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## ENHANCEMENT OF PHOTOVOLTAIC PERFORMANCE IN COPPER PHTHALOCYANINE THICK FILM SOLAR CELLS

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### ABSTRACT

Copper phthalocyanine (CuPc) thick film solar cells were fabricated by spin coating and their photovoltaic behavior was studied. Polyvinylidene fluoride (PVdF) was used for the binder. Aluminum and indium were employed as electrode metals to form Schottky contact to CuPc layer. The cells showed rectifying J-V characteristics in the dark and photovoltaic effect associated with white light irradiation. The photovoltaic performance of the cells strongly depended on contact metals, in which the formation of oxide layer between binder layer and electrode interface affected the solar cell. Influence of the CuPc layer thickness, CuPc/PVdF ratio on the photovoltaic performance of the cells were also examined.

### INTRODUCTION

Recently, many studies have been made to utilize organic materials for photovoltaic devices because of their wide capability and low cost. Phthalocyanines are green to blue pigments and expected to be promising organic semiconductors for photovoltaic devices because of their high stability and spectral fitting to sun light. Various reports were made on application of phthalocyanines to organic solar cells<sup>[1, 2]</sup>. Most workers fabricated phthalocyanine solar cells by preparing a phthalocyanine layer and a metal contact both by vacuum deposition. However, another approach was also reported by Loutfy and Sharp to fabricate low cost organic solar cells, namely, the use of particulate organic semiconductors<sup>[3]</sup>. Their devices were based on a

solvent casted dispersion layer of phthalocyanine particles in a polymer binder. There are several factors which affect the cell performance such as kinds of phthalocyanines, electrode materials, cell structures, etc. Many attempts have been carried out to improve energy conversion efficiency both in thin layer cells<sup>[4-6]</sup> and binder layer cells<sup>[7-9]</sup>. However, further investigation for the improvement of photovoltaic performance in organic solar cells are in demand.

Copper phthalocyanine (here after, CuPc) is one of the typical phthalocyanines widely used for organic solar cell studies, which shows p-type conduction and photoconductivity in the visible region. This paper describes several attempts to improve capabilities of CuPc thick layer solar cells, manufactured in air, except for the electrodes and dis-

cuss the effect of metal electrodes, CuPc layer thickness, etc. on photo-electronic behavior of the solar cells.

## EXPERIMENTAL

The basic structure of the photovoltaic cell fabricated in this study was illustrated in Fig. 1, in which Schottky barrier was formed based on a CuPc binder layer-metal contact and where the CuPc binder layer was prepared by spin coating. A CuPc power of  $\alpha$ -form( $\alpha$ -CuPc) and polyvinylidene fluoride (PVdF) which promotes photogeneration of carriers by its dipole field, were employed as a photoactive particulate semiconductor and binder, respectively.

The device was fabricated as following sequence. A specific weight of the CuPc powder, PVdF and solvent(N,N-dimethyl acetamide)were mixed ultrasonically in reservoir. A drop of the slurry, achieved by the mixture, was put on the indium-tin oxide(ITO) glass substrate, and spin coating was carried out to form a CuPc-PVdF layer. The layer was dried in the air at 60°C for 24h. After drying, a thin semitransparent metal contact was vacuum deposited on the CuPc-PVdF layer. Aluminum(Al)and indium(In) were used for the thin metal contact, of which transmittance was 0.2-20%.

Photovoltaic characteristics of the solar cells fabricated were measured with light irradiation through the semitransparent metal

electrode in a evacuated chamber( $10^{-3}$  Torr) at room temperature. A 150W incandescent lamp with an IR-cut filter was employed as the light source.

## RESULTS AND DISCUSSION

At the beginning, effects of contact metals, i.e., aluminum (hereafter, Al-cell) and indium(hereafter, In-cell) to the CuPc layer on the photovoltaic performance were examined. Figure 2(a) shows current-voltage(J-V) characteristics for both kinds of cells in the dark. The abscissa indicates the voltage applied to the ITO electrode. It should be noted that the ITO-CuPc layer contact is ohmic. Both cells showed rectifying behavior and generated photovoltage associated with white light irradiation, as the metal electrode was negative.

