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Control of C₆₀ Thin Film Surface and Its Photovoltaic Properties

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Introduction

Since the discovery of conducting polymers (CPs) with extended π -conjugation in their main chains, CPs have attracted considerable attention not only from a fundamental view point but also from a practical viewpoint¹⁾ as materials suitable for electronic and optoelectronic devices such as photodiodes and solar cells²⁻⁴⁾. Among various CPs, regioregular poly(3-hexylthiophene) (PAT6) is attractive for the fabrication of photovoltaic cells due to characteristics such as high hole mobility, low band gap and good processability.

Recently, we reported that the surface morphologies of C₆₀ films differ markedly depending on the organic solvents used in the spin-cast treatment and the photovoltaic properties of the photovoltaic cell with the structure of indium-tin-oxide (ITO)/C₆₀/MEH-PPV/Au are affected by the morphology of the C₆₀/MEH-PPV interface⁵⁾. We also found that nanorod-shaped surfaces of C₆₀ films, which have more complicated rough surface, were easily formed⁶⁾. Using trans-1,2-dichloroethylene or a mixture of chloroform and toluene as a solvent for spin-cast treatment onto a C₆₀ film, we succeeded in preparing nanorod-shaped surfaces of C₆₀ films⁷⁾. However, detailed studies on correlation between the C₆₀/CPs interface and photovoltaic properties remain to be carried out.

In this study, we report on the photovoltaic properties of the photovoltaic cell with a structure of ITO/C₆₀/PAT6/Au, the C₆₀/PAT6 hetero-junction of which was fabricated by spin-coating the mixture of chloroform and toluene solution of PAT6 onto the C₆₀ thin film, and discuss the photovoltaic properties by taking the optical properties of the unique C₆₀/PAT6 hetero-junction and the direct observation of the C₆₀ film surface after the mixed solvent spin-cast treatment into consideration.

Experimental

Regioregular PAT6 (Aldrich Ltd.) and C₆₀ (MTR Ltd.) in this study were used as purchased. The photovoltaic cell with the structure of ITO/C₆₀/PAT6/Au was fabricated in the following way.

The C₆₀ layer with a thickness of about 170 nm was deposited by thermal evaporation onto the ITO electrode under a pressure of 10⁻⁴ Pa. The solution of PAT6 was spin-coated onto the C₆₀ layer. Mixtures of chloroform and toluene were used as solvents of the solutions of PAT6 and the mixture ratios of chloroform and toluene are 1:0, 4:1, 1:1 and 1:4. The typical film thickness of active layer (C₆₀/PAT6) was around 300-400 nm as determined from the cross-sectional SEM image. The Au electrode was deposited on the PAT6 layer by thermal vacuum evaporation at pressures below 10⁻⁴ Pa and patterned with a shadow mask to define active areas of 1 x 1 mm². In the photovoltaic cell, ITO and Au electrodes play roles in electron and hole collections, respectively.

Current-voltage characteristics were measured with Keithley 237 a high-voltage source measurement unit, under dark and illuminated conditions at a wavelength of 500 nm with an intensity of 0.3 mW/cm². From the current-voltage characteristics under the illuminated conditions, the fill factor (*FF*) and the power conversion efficiency (η) were estimated by the following definition. $FF = I_{max}V_{max}/I_{sc}V_{oc}$ and $\eta = I_{sc}V_{oc}FF/P_{in}$, where I_{sc} is the short-circuit current density, V_{oc} is the open-circuit voltage, I_{max} and V_{max} are the current and voltage for the maximum output power, and P_{in} is the incident light power. Photocurrent spectra were measured using a Xe lamp light passing through a monochromator as a light source with a Keithley 617 programmable electrometer. The external quantum efficiency (EQE) was estimated according to $EQE (\%) = 1240 \times I (A/cm^2) \times 100 / (\lambda (nm) \times P_{in} (W/cm^2))$, where I is the photocurrent density and λ is the excitation wavelength. The current-voltage characteristics and photocurrent spectra were measured in vacuum at room temperature. Absorption spectra of the thin films were measured at room temperature using a Hewlett Packard HP8452A spectrophotometer. Electron micrographs of the thin films were taken with a JEOL JSM-6320F scanning electron microscope (SEM).

