CHEMISTRY LETTERS, pp. 1717-1720, 1992.

Three-Layer Organic Solar Cell

Tokushige SHICHIRI,* Minoru SUEZAKI, and Takeshi INOUE
Advanced Polymer Research Laboratory, Corporate Research Institute,
Sekisui Chemical Co., Ltd., Shimamoto, Osaka 618

Three-layer organic cells composed of perylene pigment/phthalocyanine/quinacridone were examined, and the photocurrent was founded to be greatly affected by the thickness of phthalocyanine layer. Furthermore, the tandem type solar cells were fabricated by combining of several units of the three-layer cell to clarify the relationship between the number of accumulated unit cells and cell characteristics.

Photovoltaic devices using organic compounds are attracting much attention as a result of the appearance of cells whose conversion efficiencies are about 1%.[1-6] Tang reported a perylene dye(Pe)/a phthalocyanine dye(Pc) two-layer cell of 0.9%,[1] but it was difficult to reproduce a solar cell of such high efficiency.[3] Besides these dyes, quinacridone dye(QA) is known as one of the photoactive pigments and is used in photovoltaic cells. Yokoyama *et al.* studied the Schottky type cell produced by the junction of QA dispersed polymer and Al metal.[4] In this study, we fabricated three-layer solar cells using Pe, Pc, and QA dyes and investigated the properties of the cells focusing on the thickness of Pc layer.[5] This three-layer cell is convenient to elucidate the function of Pc more in detail than Pe/Pc two-layer cell since the absorption of Pc is quite different from that of QA and Pe, *i.e.*, the absorption of QA and Pe is in the range of 400 to 600 nm, while Pc absorption ranges from 600 to 800 nm. We found that the photocurrent of the three-layer cell is very sensitive to the thickness of the Pc layer when the layer is more than 30 Å.

When Pc layer of the three layer cell is very thin, the absorption of Pc is so weak that the light passed through could be used efficiently in other cells behind the front cell. Yokoyama *et al.* also studied the tandem type cell in which two Pc/Pe unit cells are connected.[6] In this tandem cell, the absorption of the front cell reduces the light intensity, so overall conversion efficiency of the tandem cell is lower than the single cell due to the restriction of current in the back cell. In the present work, we fabricated tandem type cells using the three-layer unit cell and found that several unit cells can be accumulated without a reduction in conversion efficiency.

N,N'-Dimethyl-3,4,9,10-perylene tetracalboxylic diimide (PTC), metal free phthalocyanine (H2Pc) and 2,9-dimethylquinacridone (DMQ) were used as photoactive dyes. All dyes were purified by the sublimation method at least twice. PTC, H2Pc, and DMQ dyes were successively deposited on an indium tin oxide(ITO) coated glass by conventional vacuum evaporation under a pressure of 1×10^{-5} Torr using melting pots made of alumina. Finally, an Au counter electrode was deposited onto the dye layer under the same condition as dyes were deposited. The thickness of the Au electrode was typically 300 Å and the active area of the electrode was 0.1 cm^2. Tandem type cells were fabricated by the successive accumulation of three kinds of dyes and thin Au layer.[6] The thicknesses of PTC, H2Pc, DMQ, and Au layers were 800,100, 800, and 30 Å, respectively.

The thickness of each layer was monitored by a CRTM-1000 quartz oscillator (ULVAC Corp.). The dark and light current density-voltage characteristics of the cells were measured under simulated air mass 2(AM2) illumination (75 mW/cm^2). Light intensity was measured by using a Thermopile (EPPLAY Laboratory Inc.). The photocurrent spectra of the cells were measured by using a P-250 monochrometer with AS-D102 Auto-Scaner (Nikon).

The three-layer cells with fixed thickness of 1500 Å in both PTC and DMQ layers and varied thickness in the H2Pc layers were examined. The relationship between the H2Pc thickness and the cell characteristics is listed in Table 1. At first, we must discuss the two-layer cell composed of PTC and DMQ(i.e. H2Pc is 0Å). These two dyes show rectifying contact from short circuit photocurrent density(J_{sc})-open circuit voltage(V_{oc}) measurement both in the dark and under the illumination. The fill factor of the two-layer cell represents a very high value(0.57). This feature indicates that the PTC/DMQ interface exhibits nearly ideal behavior, *i. e.*, there are few trapping levels of carriers on the interface. Figure 1(a) shows the photocurrent spectrum of the two-layer cell under the illumination from the ITO electrode side. A photocurrent around a wavelength of 590 nm corresponds to the absorption spectra of DMQ. The contribution of PTC is also seen in the photocurrent spectra in the range of 400-600 nm, but the shape is somewhat different from the absorption spectra as a consequence of the filtering effect of PTC. These facts indicate that the photoactive region lies in the PTC/DMQ interface. Conversion efficiency of this cell is lower than conventional Pe/Pc cells probably because the absorption of DMQ and PTC exists in the same region and/or because the quantum efficiency of DMQ is lower than that of Pc.

