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ORGANIC SOLAR CELL FABRICATION USING QUINACRIDONE PIGMENTS

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The photovoltaic characteristics of quinacridone pigments dispersed in the polymer binder in the Schottky type solar cells are reported. The relatively high power conversion efficiency of 0.34% has been obtained at 550 nm and 200 $\mu W \cdot cm^{-2}$ with a light exponent of 0.6 - 0.7 for the short circuit photocurrent.

A large number of studies have been made on the photovoltaic effects in organic photoconductors for converting solar radiation directly into electrical energy since a high power conversion efficiency was reported in merocyanine dye.[1] In recent years, phthalocyanine pigments have been investigated extensively as photoactive materials in organic photovoltaic cells.[2-5] The much attention to such pigments is mainly due to their high absorption in the visible region and their chemical stability as well as their good photovoltaic properties. It seems to be the right way to search chemically stable pigments for new photovoltaic materials.

In the present letter, the photovoltaic characteristics of the Schottky type solar cells using quinacridone pigments as a photoactive material are reported. Relatively high conversion efficiency obtained in the present quinacridone system is convinced to provide a new candidate for organic photovoltaic materials. The qualitative assessment of the solar cell performance for the methyl- and chloro-substituted quinacridone pigments are also presented.

Qunacridone pigments are insoluble in most solvents. In the present work, pigments were dispersed in polymer binder to fabricate thin film on electrode. Commercially available 2,9-dimethyl quinacridone (Fig.1, Hostaperm Pink E, Hoechst Co.) was first used as a quinacridone pigment. Thin film (≈0.2 μm thick) on an In_2O_3 coated glass electrode was prepared by the spinning coat from the slurry of the ball-milled pigments with the polymer binder (pigment : polymer = 0.5:1 - 3:1 in weight) in dichloroethane or tetrahydrofuran. After dried, an Al electrode was evaporated on the free film surface to form a sandwich-tpyed photovoltaic cell as shown in Fig. 2. As the polymer binder, polycarbonate (Panlite L1250, Teijin Co.) and

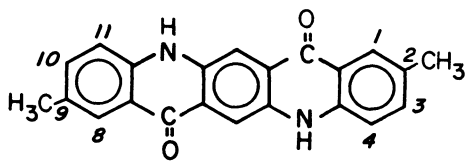


Fig. 1. 2,9-Dimethyl quinacridone.

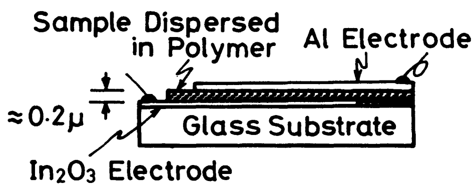


Fig. 2. Side-view of a photovoltaic cell.

polyester (Vylon 200, Toyobo Co.) resins were chosen to give the uniform dispersion of the pigments. The photovoltaic properties were measured using an electrometer (TR-8651, Takedariken Co.) by irradiating monochromatic light (550 nm) from a 250 W metalhalide lamp (Toshiba Co.) on a transparent Al electrode (front illumination). The incident light power was monitored by a thermopile (Eppley Lab. Inc.).

The power conversion efficiency η'(%) referred the conversion efficiency for the light energy which is transmitted through the Al electrode in the following equation,

$$\eta'(\%) = \frac{(J_{SC})\cdot(V_{OC})\cdot(ff)}{(I_0)\cdot(T_{Al}(\%))} \times 100$$

where J_{sc} is the short circuit photocurrent, V_{oc} the open circuit voltage, ff the fill factor, I_0 the incident photon power, and T_{Al}(%) the transmittance of the evaporated Al electrode.

Figure 3 shows the spectral dependence of the short circuit photocurrent J_{sc} and absorption spectrum of the pigment dispersed in a thin polymer film. The action spectrum on irradiation through the Al electrode gave a maximum near at 550 nm, well-corresponding to the absorption spectrum of the pigment, while that on irradiation through the In_2O_3 electrode exhibited the antibatic relation to the absorption spectrum due to the filter effect of the pigment. These results indicate that the active region exists in the pigment layer at the Al electrode interface.

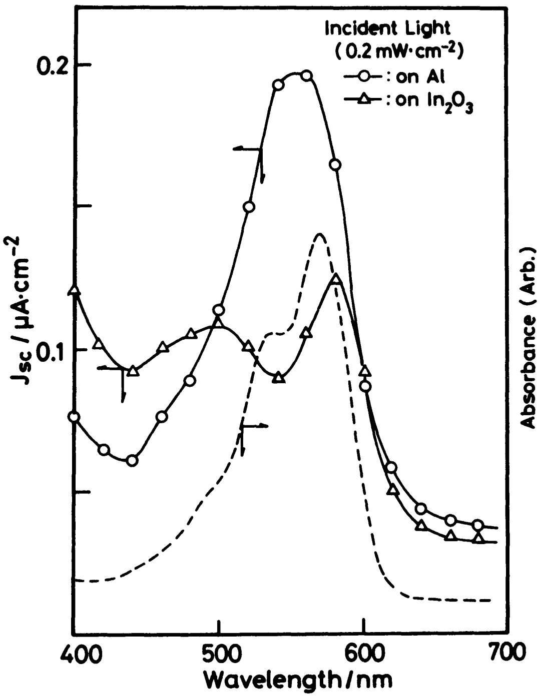


Fig. 3. Spectral dependence of the short circuit photocurrent J_{SC}. The dashed curve represents absorption spectrum of the pigment.

