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Effect of crystalline microstructure on the photophysical performance of polymer/perylene composite films*

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To obtain high carrier mobility, better charge injection capability, and high photovoltaic device conversion efficiency, a powerful strategy is to improve the morphology of the polymer/dye composite films. Conjugated conducting polymer (CP) thin films doped with perylene derivative (PV) of various concentrations were prepared by spin-casting method, and their morphology and photovoltaic characteristics were examined. The change in morphology and molecular reorientation occurring in CP-PV composite films upon annealing at different temperatures was investigated using scanning electron microscopy, x-ray diffraction, Fourier transform infrared and UV-vis absorption. By changing the annealing temperature, PV microcrystallines of 8–10μm in size lying parallel to the substrate surface can be obtained. Annealing effect improved the photovoltaic performance of ITO/CP-PV/Al Schottky-type solar cells, which can be attributed to the formation of an electron conducting PV crystal network. Preliminary studies indicate that the morphological structure in CP-PV composite films has an important influence to their photovoltaic properties.

Keywords: morphology, organic photovoltaic device, conducting polymer composite, perylene, annealing

PACC: 7240, 7860, 8630J

1. Introduction

Organic solar cells based on organic molecules and conjugated polymers are currently attracting growing interest worldwide.[1−4] One essential reason for this is the possibility to realize flexible and low-cost photovoltaic cells. Especially, polymer -based solar cells could offer many advantages in fabrication, such as low-cost roll-to-roll production of large-area flexible solar cells. Because of these advantages, the development of polymer solar cells is supposed to have a major impact. However, in many conjugated polymers, the poor photo-induced charge separation and transport of photogenerated charges are considered responsible for the low efficiencies of energy conversion.[5] In order to maximize the photo-induced charge separation, the introduction of another material into polymer photovoltaic devices for improving electron transport is a powerful strategy. The presence of a second material also provides interfaces and pathways for charge transfer. The discovery of photo-induced electron transfer in composites of conducting polymers as donors and organic molecules as acceptors has provided a molecular approach to highly efficient photovoltaic conversion.[6−8]

In our previous work, higher photovoltaic conversion efficiency was realized by blending solubilized poly (2,5-dialhoxyphenylene vinylene) (ROPPV) or poly (3-alkylthiophene) (PAT) (acting as photoexcited electron donors) with perylene derivatives (acting as electron acceptor).[9,10] Perylene derivatives like the MePTCDI (N, N'-dimethyl-perylene-3, 4,

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9, 10-biscarboximide), PV (N,N'-diphenyl glyoxaline-3,4,9,10-perylene tetracarboxylic acid diacidamide) and PTCDA (perylene-tetracarboxylic dianhydride) have high electron affinity, large visible extinction coefficients, photostability, low cost of fabrication, and show n-type behaviour,[11−13] which is of interest not only for fundamental research but also for their possible application in new integrated gas sensors with multiple sensitivity, or photovoltaic and light-emitting cells.[14−16] It has been shown that in these polymer-perylene composite systems exciton dissociation and photo-excited electrons transfer on to the perylene occurs efficiently at interfaces between conjugated polymer and perylene.[17,18] Moreover, thermal annealing can often be used to restructure the morphology of composite films by inducing crystallization,[19] which is responsible for the improved efficiency of solar cells[20] and enhancement of their carrier mobility.[21]

Most of the studies so far published deal with the photovoltaic characteristics of such composite films. The morphological characteristics of composite films as well as their changes when annealed, however, have been studied only to a limited extent.[22] The investigation on the relation between the molecular orientation and composite films morphology when annealed is of considerable interest because of its importance in describing the physical properties of these thin composite films.

In this paper the morphologic structure of PAT-PV thin composite films prepared by spin-casting was characterized. The effect of annealing on morphological changes and photovoltaic performance of PAT-PV composite thin film cells was also described.

