a6T as an electron blocking layer. The band gap shows a change for the TiOPc thin film solvent vapor annealed with various solvents, which may be due to the phase transition from amorphous to α -phase, β -form or α + β -form. The phase separation could be responsible for the variations of the optical properties. No significant change is observed in the π - π^* transition at various phase behaviors. Device performance of hybrid solar cells could be improved and open-circuit voltage (VOC), short-circuit current (ISC) and power conversion efficiency (η) were enhanced by solvent vapor annealing, which originated from amorphous TiOPc films transformed into crystalline α -phase, β -form or α + β -form. At α -TiOPc, the device achieved the highest performance with VOC, ISC and η of 0.57 V, 1.40 mA/cm², and 0.22 %, respectively, which originated from α -TiOPc with the widest red and near-IR absorption band.

Index Terms— Organic thin films, Solvent vapor annealing, Hybrid solar cells, Optical absorption.

I. INTRODUCTION

Metal phthalocyanines (MPcs) are organic dye materials, used in printing inks, as colorants for plastics and fibers, and their semiconducting properties are exploited for applications such as thin film transistors (TFTs), light emitting diodes, solar cells and gas sensors.[1-16] Titanyl phthalocyanine (TiOPc), one of non-planar phthalocyanines, has five polymorphs with different preparation and treatment procedures.[8-16] Amorphous or nearly amorphous TiOPc films were obtained for vacuum deposition at substrate temperature below 0 °C while β -form (phase I) or a mixture of α -form (phase II) and β -form polycrystalline films at substrate temperature above 20 °C and crystallinity increased with increasing of substrate temperature, and at substrate temperature of above 170 °C only α -form films were obtained. Moreover, amorphous TiOPc films could be transformed into crystalline α -TiOPc film through thermal annealing or vapor exposure. [13, 15] It has been known that α -TiOPc presents a particularly efficient charge photogeneration and a strong optical absorption in the red and near-IR spectral regions and a very promising organic semiconductor with high mobility due to showing the pi-stacking structure with concave pair and convex pair with significant molecular overlaps and very short intermolecular distance.[16] Compared with thermal annealing, solvent vapour annealing is demonstrated as an attractive method to anneal organic thin films at low temperatures. It is especially

suitable for organic electronics, where sensitive materials with strong intermolecular interactions are used. In this study, we report on effect of solvent vapor annealing on TiOPc thin films and the application on hybrid solar cells.

II. EXPERIMENTAL DETAILS

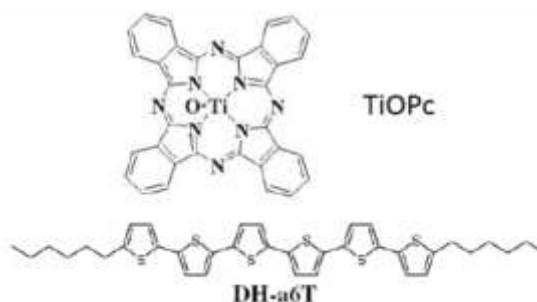
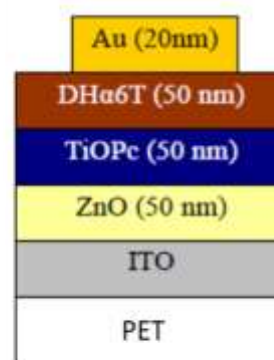


Figure 1 Schematic cross-sectional view of a hybrid solar cell, and molecular structures of TiOPc and DH-a6T.

A schematic cross-sectional view of a hybrid solar cell is shown in Fig. 1. All devices were prepared on indium-tin oxide (ITO) coated plastic substrates that used for the front electrode of hybrid solar cells. ZnO thin films of approximately 50 nm thickness were deposited on ITO glass substrates by r.f. sputtering technique (Anelva, SPF210H) with 50 W at 0.8 mTorr Argon gas pressure. TiOPc thin films of approximately 50 nm thickness (first p-type layer), DH-a6T thin films of approximately 50 nm (second p-type layer) and Au as a back electrode of 20 nm thickness were vacuum-deposited, respectively. Improving performance of hybrid devices, TiOPc thin films were solvent vapor annealed with THF at room temperature (RT) and 35 °C. The absorption spectra were recorded with UV/VIS spectrophotometer (V-550, JASCO) at RT. The current-voltage (I-V) characteristics of hybrid solar cells were performed using a source/meter Keithley 2400 and a Newport solar simulator equipped with a xenon short arc lamp with a power of 300 W under the ambient laboratory air conditions. The area of all devices is 0.2 x 0.4 cm².

