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# Long-life Organic Solar Cell Fabrication Using Quinacridone Pigment

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A hetero-junction organic solar cell coupled with electrochemically deposited CdS and 2,9-dimethyl quinacridone pigment was fabricated. Open-circuit voltage of 0.61 V and short-circuit photocurrent of 127 μA/cm$^2$ with large fill-factor of 0.32 were obtained under 71 mW/cm$^2$ white light, giving conversion efficiency of 0.04%. No fatigue was observed over a month continuous irradiation of 15 mW/cm$^2$.

There has been much attention paid to organic photoconductors as an attractive material from the viewpoint of its low cost and easy processability for the practical application in the field of photo-electrical energy conversion. Many organic solar cells have been examined but mainly in the Schottky-type photovoltaic cells coupled with metal electrodes of low work-function and organic pigments or dyes such as phthalocyanine and merocyanine derivatives. In addition to low conversion efficiency compared with inorganic solar cells, such organic solar cells also have a serious problem with their lifetime. Particularly, the use of low work-function metals such as Al or In as a barrier electrode results in a short lifetime in the order of hours, which is considered to be due to the oxidation of the metal electrodes. However, the use of thicker evaporated metal electrodes would give rise to poor light transparency. In order to improve such problems, stable inorganic n-type semiconductors of wide-bandgap II-VI compounds such as CdS or ZnO have been proposed to make p-n hetero-junction organic solar cells. Loutfy et al.[1] reported that a ZnO/x-$H_2$Pc cell showed the efficiency of 0.04% under AM0 sunlight simulator and to be stable only to 5% of the initial efficiency dropped in 150 days. Similar stability was reported in a ZnO/merocyanine cell by Moriizumi et al.[2]

We have already reported that quinacridone pigments (Fig.1) show photovoltaic properties as well as phthalocyanine dyes,[3] and by adopting a double-layered structure of Al/2,9-dimethyl quinacridone/carrier transport layer for Schottky-type photovoltaic cell, the conversion efficiency was shown to be attainable up to about 0.1%.[4] In the present paper, from a viewpoint of establishing a long-life organic solar cell we attempted to fabricate a 2,9-dimethyl quinacridone/CdS p-n hetero-junction solar cell, which would exhibit good photovoltaic properties even

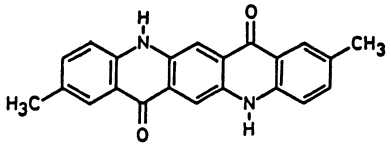


Fig. 1. 2,9-dimethyl quinacridone.

in highly intense light irradiation and good stability in air.

Figure 2 shows the side-view of the present cell. The CdS thin film (≈1000 Å) was cathodically deposited onto the transparent ITO glass substrate from dimethyl sulfoxide (DMSO) solution containing 0.055 mol $dm^{-3}$ $CdCl_2$, 0.19 mol $dm^{-3}$ sulfur at a current density of 3 $mA/cm^2$ at 110 °C for 2 min.[5] To obtain homogeneous CdS film the addition of tetrabutylammonium tetrafluoroborate (0.1 mol $dm^{-3}$) was important as supporting electrolyte. The CdS thin film thus obtained is transparent in the wavelength region longer than 500 nm, providing the window for the absorption of the pigments. The 2,9-dimethyl quinacridone (Fig.1, Commercially available Hostaperm Pink E, Hoechest Co.) films onto it were prepared by two methods; (1) vacuum deposition film (≈2000 Å) and (2) dispersion film (≈0.5 μm) by spin coating technique from a slurry containing the pigment and polycarbonate binder resin by weight ratio of 3:1 in dichloromethane. The Au electrode was provided by vacuum evaporation on it to form ohmic contact. The effective area of the cell was 1 $cm^2$.

Figure 3 shows the typical J-V characteristics of the pigment-evaporated cell. In the dark, the cell shows good rectification of greater than 150 at ±1 V in the ratio of forward to reverse currents. By fitting to Schockley equation the ideal factor of n = 3.1 and reverse saturation

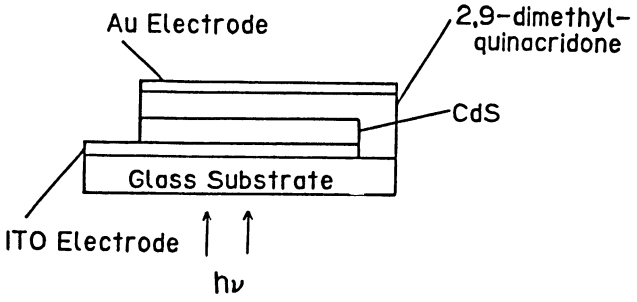


Fig. 2. Side view of the sample cell.