2. Experiments

The poly (3-dodecylthiophene) (PAT12) was synthesized according to the method already described.[23] PAT12 is highly soluble in toluene and chloroform. PV was synthesized according to the method already described in Ref.[9]. The chemical structures of PAT-12 and PV are shown in Fig.1. PAT12-PV composite at appropriate weight ratios is dissolved in chloroform and spin-coated on a glass plate.

The photovoltaic device was prepared by spin-coating the solution of PAT12-PV on a patterned ITO-coated glass substrate with a sheet resistance of $10\Omega/\square$ and followed by deposition of Al contact-layer by thermal evaporation through the shadow mask. The active area of the device was 1×1 mm^2. The typical thickness of PAT12-PV film was about 0.1–0.2μm.

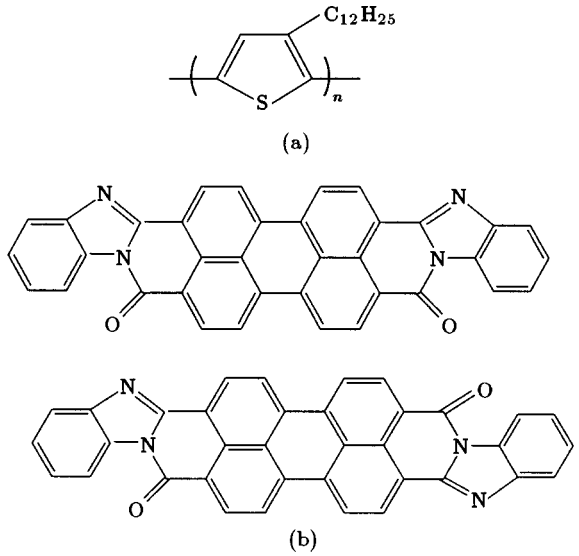


Fig.1. Molecular structures of poly (3-dodecylthiophene) (PAT12) (a) and perylene tetracarboxylic derivative (b).

The absorption was measured using a Hitachi 330 UV-vis spectrophotometer. Measurements of morphology of PAT-PV composites film before and after annealing at different temperatures were performed using a Hitachi 8000 transmission–electron microscope and Hitachi S-2100A scanning electron microscope (SEM). Fourier transform infrared spectroscopy (FTIR) measurement of the composite was carried out by JASCO corporation FT/IR-300E. X-ray diffraction (XRD) pattern was measured by RINT x-ray diffractometer. Photoelectrical measurements were carried out in a vacuum optical cryostat in vacuum of about 1.33×10^{-3} Pa. Current-voltage characteristics were measured by a Keithley 617 picoammeter. A high-intensity Xenon lamp (500 W) was used as UV-visible light source. The spectral response of the device was corrected for the response of the lamp-monochromator system by measuring the calibration spectrum with a UV-enhanced Si photodiode placed at the sample position.

3. Results and discussion

For photoconducting pigments, it is known that the heat-induced crystal packing can change the absorption spectrum and affect photogeneration efficiency and carrier mobilities. Therefore, thermal annealing was performed in an attempt to increase the crystallinity of the PAT-PV composite film. Figure 2 shows the UV/vis absorption spectra of the composite film containing 50% weight per cent of PV before and after annealing.

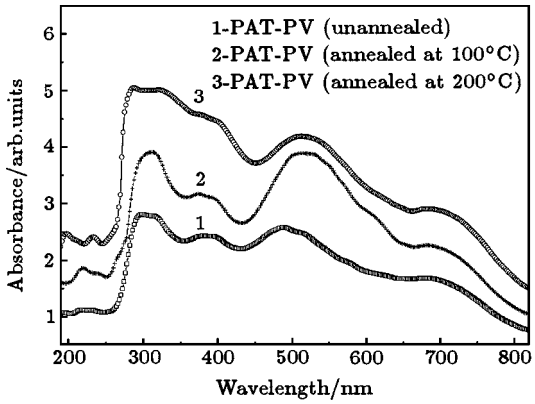


Fig.2. The absorption spectra of PAT12-PV composite film, unannealed (curve 1) and annealed at 100°C (curve 2) and 200°C (curve 3).

