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Effect of Thin Gold Interstitial-layer on the Photovoltaic Properties of Tandem Organic Solar Cell

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Tandem type organic solar cell consisting of two combined unit cells was fabricated. Each unit cell was two-layer organic solar cell composed of metal-free phthalocyanine and perylene tetracarboxylic derivative. When ultra-thin Au layer was inserted between unit cells, photovoltage increased about 2 times, while photocurrent density was much dependent on the thickness of the inserted Au layer.

Organic solar cells using organic pigments or dyes have been studied from the standpoint of the photo-electrical solar energy conversion.[1-3] Recently, Tang[4] reported the two-layer organic solar cell belonging to the category of organic p-n junction and showed high conversion efficiency of about 1% under solar simulated AM2 light. We have reported the pronounced doping effects of H_2 on the photovoltaic properties of the two-layer organic solar cell composed of metal-free phthalocyanine (H_2Pc) and perylene tetracarboxylic derivative (Me-PTC, Fig. 1).[5] Though this two-layer organic solar cell showed large photocurrent density of the order of milli-amperes, their photovoltage (about 0.5 V) is rather small for the organic solar cells. On the other hand, nearly the half of the incident light transmitted through the cell since the thickness of the active region responsible for the photovoltaic effect is very thin. In order to utilize the whole light energy and to attain larger photovoltage, a tandem type cell seems to be advantageous. The goal of this study is to obtain higher conversion efficiency by combining different kinds of cells which respond to the different region of solar spectrum. As for the first step, we combined the same type cells in the present

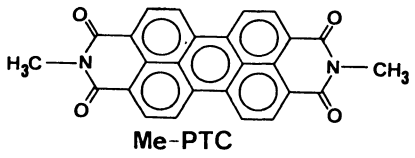

Fig. 1. Chemical structure of Me-PTC.

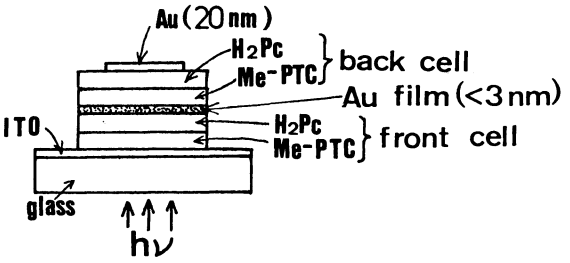

Fig. 2. The structure of tandem organic solar cell. A unit cell is Me-PTC/H_2Pc. Thin Au film was inserted between two unit cells.

work. The structure of the tandem cell is shown in Fig. 2. In the H_2Pc/Me-PTC interface, organic p-n junction is formed. Since an inverse junction, however, is inevitably formed between H_2Pc of the front cell and Me-PTC of the back cell, it is necessary to make an ohmic contact between two unit cells. For this purpose, we examined to insert ultra-thin Au interstitial-layer (< 3 nm) between unit cells. Interestingly, the photovoltaic properties of tandem type organic solar cell much depends on the thickness of the inserted Au layer.

Me-PTC (BASF) and H_2Pc (Tokyo Kasei Co. Ltd.) were purified three times by train sublimation.[5] The tandem cells were fabricated by the successive vacuum deposition of Me-PTC, H_2Pc, and Au on an ITO glass under 1.3×10^{-3} Pa. The film thickness was monitored by the oscillating quartz thickness meter (ULVAC, CRTM-1000).

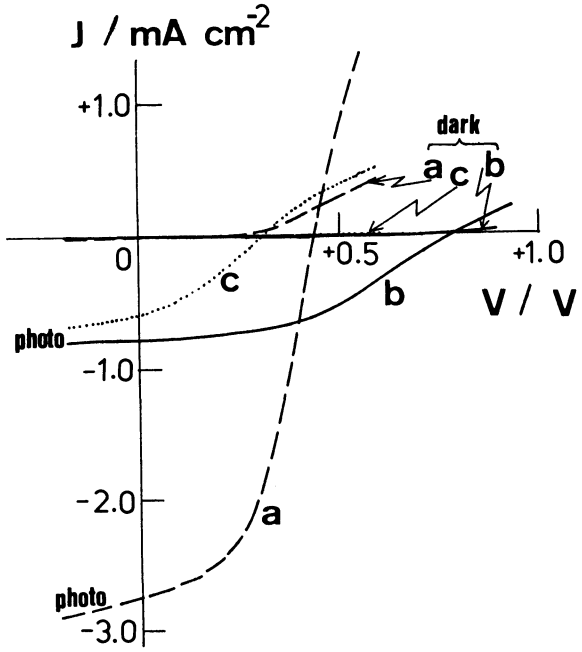

Fig. 3. J-V curves of a single cell (a), a tandem cell with 2 nm-thick Au interstitial-layer (b), and a tandem cell without Au layer (c). The film thickness of a single cell, a front cell, and a back cell are the same (Me-PTC 70 nm, H_2Pc 50nm). White light (78 mW cm^{-2}) was irradiated through ITO glass. The voltage indicated is referred to that of Au electrode.

