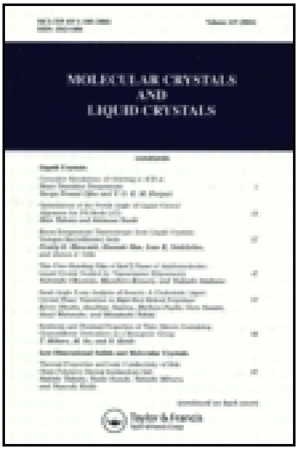

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Efficient Organic p-i-n Solar Cells Having Very Thick Codeposited i-Layer Consisting of Highly Purified Organic Semiconductors

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Efficient Organic *p-i-n* Solar Cells Having Very Thick Codeposited i-Layer Consisting of Highly Purified Organic Semiconductors

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p-i-n organic solar cells having very thick codeposited i-interlayer reaching 1.2 μm were successfully fabricated by using fullerene purified by means of the single-crystal formed sublimation. Short-circuit photocurrent density of 19 mAcm^{-2} and photo-electric conversion efficiency of 5.3% were observed.

Keywords: fullerene; organic *p-i-n* solar cells; photo-electric conversion efficiency of 5.3%; single-crystal formed sublimation; very thick codeposited *i*-interlayer

INTRODUCTION

In 1991, we proposed *p-i-n* organic solar cells in which the *i*-interlayer is a codeposited film composed of *p*- and *n*-type organic semiconductors [1,2]. In organic *p-i-n* cells, *i*-interlayer acts as an efficient photocarrier generation layer. Therefore, if this codeposited *i*-interlayer could be thick enough to be able to absorb entire irradiated solar light, organic *p-i-n* cells would show the magnitude of photocurrent density of about 20 mAcm^{-2} comparable to inorganic solar cells. Unfortunately, *i*-interlayer has been inevitably very thin, i.e., several tens nm, in the reported organic *p-i-n* cells [1–5] since cell performances were severely lowered by using thicker *i*-interlayer.

On the other hand, the electrical properties of organic semiconductors are strongly influenced by various unidentified impurities. On the

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analogy of the case of inorganic silicon which is usually purified to eleven-nine, we convinced that the purity of organic semiconductors should be reached to ppm or ppb level in order to draw out their essential nature. Thus, we decided to increase the precision of purification for organic semiconductors used in *p-i-n* cell. Conventionally, organic semiconductors have been purified train sublimation method under vacuum [6] and purified samples were obtained as the shape of particles. On the contrary, when the sublimation is performed under 1 atm gas, purified samples were obtained as the shape of single crystals with the help of gas convection [7]. We expected that the organic semiconductors obtained as the shape of large single crystals would possess extremely higher purity compared to those obtained by conventional train sublimation. Therefore, we decided to apply the single-crystal formed purification method to the organic semiconductors in order to draw out the genuine performances of organic *p-i-n* cells.

Here, we report the successful fabrication of organic *p-i-n* cells with 1 μm-thick *i*-interlayer incorporating C_{60} purified by the single-crystal formed sublimation. Short-circuit photocurrent density and photoelectric conversion efficiency reached 19 $mAcm^{-2}$ and 5.3%, respectively.

EXPERIMENTAL

C_{60} sample (Aldrich, 99.5%) was purified three times by the single-crystal formed sublimation based on the method of Kloc [7]. Crystal growth was performed in the quartz tube under 1 at in N_2 flow. Temperature gradient was formed by using three-zone furnace (Thermo Riko, GFB-460-3Z). C_{60} sample was set at 760°C and single crystals were grown at around 500°C. Taking the very large crystal size reaching 2 mm × 2 mm and strict agreement with reported crystal structure of C_{60} into consideration, we concluded that C_{70} was not included in the obtained crystals. H_2Pc samples (Dainippon Ink and chemicals, Inc.) were thoroughly purified 4 times by conventional train sublimation [6] in the quartz tube. Naphthalene tetracarboxylic anhydride (NTCDA (Aldrich), Fig. 1) sample was purified 2 times by the single-crystal formed sublimation. In this case, plate-like crystals having size of about 1 cm × 1 cm were obtained.

p-i-n cell structure is shown in Figure 1. *p*-type layer of H_2Pc (20 nm), codeposited *i*-interlayer composed of C_{60} and H_2Pc, and *n*-type layer of NTCDA were successively deposited by vacuum evaporation technique at 1×10^{-3} Pa onto indium tin oxide (ITO) glass substrate. A 100 nm-thick Ag was then deposited as a metal counter electrode. Thick NTCDA layer (600 nm) also acts as a transparent protection layer which prevents electrical shorting of cells caused by metal