Spectra 1, 2 and 3 correspond to unannealed pristine film, and the annealed films at temperatures of 100°C and 200°C, respectively. The principal structure of the spectra is the same, indicating that the components of the films are unchanged after annealing. Four absorption peaks with the maxima at around 300, 383, 487 and 693 nm are observed in the pristine composite film. The spectrum in the annealing state at 100°C is redshifted in comparison with the pristine film, and the peak at 487 nm shifts to 518 nm by an amount of 31 nm in the visible range, indicating the physical changes in morphology and a higher degree of PV overlapping. Moreover, the overall absorption intensity is increased remarkably after annealing. Heating the film at 200°C for 1 h has some influence on the principal structure of spectra. The two peaks of 300 and 383 nm combine into a broader one with its shoulder at 375 nm. These phenomena can be explained as follows.

The PAT chain is more flexible than many other conjugated polymers. When annealed, PAT chains rearrange to reach an ordered state that exhibits absorption in the long-wavelength range.[24] The PAT chains in the composite film could also have a chance to relax and display a more ordered state through the thermal process. So the PAT/PV composites film in a morphology characterized by the most redshifted and broadened absorption band would show a greater photosensitivity than the pristine film.

In parallel with the change of optical behaviour, the morphology and the structure may also change in PAT-PV composite films upon annealing at different temperatures. Figure 3 illustrates the SEM images of samples with 50% PV content annealed at different temperatures. Figure 3(a) is the SEM image of a pristine film, while 3 (b) and 3 (c) are those of the sample of PAT-PV annealed at temperatures 100 and 200°C, respectively.

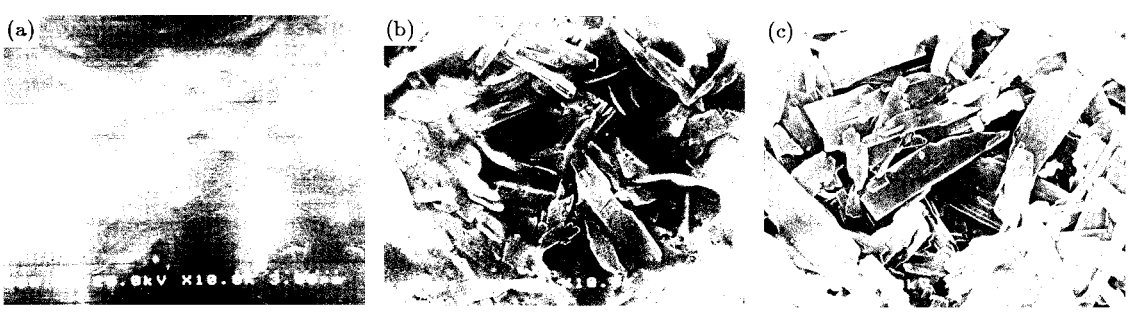


Fig.3. SEM images of PAT-PV composite films. (a) SEM image of unannealed film; (b) annealed at 100°C; (c) annealed at 200°C.

A general problem connected with the annealing process is the high mobility and crystallinity of the PV molecules in the composite samples occurring at an elevated temperature. For the pristine sample (Fig.3(a)), the crystallites are quite small on the order of 1–2μm in size and have a shape of rectangular leaf. Comparing 3(a) and 3(b), we can find that the surface roughness of composite films increases with increasing annealing temperature. During volatilization of PAT-PV solution and formation of composite films, the PV molecule tends to crystallize and rearrange its morphology. Therefore, the surface roughness of the composite film is higher than that of the pristine film. When the composite film is heated at 100°C for 1 h, larger crystals will grow about 6–8μm. This suggests that both PV and PAT molecular chains have rearranged to reach an ordered state during the annealing process. At 200°C, the crystallites increase in number and in size to about 10μm, as can be confirmed by the SEM observation (Figs. 3(b) and 3(c)). These

results can be attributed to the rearrangement process of PV crystallite proceeding adequately at higher annealing temperatures. SEM images of thermally annealed PAT/PV composites on Cu substrates have shown elongated crystallites (up to ten microns long), having their long axes in a direction roughly parallel to the substrate surface.

