

Organic Solar Cells

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Organic EL television was commercialized last year. Next target of organic electronics is organic solar cell. Our group accomplished the world record conversion efficiency of 5.3% based on the fundamental research on the organic semiconductors such as ultra-high purification, nanostructure design. Moreover, 1000 h (42 days) operation of organic solar cell without degradation was accomplished.

1. Efficient Organic *p-i-n* Solar Cells Having 1 μm -Thick Codeposited *i*-Layer Incorporating Seven-Nine (7N) Purified Fullerene¹⁾

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.^{2,3)} Since *i*-interlayer acts as an efficient photocarrier generation layer, 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 comparable to inorganic solar cells.

Unfortunately, *i*-interlayer has been inevitably very thin. For example, we have reported *p-i-n* organic solar cells in which the *i*-interlayer is nanostructure-optimized codeposited film composed of fullerene and metal-free phthalocyanine ($\text{C}_{60}\text{:H}_2\text{Pc}$).⁴⁾ At that time, thickness of $\text{C}_{60}\text{:H}_2\text{Pc}$ *i*-interlayer was limited below 180 nm since the fill factor (FF) was seriously decreased for thicker *i*-interlayer due to the increase of internal resistance of *i*-layer.

On the analogy of the case of Si which is usually purified to eleven-nine (11N), we convinced that the purity of organic semiconductors should be reached to ppm level at least in order to draw out their essential nature.

In this study, we performed the single-crystal formed sublimation under N_2 gas of 1 atm (Figure 1). Due to the gas convection, in the case of C_{60} , single crystals of the maximum size of 2 mm \times 2 mm were obtained (Figure 2). C_{60} purity was determined by the secondary ion mass spectroscopy (SIMS), which has been used for the analysis of dopants in Si wafer. Purity of C_{60} crystals purified three times was more than 0.1 ppm, *i.e.*, seven-nine (7N). On the other hand, purity of H_2Pc



Figure 1. Photograph of single-crystal formed sublimation apparatus.

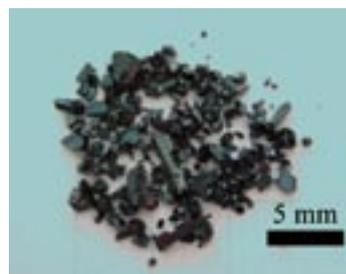


Figure 2. Photograph of C_{60} single crystals. Crystal size reached 2 mm \times 2 mm.

sample purified four times was five-nine (5N).

p-i-n cell structure is shown in Figure 4. *p*-type layer of H_2Pc , codeposited *i*-interlayer composed of C_{60} and H_2Pc , and *n*-type layer of NTCDA, which also acts as a transparent protection layer, were successively deposited by vacuum evaporation on ITO glass substrate. Codeposited films were fabricated by the coevaporation from two separately controlled sources on the substrate heated at +80 °C.

Figure 3(a) shows the dependence of fill factor (FF) on *i*-interlayer thicknesses (*X*). Surprisingly, FF hardly decreased

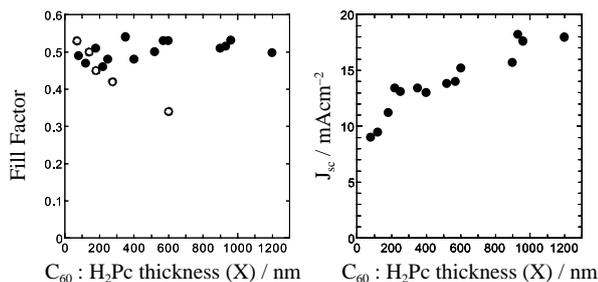


Figure 3. Dependence of fill factor (FF) and short-circuit photocurrent (J_{sc}) on i -interlayer thickness (X) for organic p - i - n cells.

even for very thick i -layer reaching 1.2 μm (closed dots). Accordingly, short-circuit photocurrent density (J_{sc}) increased with X and reached maximum value of 19.1 mAcm^{-2} at $X = 1 \mu\text{m}$ (Figure 3(b)). When we used C_{60} of low-purity by the conventional sublimation under vacuum, FF monotonically decreased with X and, as a result, thick i -layer could not be fabricated (Figure 3(a), open dots).