Figure 2(b) shows typical photo J-V curves with white light irradiation of 13mW/cm<sup>2</sup> for both cells. Open circuit voltages(Voc) of Al-cell and In-cell were about 0.5V and 0.18V, respectively. On the other hand, short circuit current(Jsc) of In-cell was 5  $\mu$ A/cm<sup>2</sup>, Higher than that of Al-cell Since aluminum has larger work function than indium, the height of Schottky barrier of Al-cell must be lower, and therefore larger current was expected in Al-cells<sup>[10]</sup>. The reason for a small current Al-cell may be attributed to the formation of an oxide layer (Al<sub>2</sub>O<sub>3</sub>) between the aluminum electrode and CuPc-PVdF layer-interface. The oxide layer formed in In-cell (In<sub>2</sub>O<sub>3</sub>) has much smaller resistivity than Al<sub>2</sub>O<sub>3</sub>. Current rising at smaller voltage (Fig. 2(a)) and smaller Voc (Fig. 2(b)) in In-cell, also opposed to the smaller work function of indium, may also be attributed to the oxidation of the indium contact.

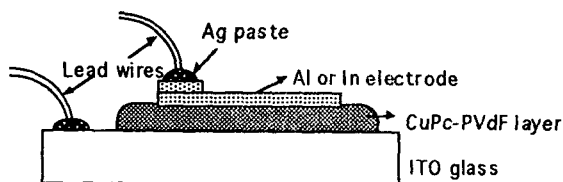


Fig. 1 Basic structure of the photovoltaic cells fabricated in this study

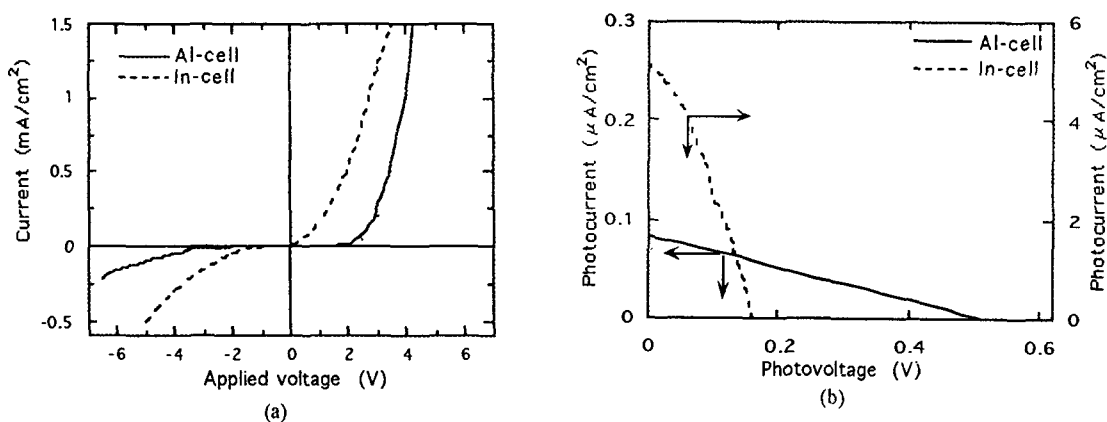


Fig. 2 (a) Current-voltage characteristics of Al or In/CuPc/ITO cells in the dark, (b) photocurrent-photovoltage characteristics of Al or In/CuPc/ITO cells.

Figure 3 shows spectral responses of  $J_{sc}$  for both Al-cell and In-cell. The action spectrum of In-cell indicates a common spectral response which matches well to CuPc and solar spectrum, however, that of Al-cell is broadened out. Since the same pigment was utilized here, i.e., CuPc, it was expected that similar spectral responses should be attained in both cells. The reason of broadening spectral response in Al-cell can be attributed to the formed oxide layer at the interface.

The formation of oxide layer can also be revealed by the fact that both the cells

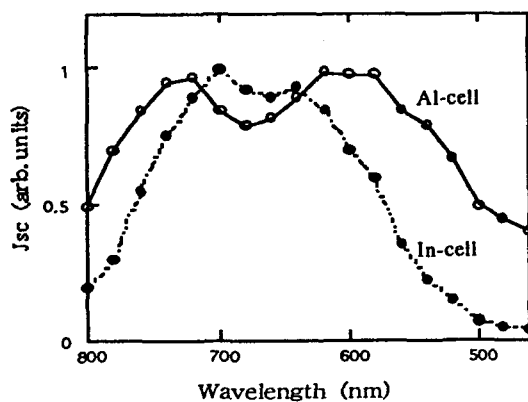


Fig. 3 Spectral responses of  $J_{sc}$  for Al and In/CuPc/ITO photovoltaic cells.

showed some voltage even in the dark.