Results and Discussion

Figure 1 shows the absorption spectra of C₆₀, PAT6 and C₆₀/PAT6 films on quartz substrates. The C₆₀/PAT6 film was prepared by spin-coating the mixture of chloroform and toluene solution of PAT6 onto the C₆₀ film. The absorption peak at around 350 nm corresponds to one of the excitation energies for C₆₀, and the absorption peak decreases somewhat after spin-coating the mixture of chloroform and toluene as a function of increasing the ratio of toluene, that is, the film thickness of C₆₀ decreases more when the ratio of toluene increases due to the higher solubility of toluene. This decrease in absorbance is caused by the mixture of chloroform and toluene encroaching upon the surface of the C₆₀ film, because

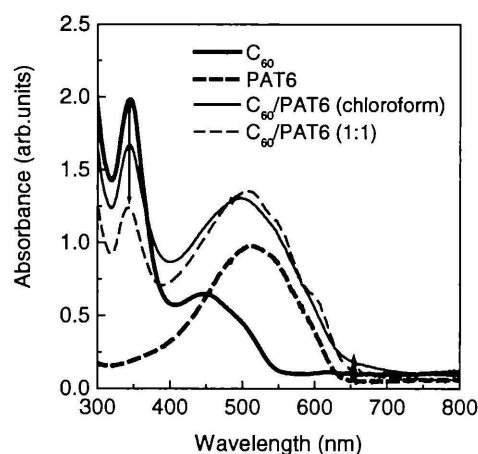


Fig. 1 Absorption spectra of C₆₀, PAT6 and C₆₀/PAT6 films on quartz substrates.

the mixture of chloroform and toluene dissolves a small amount of C₆₀.

The EQE spectra of the photovoltaic cells with the structures of ITO/C₆₀/PAT6/Au almost correspond with the overlapping of the absorption spectra of PAT6 and C₆₀ film, as shown in Fig. 2. In these photovoltaic cells, both absorption of PAT6 and C₆₀ layers contribute to photo-induced carrier generation, which suggests that part of the incident light passed through the C₆₀ layer and reaches the PAT6 layer; however obvious differences in EQE exist, depending on the used solvents. Using the mixture solvent of chloroform and toluene in a ratio of 4:1 and 1:1, the EQE around 500 nm reached over 40%, which was almost 25% larger than that of the photovoltaic cells fabricated using chloroform and toluene in a ratio of 1:0 and 1:4. It is suggested that the fabrication technique by spin-coating the solution of CP onto the C₆₀ film and its solvent dependence should be significant for the achievement of the high efficiency in photovoltaic cells with CP and C₆₀ systems.

In the photovoltaic cells with the structures of ITO/C₆₀/PAT6/Au prepared by the mixture of chloroform and toluene in a ratio of 1:1, *I*_{sc} of 57.0 μA/cm², *V*_{oc} of 0.27 V, *FF* of 0.50 and the monochromatic power conversion efficiency of 2.32% were obtained from the results of the current-voltage characteristics under the illuminated conditions at the wavelength of 500 nm with the intensity of 0.3 mW/cm² as shown in Fig. 3.

In order to investigate the interface of the C₆₀/PAT6 heterojunction, these four mixed solvents without PAT6 were spin-cast onto the C₆₀ films prepared on glass substrates, and the surface observation by SEM was carried out. As shown in Fig. 4, various surface morphologies of C₆₀ films were found to depend on the solvents used in the spin-cast treatment. The 1:4 solvent treatment produced the roughest surface of the C₆₀ film followed by 1:1, 4:1 and 1:0.

By spin-coating the solution of PAT6 onto the C₆₀ thin film, the C₆₀/PAT6 interfaces with such various morphologies should be also formed, depending on the used solvents, which implies that the formation of the C₆₀/PAT6 interfaces with various contact areas could be controlled by solvents.