Figure 4 shows the current-voltage (J-V) characteristics for p - i - n cell having 1 μm -thick i -interlayer. J_{sc} of 18.3 mAcm^{-2} , open-circuit photovoltage (V_{oc}) of 0.402 V, FF of 0.532, and conversion efficiency 5.3% were observed.

Since the present cell ($X = 1 \mu\text{m}$) absorbs whole visible light, cell color is black (Figure 5(a)). On the contrary, cell having thin i -layer ($X = 180 \text{ nm}$), cell color is transparent green (Figure 5(b)), namely, large portion of irradiated light can not be utilized. Utilization of entire visible light of solar spectrum without decreasing FF by incorporating very thick C_{60} - H_2Pc i -interlayer is essential to obtain large J_{sc} value close to 20 mAcm^{-2} and efficiency of 5.3%.

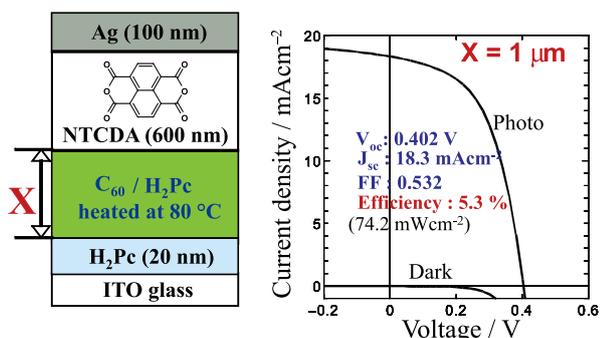


Figure 4. Cell structure and current-voltage (J-V) characteristics for p - i - n cell having 1 μm -thick i -layer.

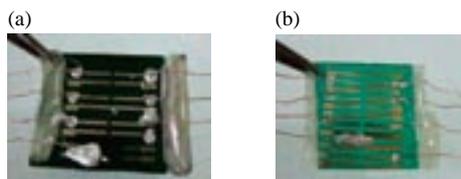


Figure 5. Photographs of cells. (a) $X = 1 \mu\text{m}$. (b) $X = 180 \text{ nm}$.

2. Long-Term Operation for 42 Days

The conversion efficiency of organic solar cells is expected to exceed the practical level (10%) within few years. However, few studies have been made on their durability.⁵⁾

In this study, we performed the long-term operation tests reaching 1000 h in high vacuum (10^{-7} Torr). White light (100 mWcm^{-2}) was continuously irradiated under the short-circuit condition. Gradual degradation within 100 h was observed for p - i - n cells having the structure of Figure 4. Detailed investigation revealed that the photodegradation of NTCDA, which acts as the transparent n -type layer, occurred.

Therefore, we replaced NTCDA with Al-doped ZnO (AZO) fabricated by electron beam evaporation on organic film (Figure 6). Fabricated AZO was transparent and showed the conductivity of 10^3 Scm^{-1} , which is comparable to ITO. Little decrease of J_{sc} and efficiency after 1000 h operation was confirmed (Figure 6). This is good news for the practical application of organic solar cells.

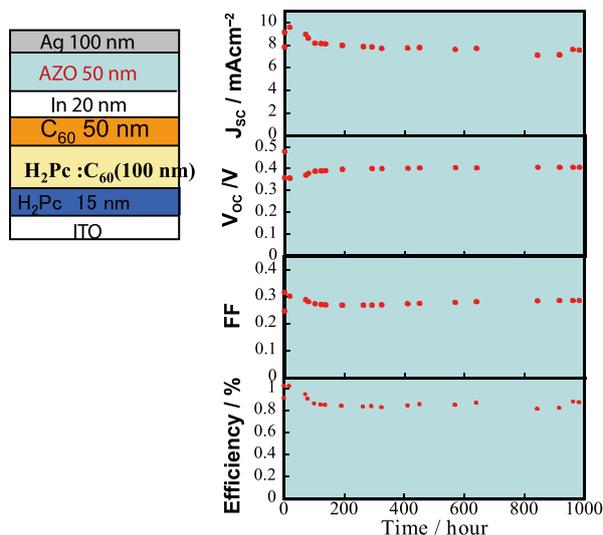


Figure 6. Cell parameters vs. operating time for a cell incorporating transparent AZO layer.

References

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