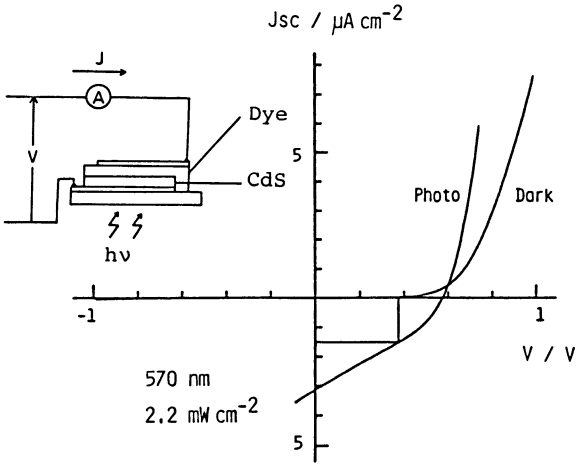


Fig. 3. Dark and photo J-V characteristics of an ITO/CdS/2,9-dimethyl quinacridone/Au cell for light incident on the ITO side.

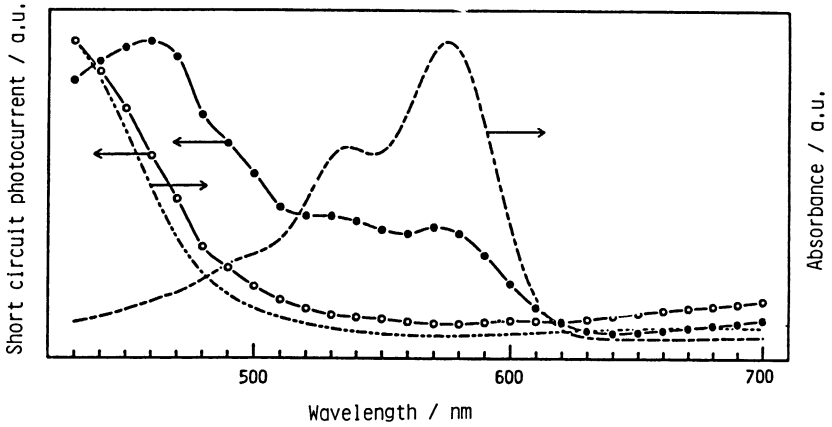


Fig. 4. Action spectra of short circuit photocurrent of an ITO/CdS/2,9-dimethyl quinacridone/Au cell for light incident on the ITO (●) and Au (○) side. Solid state absorption spectra of 2,9-dimetyl quinacridone (---) and CdS (----).

current of $2.5 \times 10^{-10}$ A/cm$^2$ were obtained. Under irradiation (570 nm, 2.2 mW/cm$^2$), the cell exhibited the photovoltaic effect so as to be positive for Au electrode. It should be noted that the fairly large fill factor is one of the characteristics of the present cells, being 0.41 and 0.32 for evaporated and dispersion films, respectively. As can be seen from the action spectra of short-circuit photocurrent shown in Fig.4, the mask effect due to the absorption of the pigment was clearly observed for the irradiation through Au electrode, which indicates that p-n junction is formed at the interface between the pigment as p-type and CdS as n-type material.

In Table 1 is summarized the performance of the present cells for 570 nm monochromatic light irradiation, which is absorption maximum of the pigment, and for 71 mW/cm$^2$ white light irradiation through the CdS window. The pigment-evaporated cell showed fairly high device conversion efficiency of 0.07% for monochromatic light and 0.04% even under white light irradiation. This lowering for the white light irradiation is only due to the narrow absorption band of the pigment but not due to non-linearity of the efficiency to the light intensity as often can be seen in the most of organic solar cells. Actually, as shown in Fig. 5, the short-circuit photocurrent gives the linear relation to the light intensity over wide range from 0.001 to 100 mW/cm$^2$ and its efficiency does not show any significant decrease under practical light intensity. This is another characteristics of the present CdS/quinacridone pigment cells.