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III. RESULTS AND DISCUSSION

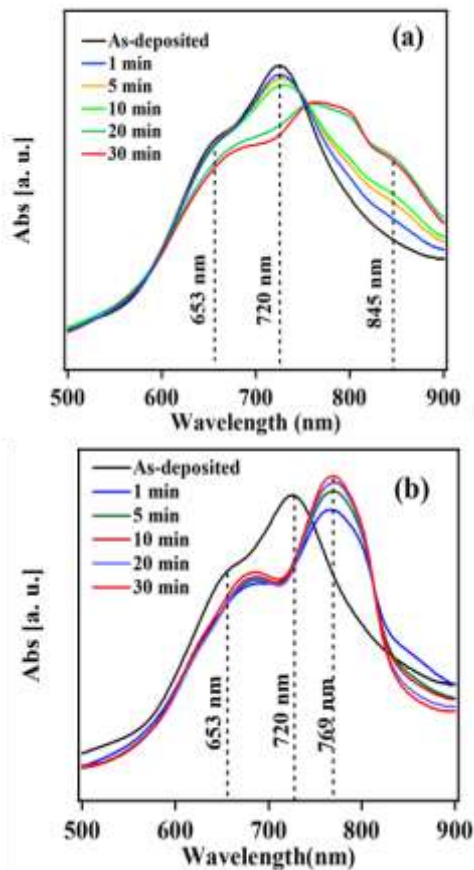


Figure 2 Absorption spectra of TiOPc thin films before and after solvent vapor annealed at various times with THF at (a) RT (20 °C) and (b) 35 °C, respectively.

Figure 2 show absorption spectra of TiOPc thin films prepared as-deposited and solvent vapor annealing for various times. The as-deposited film was amorphous and its absorption spectrum consists of the Q-band peaking at 720 nm with a well-defined vibronic replica at 653 nm. As shown in Fig. 2a, these sequence absorption spectra reveal the gradual formation of the crystalline α -phase, as evidenced by the development of a red-shifted absorption band, peaking 845 nm, and the corresponding reduction of the 720 nm amorphous phase peak when the film was solvent vapor annealed with THF at RT. The 845 nm peak, which is a spectroscopic signature of α -phase, has been attributed either to excitonic delocalization induced by the formation of J aggregates in the crystalline phase or to molecular distortion lifting the degeneracy of the fundamental electronic transition. On the other hand, these sequence absorption spectra in Fig. 2b reveal the gradual formation of the crystalline β -phase, as evidenced by the development of a red-shifted absorption band, peaking 769 nm, and the corresponding reduction of the 720 nm amorphous phase peak when the film was solvent vapor annealed with THF at 35 °C. From the above-mentioned results, phase behaviors of TiOPc thin film could also be transferred by controlling the solvent annealing temperature. Furthermore, a mixture of α -form and β -form films (as shown in Fig. 3d) could be obtained by ethanol at RT, but a longer solvent annealing time is needed than that of THF.

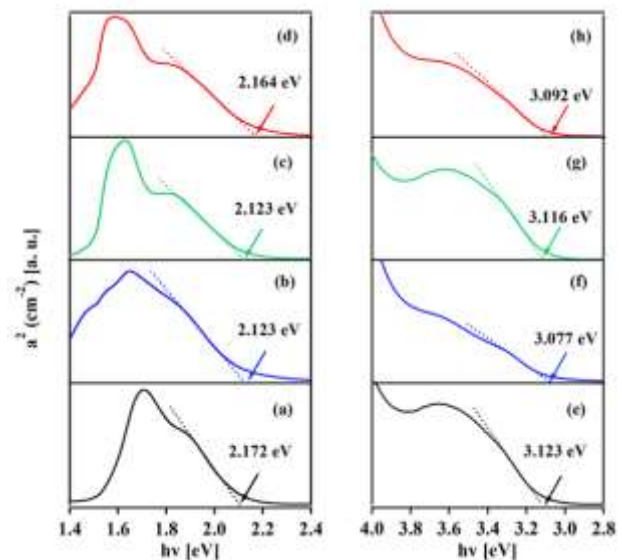


Figure 3 The photon energy dependence of α^2 for TiOPc thin films before (a, e) and after solvent vapor annealed with (b, f) THF (RT, 30 min), (c, g) THF (35 °C, 30 min) and (d, h) ethanol (RT, 4 h), respectively.