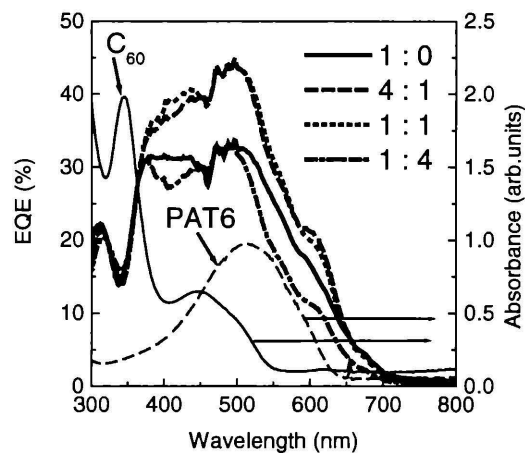


Fig. 2 EQE spectra of the photovoltaic cells with the structures of ITO/C₆₀/PAT6/Au. Mixtures of chloroform and toluene were used as solvents of the solutions of PAT6 and the mixture ratios of chloroform and toluene are 1:0, 4:1, 1:1 and 1:4.

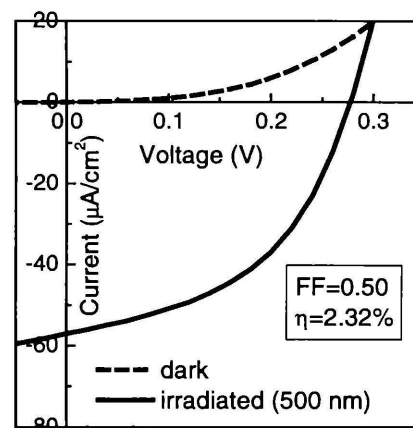


Fig. 3 Current-voltage characteristics of the photovoltaic cell with the structure of ITO/C₆₀/PAT6/Au under illuminated conditions at the wavelength of 500 nm with the intensity of 0.3 mW/cm².

Considering the poor solubility of C_{60} in these mixed solvents, the surface of the C_{60} layer is modified by the solution of PAT6, resulting in the C_{60} /PAT6 bilayers with various contact areas, that is, with various C_{60} /PAT6 interpenetrating interfaces. In such a C_{60} /PAT6 interpenetrating system, not only the photo-induced carrier generation but also the carrier transport are considered to be affected by the morphology of the C_{60} /PAT6 interface, for the electrons produced on C_{60} by the photo-induced charge transfer at the C_{60} /PAT6 interface are transported through the C_{60} layer to the ITO electrode and the holes produced on PAT6 by the photo-induced charge transfer are transported through the PAT6 layer to the Au electrode, respectively. It is, therefore, considered that the photo-induced charge generation occurs near the heterojunction between C_{60} and PAT6 layers.

Conclusion

We investigated the photovoltaic properties of a photovoltaic cell with a structure of ITO/ C_{60} /PAT6/Au, the C_{60} /PAT6 heterojunction of which was fabricated by spin-coating the mixed organic solution of PAT6 onto the C_{60} thin film. The photovoltaic properties of the photovoltaic cell were improved by the C_{60} /PAT6 interface control. The results demonstrate that this interface control is a promising technique and is expected to accelerate the realization of low cost and high efficiency solar cell.

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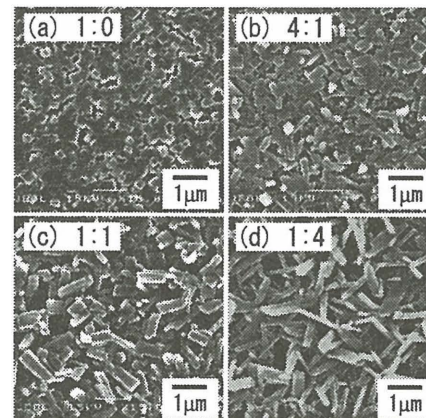


Fig. 4 SEM images for four kinds of C_{60} films on glass substrates after spin-cast treatment with mixed solvents of chloroform and toluene in a ratio of (a) 1:0, (b) 4:1, (c) 1:1 and (d) 1:4.