Table 1. Cell performance

| Sample | Light (L/mW cm$^{-2}$) | Jsc/μA cm$^{-2}$ | Voc/V | f.f. | η/% |
|---|---|---|---|---|---|
| Vacuum-evaporated Film | 570 nm (2.2) | 6.7 | 0.52 | 0.41 | 0.07 |
| | White ( 71) | 127 | 0.61 | 0.32 | 0.04 |
| Dispersion Film | 570 nm (2.2) | 4.8 | 0.60 | 0.32 | 0.04 |
| | White ( 71) | 47 | 0.63 | 0.29 | 0.01 |

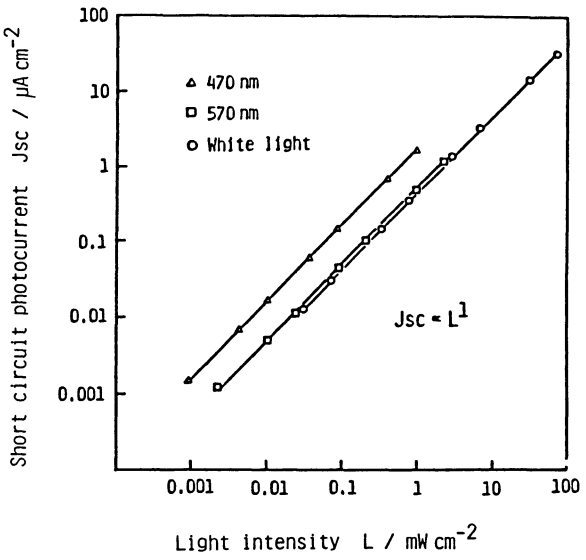


**Fig. 5. Light intensity dependence of short circuit photocurrent of an ITO/CdS/2,9-dimethyl quinacridone/Au cell.**

When the pigment-evaporated and dispersion cells are compared, the latter gives a little poor photovoltaic properties, particularly in fill factor as shown in Table 1. This seems to be due to the high resistance of the pigment-dispersion film. Estimating from J-V characteristics, higher series resistance by one order was obtained, 26 kΩ for the evaporated film and 110 kΩ for the dispersion film, respectively. Taking it into account for dispersion film to give not so low conversion efficiency of 0.01% under the practical light intensi-

ty, the advantage of easy fabrication in dispersion films will be still useful for the practical application.

The third characteristics of the present cell is in the point of improvement of lifetime. As shown in Fig. 6, the durability of the present cell was tested by monitoring the short-circuit photocurrent under continuous irradiation of 15 $mW/cm^2$ white light. Over a month the photocurrent did not show any decrease but the tendency to increase slightly during irradiation. Thus, replacing low work-function metal electrode in Schottky-type organic cell by n-type CdS, the better photovoltaic properties were obtained. It should be noted here that the photovoltaic properties remained unchanged for the sample kept in the ordinary environment after several months from its fabrication. The present pigment evaporated cell could continuously drive a LCD clock (5 μW, 1 V driven) by connecting two cells (active area: 1 $cm^2$) in series under room fluorescent lamp.

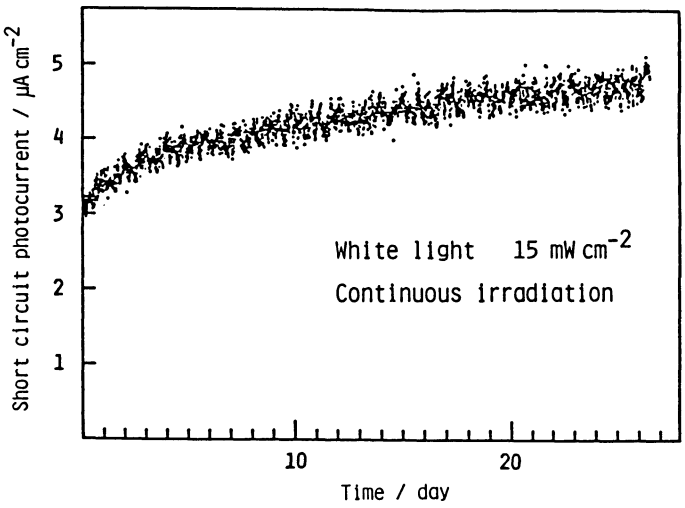


Fig. 6. Life time test monitored by short circuit photocurrent.

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