Figure 4 shows the temperature dependence of short circuit current in the dark. This dark current is considered to be generated by chemical or electrochemical reaction which results in formation of oxide layer. The results of Fig. 4 confirm that oxide layer is more actively formed in Al-cell than In-cell.

Figure 5 shows the dependence of photovoltaic characteristics on light intensity for both cells. The  $J_{sc}$  of Al-cell and In-cell are pro-

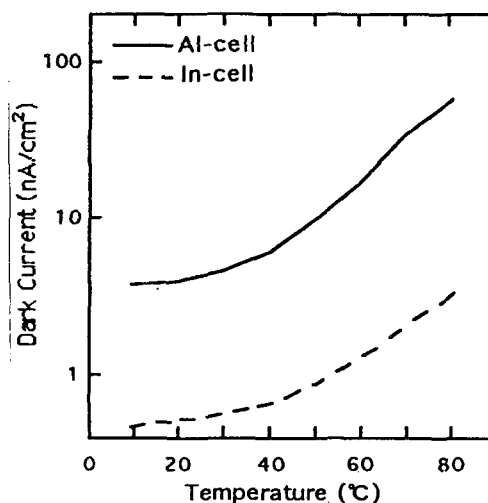


Fig. 4 Temperature dependence of output for Al and In/CuPc/ITO photovoltaic cells.

portional to 0.7 and 0.8 power of light intensity, respectively. The fill factor(ff) and  $V_{oc}$  of In-cell are approximately independent of light intensity, which is preferable to solar cell parameters. The ff of Al-cell is very low and decrease as intensity increases. In Al-cell, the moderate photovoltaic performance at low light intensity is considered to be supported by electrochemical reaction and most of photogenerated excitons or carriers at high light intensity are trapped by polarized oxide layer.

Ratio of CuPc to PVdF is one of the important parameters which affect the photovoltaic performance of the cells. If the CuPc concentration is low, the CuPc layer is not photoactive enough for photo-generation of carriers, while a CuPc rich layer is not smooth for carrier transport. It was found that the weight ratio of CuPc to PVdF of 3:2 was optimal, at which the maximum current was obtained in most cells

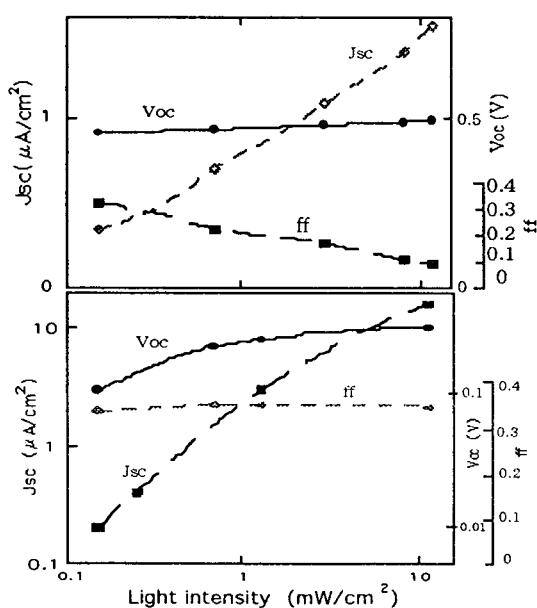


Fig. 5 Light intensities dependance of  $J_{sc}$ ,  $V_{oc}$  and for Al and In/CuPu/ITO photovoltaic cells.

The thickness of the CuPc-PVdF layer is also another important parameter for the cell performance. Our results of layer thickness dependance of out put power is shown in Fig. 6. A maximal photocurrent wa obtained at the layer thickness of 3  $\mu\text{m}$  and 4  $\mu\text{m}$  for Al-cell and In-cell, respectively. The thin layer cells contain not enough CuPc for photogeneration of carriers, while thick layer cell has large internal resistance.