The curves b and c in Fig. 3 show the photocurrent density - voltage (J - V) curves of the tandem cells. The thickness of the front cell and the back cell are the same (H_2Pc: 50 nm, Me-PTC: 70 nm). The pigment film of this thickness transmits about 40% light on an average. The tandem cell without Au interstitial-layer (curve c) showed smaller photovoltage (V_{oc}) and photocurrent density compared to a single cell having a structure of ITO/Me-PTC/H_2Pc/Au (curve a). When 2 nm-thick Au layer was inserted between unit cells of the tandem cell, V_{oc} drastically increased to 0.78 V which is about twice to that for a single cell (0.44 V). Only 0.6 nm-thick Au film was sufficient to double V_{oc} as shown in Fig. 5. This result shows that the deposited Au can provide the ohmic contact between H_2Pc of the front cell and Me-PTC of the back cell. Without Au film, V_{oc} did not increase because of the inverse photovoltage generated by the junction between unit cells.

Short-circuit photocurrent (J_{sc}) of the tandem cell was about one-third compared to that of a single cell. As shown in Fig. 4, the shape of the action spectrum of a tandem cell (curve b) was different from that of a single cell (curve a). Since the photocurrent density was confirmed to be proportional to a wide range of the light intensity, J_{sc}^{b} for the back cell which works under the light intensity attenuated by the front cell and the inserted Au layer can be calculated by Eq. 1.

$$J_{sc}^{b} = T_f \cdot T_{Au} \cdot J_{sc}^{s} \qquad (1)$$

Here, J_{sc}^{s} is J_{sc} for a single cell having a structure of ITO/Me-PTC(70 nm)/H_2Pc(50 nm)/Au and T_f is the transmittance of the pigment film of the front cell and T_{Au} is that of inserted Au layer. The shape of the action spectrum for calculated J_{sc}^{b} (Fig. 4, curve c) well agrees with that of the tandem cell (curve b). Thus, we concluded that the photocurrent density of the tandem cell was mainly determined by that of the back cell working under the light intensity attenuated by the front cell. In order to increase the photocurrent density of the tandem cell, the thickness of the front cell, namely the light absorption by the front cell, has to be reduced.

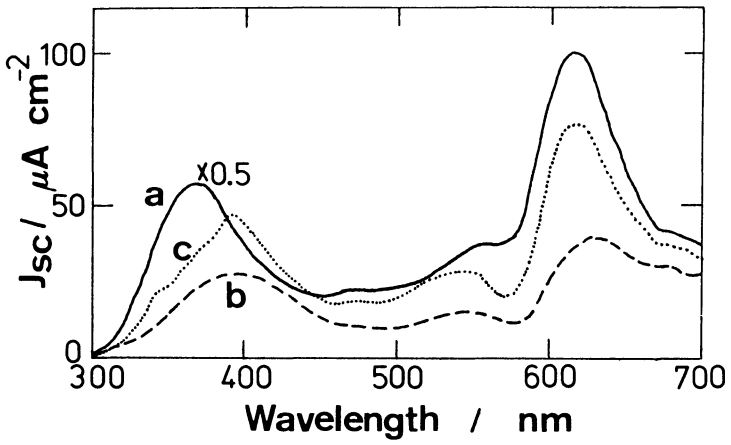

Fig. 4. Action spectra of J_{sc} for a single cell (a) and a tandem cell with 2 nm-thick Au interstitial-layer (b). Action spectrum of J_{sc} for a back cell calculated by Eq. 1 is also shown (c).

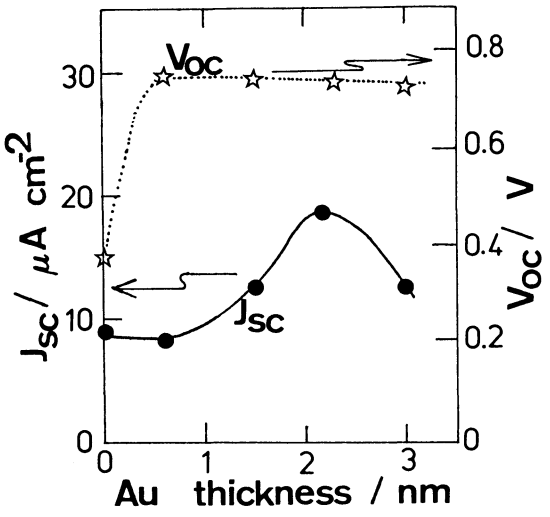

Fig. 5. Dependence of J_{sc} and V_{oc} of the tandem cell on the thickness of the inserted Au layer. Thickness of the pigment layer is the same as in Fig. 3. J_{sc} was measured under 630 nm light (0.62 mW cm^{-2}) and it was corrected for the transmittance of the Au layer. V_{oc} was measured under white light (76 mW cm^{-2}).