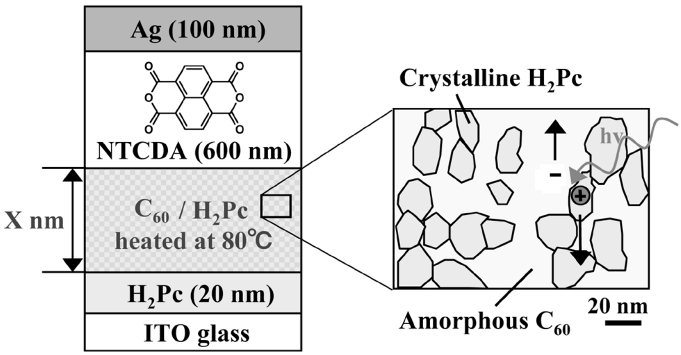

FIGURE 1 Structure of organic *p-i-n* solar cell. C_{60}:H_2Pc *i*-interlayer (X nm) is sandwiched between *p*-type H_2Pc (20 nm) and *n*-type NTCDA (600 nm). C_{60}:H_2Pc layer codeposited to the substrate heated at +80°C has the crystalline H_2Pc-amorphous C_{60} nanocomposite structure.

migration into organic film during metal deposition [8,9]. Codeposition was performed coevaporation from two separately controlled sources on the substrate heated at +80°C using a substrate heater (ULVAC Kiko, Inc.).

The current-voltage (J-V) characteristics were measured under the simulated solar light (Yamashita Denso, Co. Ltd., YSS-50A). The intensity of the solar light was monitored using a silicon photodiode.

RESULTS AND DISCUSSION

Photovoltaic properties of organic *p-i-n* cells incorporating C_{60} purified by single-crystal formed sublimation were measured for various *i*-interlayer thicknesses (X). Figure 2(a) shows the dependence of fill factor (FF) on X (closed dots). Surprisingly, FF hardly decreased even for very thick *i*-layer reaching 1200 nm. Accordingly, short-circuit photocurrent density (J_{sc}) increased with X and reached maximum value of 19.1 mAcm^{-2} at X = 960 nm (Fig. 2(b), closed dots). On the contrary, in the case of *p-i-n* cell incorporating the C_{60} purified by conventional train sublimation under vacuum, FF monotonically decreased with codeposited layer thickness (Fig. 2(a), open dots) [10].

Figure 3(a) shows the current-voltage (J-V) characteristics for *p-i-n* cell having very thick *i*-interlayer (X = 960 nm). J_{sc} of 18.3 mAcm^{-2}, open-circuit photovoltage (V_{oc}) of 0.402 V, FF of 0.532, and photoelectric conversion efficiency 5.3% was observed for the simulated solar light transmitted through ITO substrate (74.2 mWcm^{-2}). Figure 3(b) shows the spectral dependence of internal quantum efficiency of J_{sc}

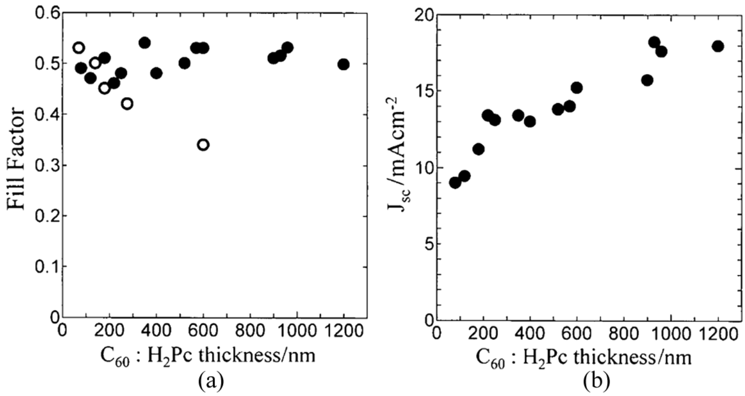

FIGURE 2 (a) Dependence of fill factor (FF) on the *i*-interlayer thickness (X) for organic *p-i-n* cells incorporating C_{60} purified three times by the single-crystal formed sublimation (closed dots) for those incorporating C_{60} purified by conventional train sublimation under vacuum (open dots). (b) Dependence of J_{sc} on X for organic *p-i-n* cells incorporating C_{60} purified three times by the single-crystal formed sublimation.