Figure 4 shows the FTIR spectra of the PAT-PV composite films. Spectra a, b and c correspond to the unannealed composite film, the films annealed at 100 and 200°C, respectively. The observed infrared absorption wavenumbers for the PAT-PV composite films are given in Table 1.

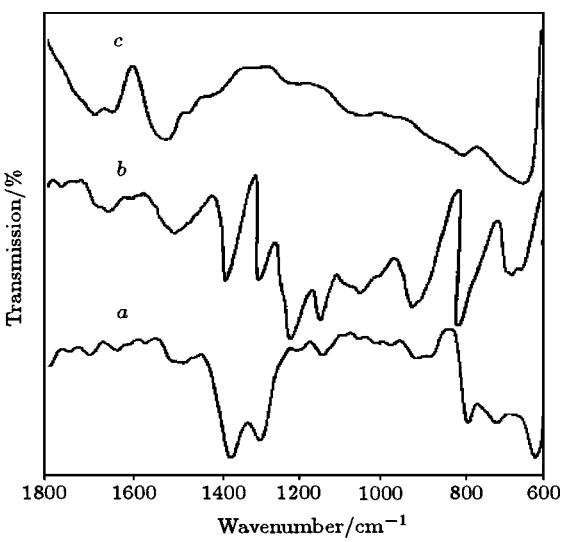


Fig.4. FTIR spectra of PAT-PV composite films. Spectra *a*, *b* and *c* correspond to those unannealed, annealed at 100 and 200°C, respectively.

Due to annealing, the remarkable differences in relative intensities and peak shifts between the unannealed and annealed films at different temperatures can be observed. The most relevant molecular vibrations of the PV group are the strong carbonyl stretching vibration at 1660 cm^{-1} and 1696 cm^{-1} which correspond to antisymmetric and symmetric C=O stretching modes, respectively. This suggests that PV molecules have two kinds of structure as shown in Fig.1. Moreover, C=C stretching mode (in plane) of PV is observed at 1562 cm^{-1}. The out-of-plane vibrations of PV ring provide a dynamic dipole perpendicular to that of the carbonyl stretching vibration. The wavenumber of 1285 cm^{-1} can be confidently assigned to the C-H bend vibration and that of 1358 cm^{-1} is also an out-of-plane mode. For transmission, the infrared active mode, the dynamic dipole moment of which is parallel to the substrate surface, is more intense than those modes with dynamic dipole moments perpendicular to the surface.[25]

Table 1. Observed infrared wavenumbers for PAT-PV composite films before and after annealing.

cm^{-1}	assignment
624	Ring deformations
732	C-H PV wagging
794	Alkyl wagging
850	C-H PV wagging
1120	C-H bending (PV)
1285	C-H bending (PAT)
1358	C-N stretching
1508	PV stretching
1562	C=C ring stretching
1604	C=O stretching
1660	C=O stretching
1694	C=O stretching

Using the preceding information, it is now possible to elucidate the molecular orientation of PV in the composite films. The PV molecule is planar as shown in Fig.1, and thus changes in orientation can be easily determined from a comparison of modes with dynamic dipoles located within the plane of the molecules (i.e. within the plane of the aromatic moiety) with fundamental vibrational modes. Since the intensity is proportional to the dot product of the electric field and the dynamic dipole, in average, the PV plane might be parallel to the substrate surface when it is annealed at a high temperature such as 200°C. It implies that the composite samples have a more ordered arrangement in morphology, which is uniform to the observation in SEM images. Through morphology control of the phase separation into interpenetrating networks, one can achieve a high interfacial area in a bulk material. The detailed studies about the molecular orientations are now in progress and will be reported elsewhere.