The absorption coefficient α is related to the photon energy $h\nu$ by $\alpha = \alpha_0(h\nu - E_g)^n$, where E_g is the optical bandgap. The plot of α^2 vs. $h\nu$ for TiOPc thin films are shown given in the Fig. 3. For allowed transition α^2 is plotted against E ($h\nu$) to yields a straight line for direct allowed transitions as shown in Fig. 3 from which the extrapolation of linear portion to $\alpha = 0$ near the absorption edge gives the band gap energy. The variations in E_g and $E_{\pi-\pi^*}$ are tabulated in **Table I**. The band gap shows a change for the film solvent vapor annealed with various solvents, which may be due to the phase transition from amorphous to α -phase, β -form or $\alpha+\beta$ -form. The phase separation could be responsible for the variations of the optical properties. No significant change is observed in the $\pi - \pi^*$ transition at various phase behaviors.

Table I E_g and $E_{\pi-\pi^*}$ of as-deposited and solvent vapor annealed TiOPc thin films

Solvent (temperature, time)	E_g (eV)	$E_{\pi-\pi^*}$ (eV)
As-deposited	3.123	2.172
THF (RT, 30 min)	3.077	2.123
THF (35 °C, 30 min)	3.116	2.123
ethanol (RT, 4 h)	3.092	2.164

Figure 4 shows J–V characteristics of ZnO/TiOPc/DH- α 6T hybrid solar cells while the TiOPc thin films were annealed at various solvents. The electrical parameters of the devices are summarized in **Table II**. By solvent vapor annealing, the device performance was improved, which originated from the phase transition from amorphous TiOPc to α -phase, β -form or $\alpha+\beta$ -form TiOPc. At α -TiOPc, the device achieved the highest performance with V_{OC} , J_{SC} and η of 0.57 V, 1.40 mA/cm², and 0.22 %, respectively, which originated from α -TiOPc with the widest red and near-IR absorption band and could be compared to that of a hybrid solar cell while TiOPc thin film was annealed at 150 °C for 3 h in the previous study. [17]

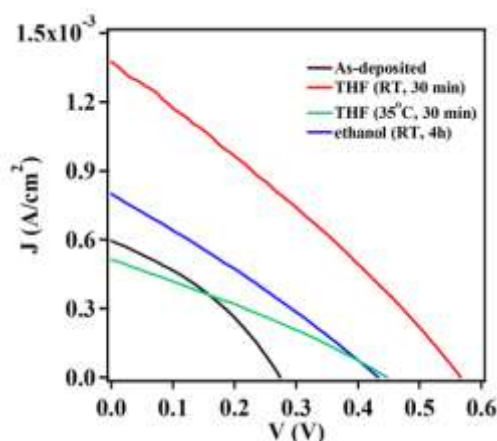


Figure 4 J–V characteristics of ZnO/TiOPc/DH-a6T hybrid solar cells at various annealed solvents of TiOPc thin films under AM1.5G simulated illumination (100 mW/cm^2).

Table II Electrical parameters (V_{oc} , I_{sc} , FF, and η) of hybrid solar cells

Solvent (temperature, time)	V_{oc} (V)	I_{sc} (mA/cm^2)	FF (%)	η (%)
As-deposited	0.27	0.61	34.6	0.06
THF (RT, 30 min)	0.57	1.40	27.8	0.22
THF (35 °C, 30 min)	0.46	0.52	27.8	0.06
ethanol (RT, 4 h)	0.44	0.81	27.0	0.09
Thermal annealing ¹⁷⁾ (150 °C, 3 h)	0.53	1.71	31.9	0.29

IV. CONCLUSION

In this study, we report on effect of solvent vapor annealing on TiOPc thin films and the application on hybrid solar cells based on ZnO/TiOPc with DH- α 6T as an electron blocking layer. The band gap shows a change for the TiOPc thin film solvent vapor annealed with various solvents, which may be due to the phase transition from amorphous to α -phase, β -form or $\alpha+\beta$ -form. The phase separation could be responsible for the variations of the optical properties. No significant change is observed in the $\pi-\pi^*$ transition at various phase behaviors. Device performance of hybrid solar cells could be improved and V_{oc} , I_{sc} and η were enhanced by solvent vapor annealing, which originated from amorphous TiOPc films transformed into crystalline α -phase, β -form or $\alpha+\beta$ -form. At α -TiOPc, the device achieved the highest performance with V_{oc} , I_{sc} and η of 0.57 V, 1.40 mA/cm^2 , and 0.22 %, respectively, which originated from α -TiOPc with the widest red and near-IR absorption band.

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