Sheet resistivities of indium layer at low thicknesses were reported to be extremely high<sup>[10]</sup>. In order to enhance the photovoltaic performance of In-cell by means of lowering its internal resistance, we added an aluminum overlayer as illustrated in Fig.7. The indium electrode was prepared in two different thicknesses, one was of 3.3% and the other 78% of transmittance, keeping the aluminum thickness constant (19% of transmittance).

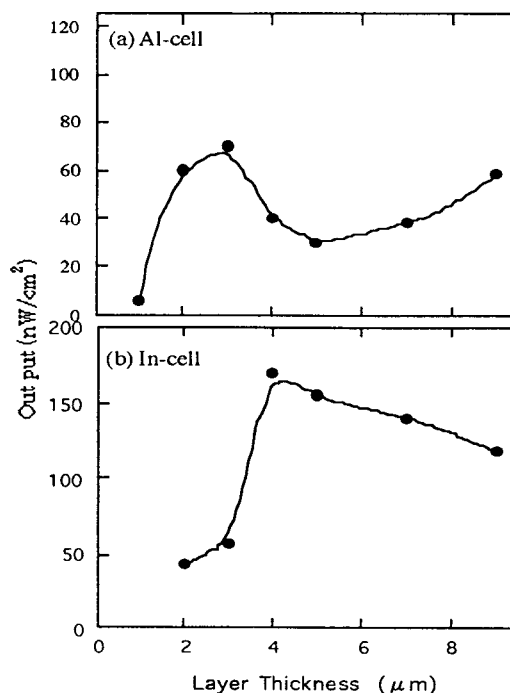


Fig. 6 Effect of CuPu layer thickness on (cells).

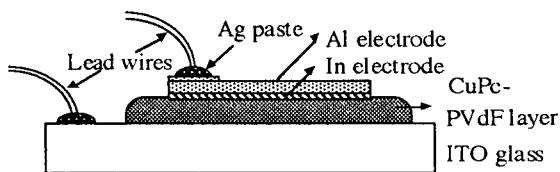


Fig. 7 Double contact metals cell, added with aluminum layer on the indium layer

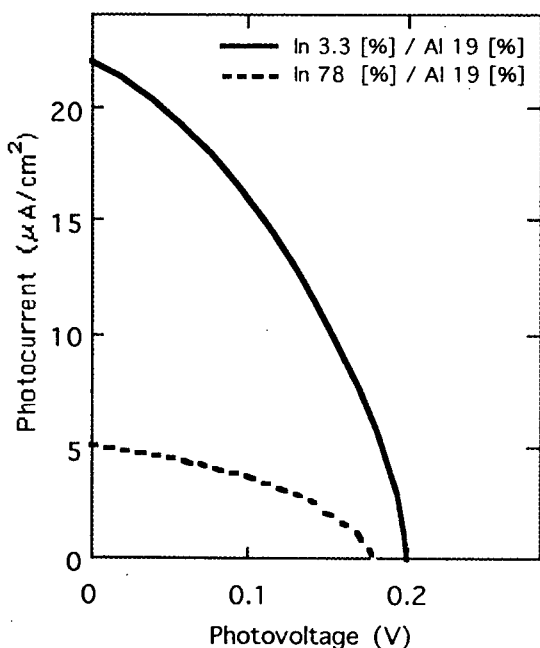


Fig. 8 Photo  $J_{sc}$ - $V_{oc}$  curve for double contact metals photovoltaic cells.

Figure 8 shows the results of photovoltaic performance with white light illumination of  $13[mW/cm^2]$ . Comparing with the basic structure In-cell, the conversion efficiency in double layered In-cell of 3.3% transmittance doubled than that of the basic one. The double layered In-cell of transmittance of 78% did not show any remarkable improvement from the basic one.

## CONCLUSION

Photovoltaic properties of copper phthalocyanine binder layer solar cells were studied,

and several attempts to improve the photovoltaic performance have been tried. The optimal CuPc/PVdF ratio and CuPc layer thickness were found to be 3:2 and  $3-4\mu m$ , respectively. The photovoltaic performance of the cells strongly depended on a contact metals, where the formation of oxide layer between binder layer and electrode interface affected those performance. Double layered metal contact of In and Al intensified the conversion efficiency of cell.

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