Table 1. Thickness of the Pc layer and cell characteristics

Thickness	Voc	J_{sc}	f.f.	eff.
Å	V	mA/cm^2		%
0	0.37	0.12	0.57	0.03
30	0.38	0.60	0.51	0.15
60	0.32	0.97	0.34	0.14
100	0.35	1.27	0.40	0.24

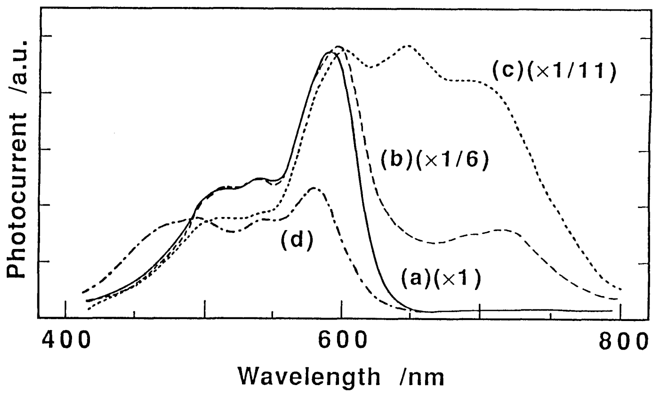

Fig. 1. Photocurrent spectra of PTC/H2Pc /DMQ three-layer cells for various kinds of H2Pc thickness. Thickness of H2Pc is (a)0 Å, (b)30 Å, and (c)100 Å. The scales of the spectra are indicated in parentheses. Absorption spectrum of the 30Å cell(b) is designated in (d).

As shown in Table 1, by the insertion of H2Pc dye in the PTC/DMQ interface, a drastic increase in J_{sc} was observed above 30 Å H2Pc thickness, though no change of V_{oc} was observed. Figures 1(b) and (c) show the photocurrent spectra of three-layer cells, whose scales were normalized at 590 nm. As seen in the spectra, the photocurrent in the region of 600 to 800 nm increases with respect to that of DMQ at 590 nm with a raise in the H2Pc layer thickness. This fact is interpreted as a result of the increase of the hole injection from H2Pc to DMQ. According to the scale of the spectra, the photocurrent of DMQ, as well as that of H2Pc, increases when the H2Pc layer becomes thicker. This indicates that H2Pc enhances the carrier density in the depletion layer. It is of interest that the photocurrent of DMQ at 590 nm appears even in the large H2Pc thickness region. When H2Pc thickness is very thin, H2Pc would have an island form or be a porous film. In this case, it is reasonable that both H2Pc and DMQ contribute to the photocurrent spectra because these dyes contact directly with PTC. When the H2Pc film is thick enough to cover the PTC layer completely, only the H2Pc/PTC interface would be active because H2Pc makes an ohmic contact with DMQ in the separated experiment and, hence, no photocarriers are generated in the H2Pc/DMQ interface. Unexpectedly, DMQ still contributes to the photocurrent spectra even in the case of a 100Å thickness H2Pc film, suggesting that the photoactive region spreads over three layers.

As seen in the absorption spectrum of this cell (Fig. 1(d)), the H2Pc absorption in 600-800 nm is very weak, so the light in this region can be utilized in the back cells of the tandem configuration. We prepared tandem cells of two to four unit cells. In the present study, we examined the tandem cells where every unit cell had the same composition. Each unit cell was combined through an ultra thin Au layer to make intercell ohmic contact.[6] Table 2 shows the characteristics of tandem cells made of various number of unit cells. V_{OC} increases in proportion to the number of unit cells while J_{SC} decreases inversely proportional to the number of unit cell. As a result the conversion efficiency does not decrease when the unit cells are added. Figure 2(a) shows the photocurrent spectrum of the tandem cell. The photocurrent is dominant in the H2Pc absorption region. The light in 600-800 nm passes several unit cells because of low H2Pc absorption, but the intensity of the light in 400-600 nm is reduced by the absorption of PTC and DMQ. This reduction in the light intensity result in the increase of the internal resistance of the PTC and the DMQ layers in the back cells. Consequently, the decrease of J_{SC} is induced with increasing numbers of unit cells.