XRD measurements have been performed to investigate the crystallinity and crystal structure of the annealed films. The XRD patterns shown in Fig.5 consist of data collected from PAT-PV composite films annealed at different temperatures, and that of the unannealed pristine composite films with the same composition is also included for comparison.

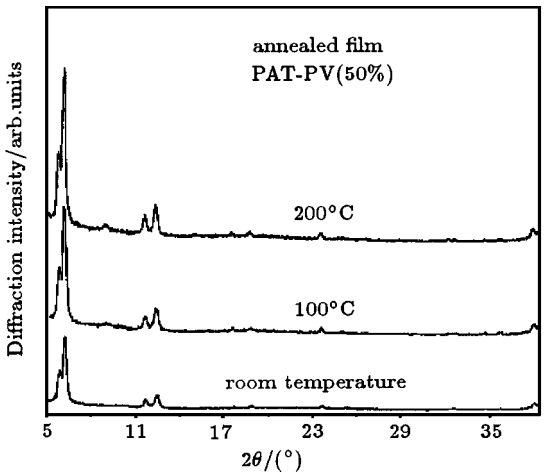


Fig.5. XRD patterns of PAT-PV composite films annealed at different temperatures.

As is evident in Fig.5, the composite films have several diffraction peaks at 2θ=5.7°, 6.1°, 11.6°, 12.3°, 18.5°, 23.2° and 37.7°, indicating a polycrystalline structure. The diffraction patterns of PAT-PV composite films annealed at different temperatures for 1 h are compared with one another. It can be seen that the relative intensities of PV diffraction peaks increase for the composite films annealed at 100°C and 200°C. Moreover, a new diffraction peak appears at 2θ=8.9° for the sample annealed at 100°C, though its intensity is comparatively weak. When the annealing temperature is raised to 200°C, the intensity of the diffraction peak at 2θ=8.9° increases. The intensity of diffraction peaks increases with increasing PV content in the composite films without appearance of new peaks, which has been confirmed by ROPPV-PV composites in our previous study.[26]

The results suggest that a higher annealing temperature causes the change in the diffraction patterns, namely the intensity of all PV diffraction peaks increases. The appearance of the new peak as well as the increase in peak intensity with annealing temperature indicates a higher degree of crystallinity formed in the composites. The XRD patterns show improved crystallinity and changes in the d-spacings upon annealing and the UV-vis absorption spectrum shows a redshift. This is an indication that the molecular packing (i.e. the degree of p-orbit overlap) is improved by annealing.

To elucidate the annealing effect on the photoexcitation process in the PAT-PV composite, photocurrent spectra of PAT-PV thin films have been measured. The result is shown in Fig.6, which reveals the photocurrent spectra of the composite films. In the unannealed film, there are two fairly strong responses at 350–450 nm and 650 nm under illumination of visible light. Compared with the spectrum of pure PAT film,[27] the result indicates that PV doping enhances the light absorption of the PAT film, which contributes to the enhancement in photo-carrier generation. This result is interpreted as follows.

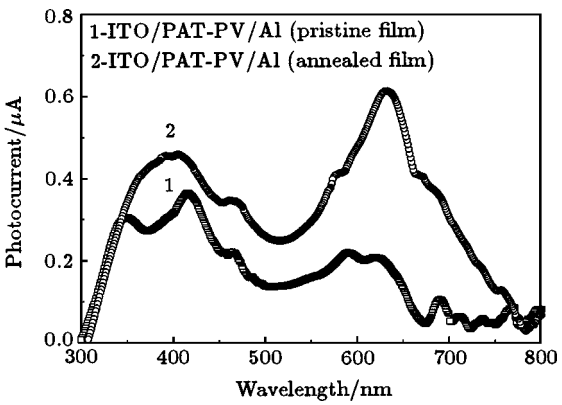


Fig.6. Photoconductivity spectra of unannealed and annealed PAT-PV composite films.