for the same cell. Internal quantum efficiency reached above 90% in the region from 400 to 700 nm. Figure 3(c) shows the spectral dependence of absorption ratio by taking the light reflection of Ag electrode into account, 95% of visible light from 300 to 800 nm can be absorbed. Based on the spectral distribution of light intensity of simulated solar light, the internal quantum efficiency (Fig. 3(b)), and the light absorption

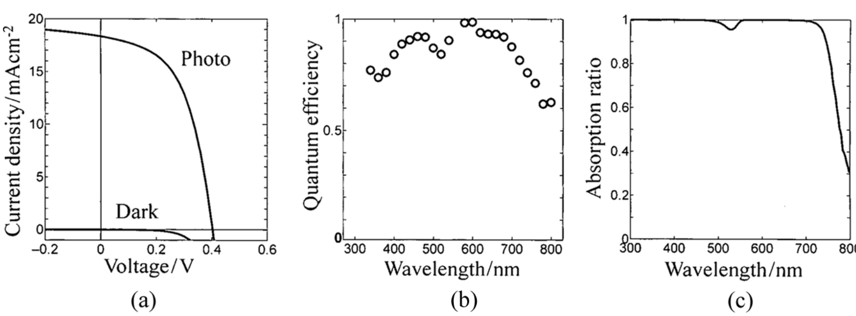

FIGURE 3 (a) Current-voltage (J-V) characteristics for *p-i-n* cell having very thick *i*-interlayer (X = 960 nm). Cell parameters; J_{sc}: 18.3 mAcm^{-2}, V_{oc}: 0.402 V, FF: 0.532, Efficiency: 5.3% (Light Intensity: 74.2 mWcm^{-2}). (b) Spectral dependence of internal quantum efficiency of J_{sc} for the same cell. (c) Spectral dependence of light absorption ratio for the same cell.

ratio (Fig. 3(c)), obtainable value of J_{sc} could be calculated to $20\,mAcm^{-2}$. This coincides well with observed maximum J_{sc} value of $19.1\,mAcm^{-2}$. Above results clearly tells us that since entire visible region of solar light can be utilized without decreasing FF by incorporating about 1 μm-thick C_{60}:H_2Pc *i*-interlayer into *p-i-n* cell, J_{sc} reached very large value close to $20\,mAcm^{-2}$ which is comparable to inorganic solar cells.

In the present *p-i-n* cell, the largest value of J_{sc} was observed for the *i*-interlayer codeposited on the substrate heated to $+80°C$. Under this condition, the codeposited film has the crystalline H_2Pc-amorphous C_{60} nanocomposite structure (see Fig. 1) [10]. This nanostructure facilitates photocurrent generation by forming the spatially separated route for electrons and holes.

However, the present results clearly shows that only the nanostructure-control of codeposited layer is not enough to realize 1 μm-thick *i*-interlayer. The utilization of extremely purified organic semiconductors is also indispensable to increase the *i*-interlayer thickness. In order to determine the purity of C_{60} samples in ppm level, we performed the secondary ion mass spectroscopy (SIMS) measurements, which has been used for the analysis of dopants in Si wafer. Only oxygen and hydrogen atoms were detected as impurities. Moreover, oxygen concentration was confirmed to decrease with the repetition number of sublimation under 1 atm N_2. For the C_{60} samples purified three times of single-crystal formed sublimation, oxygen concentration was confirmed to less than 0.1 ppm, i.e., the purity was confirmed more than seven-nine level.

Based on these results, we suspect that oxidized C_{60} ($C_{60}O_x$) acting as electron trap [11] is the main impurity of C_{60} samples purified by the conventional sublimation under vacuum. By removing such impurity acting as traps by single-crystal formed sublimation, carrier transport in the C_{60}:H_2Pc codeposited layer greatly enhanced. As a result, fill factor hardly decreased even for the very thick C_{60}:H_2Pc codeposited layer reaching 1 μm. Investigation of detailed transport mechanism in thick C_{60}:H_2Pc codeposited layer is now in progress.

CONCLUSION

We successfully incorporated 1 μm-thick *i*-interlayer which can utilize entire visible region in the solar spectrum into *p-i-n* organic solar cells. J_{sc} and conversion efficiency reached $19\,mAcm^{-2}$ and 5.3%, respectively. High performance was accomplished by using C_{60} purified to seven-nine by single-crystal formed sublimation. This results strongly suggests that the strict purification method similar to silicon reaching the purity of eleven-nine should be developed also for the organic semiconductors. Taking the observed J_{sc} value close to 20 $mAcm^{-2}$ into account, organic *p-i-n* cells have sufficient potential to compete with the inorganic solar cells.

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