Table 2. Number of unit cell and cell characteristics of the tandem cell

Number of unit cell	Voc	J sc	f.f.	eff.
	V	mA/cm^2		%
1[a)]	0.35	1.27	0.40	0.24
2	0.68	0.78	0.39	0.27
3	0.94	0.55	0.39	0.26
4	1.21	0.40	0.46	0.30

a) Thickness of PTC and DMQ are both 1500 Å.

Figure 3 shows the proposed energy profile of the three-layer cell based on the results above. These results are itemized as follows; (1) Both H2Pc and DMQ make a rectifying contact with PTC. (2) PTC and DMQ have similar energy gaps according to their absorption spectra. (3) H2Pc makes an ohmic contact with DMQ. Differing from the conventional two-layer cell, this cell has a QA layer at the back of those two layer. The QA layer has the highest conduction band (CB) level among the three dyes, and the electrons excited to CB of QA and H2Pc transfer to the PTC layer. Thus, the three-layer cell has the possibility to enhance conversion efficiency when compared with the conventional two-layer cell.

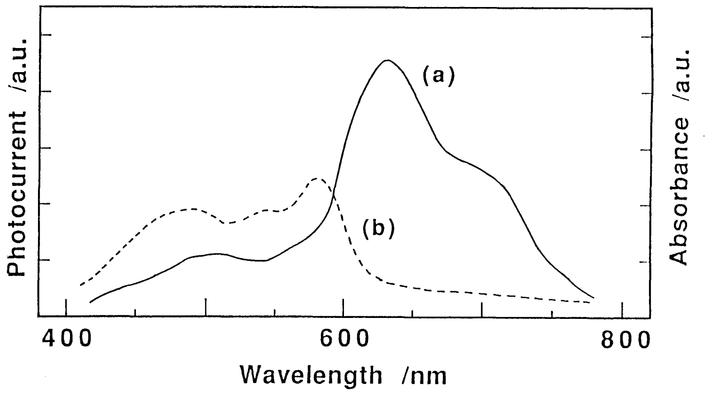

Fig. 2. Photocurrent spectrum of the tandem cell composed of four unit cells (a) and absorption spectrum of the cell (b).

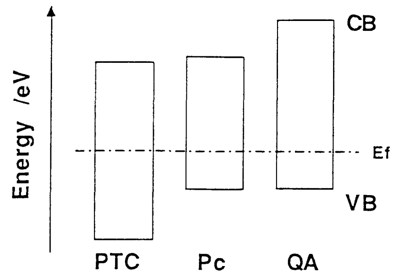

Fig. 3. Schematic representation of the energy diagram of the three layer cell.

In summary, the three-layer organic cell was examined by focusing on the relationship between cell characteristics and thickness of the Pc layer. Since three dyes used in this cell have different absorption regions relative to each other, the function of each dye can be determined more easily in the photocurrent spectra than in the conventional two-layer cell. It was found that the thickness of Pc layer was very sensitive to the photocurrent and that the three dyes make junctions effectively so that the depletion layer spreads over all three layers. Furthermore, we fabricated the tandem cells by multijunction of the three layer-cells and found that several unit cells could be accumulated without lowering the overall conversion efficiency. Conversion efficiency of the cells studied here can be improved by the optimization of the thickness of layers.

References

1) C. W. Tang, *Appl. Phys. Lett*, **48**, 183 (1986).
2) H. J. Wagner and R. O. Loutfy, *J. Vac. Sci. Technol.*, **20**, 300 (1982).
3) M. Hiramoto, Y. Kishigami, and M. Yokoyama, *Chem. Lett.,* **1990**, 119.
4) M.Tomida, S. Kusabayashi, and M. Yokoyama, *Chem. Lett.*, **1984**, 1305.
5) T. Shichiri, M. Suezaki, T. Inoue, M. Minami, and M. Asai, The Japan Society of Applied Physics, Extended Abstracts (The 51st Autumn Meeting, 1990), p.1043 (in Japanese).
6) M. Hiramoto, M. Suezaki, and M. Yokoyama, *Chem. Lett.*, **1990**, 327.

(Received May 14, 1992)