Photogenerated excitons in the PAT-PV composite film can diffuse to the interfaces between PAT and PV, where they dissociate by electron transfer from PAT to PV. That is, the dissociation of excitons occurs predominantly at the interface between PAT and PV, which plays an important role for the photovoltaic characteristics of composite films. It should also be mentioned that the morphology and texture of the composite films play a crucial role in efficient charge generation and charge carrier transport. The photovoltaic performance of the composite film can be improved markedly after annealing at 200°C for 1 h. This can also be attributed to the change in morphology of PV-doped PAT thin films as described above. As expected by our estimate, the marked increase of photocurrent of the annealed composite film appears in the spectral range from 350 nm to 750 nm with the highest peak at 630 nm. From the photocurrent spectra of the devices we can infer that interpenetrating networks will form in the composites film, leading to a large interfacial area on a scale comparable to the exciton diffusion length. Thus, charge separation and charge transport are efficient in the polymer composite system. The corresponding current-voltage characteristics of the unannealed and annealed films under illumination are shown in Fig.7. All devices are irradiated with the light with 635 nm in wavelength and 69μW/cm^2 in intensity from the ITO electrode. The

experimental results show that the annealed film exhibits a higher open-circuit voltage, short-circuit current and fill factor than the unannealed film under irradiation of a monochromatic light of 635 nm.

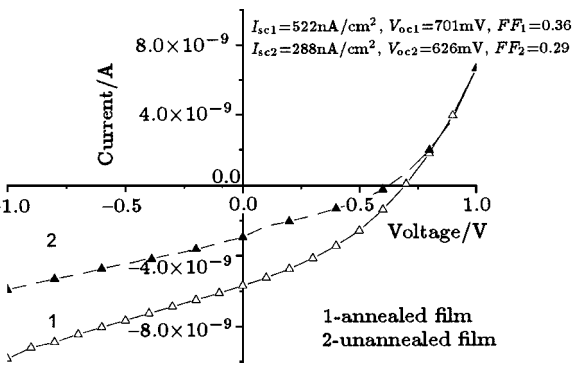


Fig.7. The current-voltage characteristics of unannealed and annealed devices. All devices are irradiated with the light of a wavelength 635 nm and an intensity of 69μW/cm^2 from the ITO electrode.

In a dispersed heterojunction device, both the photocurrent generation and charge transport are functions of morphology. Photocurrent generation requires uniform blending on the scale of the exciton diffusion length, while charge transport requires continuous paths from interfaces to contacts. Upon annealing, both PAT chains and PV molecules have chances to relax and rearrange themselves in a more ordered state. Moreover, heating seem to be able to induce better and larger interfaces between PAT and PV; and PV crystallites can also play an important role in efficient electron transports during the photoconduction process. This is probably related to the large increase in charge carrier density, and the corresponding decrease in bulk resistance in the molecular semiconductors upon annealing. Therefore, the improved photophysical and electronic properties of the composite films are attributed to the increased exciton migration lengths, the charge carrier mobilities, and other factors. And the increased exciton migration lengths in thermal-annealed PAT/PV films are attributed to the crystallinity of the PV. Taken all together, these results indicate that the annealed composite film has the major effect of enhancing the morphological microstructures of both components that form the interpenetrating networks. This may bring about a higher effective diffusion length for excitons in PAT/PV composite films.

4. Conclusion

PV doping can improve the photovoltaic performance of PAT thin film due to the annealing effect. We have also analysed in detail the changes in the composite morphology, crystallinity and photoresponse after annealing by the observation with SEM, FTIR, UV-vis absorption and x-ray diffraction.

The PV microcrystalites with 8–10μm in size can be obtained by thermal annealing treatment. Characteristic vibrational frequencies in the infrared spectra were observed and assigned for analytical application. In particular, by the annealing of the PAT-PV composites, the absorption and the photocurrent were enhanced in intensity and in their spectral response. The PV doping and annealing effects can be interpreted in terms of the growth of PV crystals in the composite and effective charge separation at the PAT-PV interface.

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