J_{sc} of the tandem cell somewhat increased by inserting thin Au layer between unit cells (Fig. 3, curves b and c). J_{sc} of the tandem cell must be affected by the absorption of the inserted Au layer because it is determined by that of the back cell as discussed previously. Figure 5 shows the dependence of J_{sc} which is corrected for the transmittance of the inserted Au layer on the thickness of the Au interstitial-layer. Interestingly, J_{sc} gradually increased with increasing the thickness of the Au layer from 0 to 2 nm and showed maximum around 2 nm. The effective recombination between electrons in Me-PTC of the back cell and holes in H_2Pc of the front cell has to take place to flow the photocurrent through the tandem cell. This result indicates that this recombination efficiency much depends on the thickness of the Au layer. Since the pigment film is polycrystalline and its surface is not uniform (Fig. 6), deposited thin Au layer on the pigment film seems to have an island structure. At only the Au sites,

the photogenerated holes in the front cell and the photogenerated electrons in the back cell can recombine. Outside of the Au sites, electrons and holes were separated each other due to the p-n junction formed between H_2Pc and Me-PTC. Thus, the photocurrent density of the tandem cell is dependent on the number of the Au effective recombination sites which increase with the Au thickness.

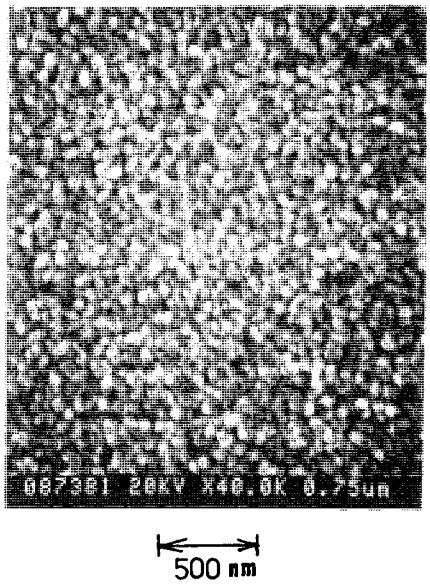

Fig. 6. SEM photograph of the surface of ITO/Me-PTC(70 nm)/H_2Pc(50 nm).

J_{sc} decreased when the thickness of the inserted Au film exceeded 2 nm. This phenomenon is possibly explained as follows. It is well-known that H_2Pc makes an ohmic contact with Au. On the other hand, if Me-PTC works as an n-type semiconductor, Schottky barrier is formed between Me-PTC and Au. This was confirmed by the fact that Me-PTC of the Au/Me-PTC junction showed negative photovoltage referred to the Au electrode. When the Schottky barrier is uniformly formed at the Au/Me-PTC junction, it repels electrons and prevents the recombination process with holes captured by Au. Since Au has small island structure below 2 nm, this barrier seems to be not uniformly formed. However, Au islands start to grow and connect to each other beyond 2 nm. This was supported by the observation that the surface resistance of the thin Au film deposited onto H_2Pc(50 nm)/Me-PTC(70 nm) film started to decrease around 2 nm of Au thickness. Thus, we concluded that the Schottky barrier between Au and Me-PTC was formed rather uniformly and prevented the electron-hole recombination when the thickness of the inserted Au layer was beyond 2 nm.

Large photovoltage was easily obtained in a tandem organic solar cell by inserting the ultra-thin Au layer between two unit cells. In order to increase photocurrent density, optimization of the thickness of inserted Au layer as well as that of the pigment layer is important.

References

1) A. K. Ghosh and T. Feng, J. Appl. Phys., 49, 5982 (1978).
2) A. M. Hor and R. O. Loutfy, Can. J. Chem., 61, 901 (1983).
3) K. Manabe, S. Kusabayashi, and M. Yokoyama, Chem. Lett., 1987, 609.
4) C. W. Tang, Appl. Phys. Lett., 48, 183 (1986).
5) M. Hiramoto, Y. Kishigami, and M. Yokoyama, Chem. Lett., 1990, 119.

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