The typical J-V curves measured in the dark and under front illumination for an Al/pigment (2.5:1 in wt) in polymer/In_2O_3 cell are represented in Fig. 4. In the dark the cell exhibited a well-defined rectification as observed in the metal-free phthalocyanine Schottky diodes.[2)] The reverse saturation current was in the order of $J_0 \approx 10^{-8}$ A·cm^{-2}. Under light illumination (550 nm, 2.7 mW·cm^{-2}, T_{Al}(%) = 17.0), the short circuit photocurrent J_{sc} = 1.58 μA·cm^{-2} and the open circuit voltage V_{oc} = 1.15 V were obtained. The fill factor was ranged within 0.25 - 0.3. Thus, the relatively high power conversion efficiency η' = 0.34% was obtained.

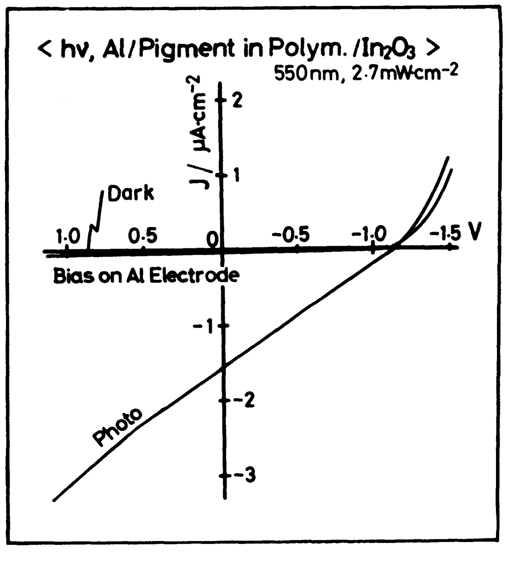


Fig. 4. The typical J-V characteristics in the dark and photo for a Al/Pigment(2.5:1 in wt) in ploymer/In_2O_3 cell.

The short circuit current as a function of the light intensity I followed the relation $J_{sc} = I^n$ with n = 0.6 - 0.7 for the intensity order order of I ≈ 0.1 $mW \cdot cm^{-2}$ througth the Al electrode at 550 nm as shown in Fig.5.

In order to confirm the Schottky barrier formation at the interface of the Al electrode, the low frequency capacitance measurements were carried out at a frequency of f = 0.0125 Hz using the method described by Twarowsky and Albrecht.[6] Figure 6(a) shows the experimental result of the dark current I as a function of the triangular applied voltage V. The capacitance at a given voltage is calculated from the current difference ΔI(V) for the up-going and down-going voltage sweep at that voltage:

$$C(V) = \Delta I(V)/8V_0 f$$

where V_0 is the amplitude of the applied voltage. As shown in Fig. 6(b), the C values plotted as C^{-2} against V gave a good linear relation, indicating the formation of the Schottky depletion region. The biuld-in potential V_{bi} = 0.83 V was obtained from the intercept with the V axis, and from the slope of the line the charge carrier density N was estimated to be the order of N ≈ 10^{17} cm^{-3}, assuming the dielectric constant ε = 4 of the material.[7] The C value at zero bias (V = 0) gave the width of the depletion region W ≈ 200 Å, according to the relation of $C = \varepsilon_0 \varepsilon / W$ (ε_0 : the permittivity of free space). These values are in good correspondence to the values reported in the metal-free phthalocyanine Schottky diodes.[2]

Figure 7 shows the effects of the dispersion ratios of the pigment on the photovoltaic properties. The values of J_{sc} and η' were averaged in five samples at least. Near the dispersion ratio of 2:1 in the polycarbonate resin the η' exhibited a maximum value. The polycarbonate resin as the polymer binder gave the small deviation in the photovoltaic characteristics from sample to sample and the relatively good quality of the thin film rather than other polymer binders.

Table 1 shows the qualitative assessment

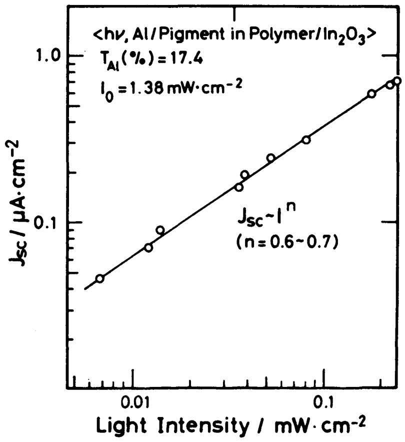


Fig. 5. Light intencity dependence of J_{sc}.

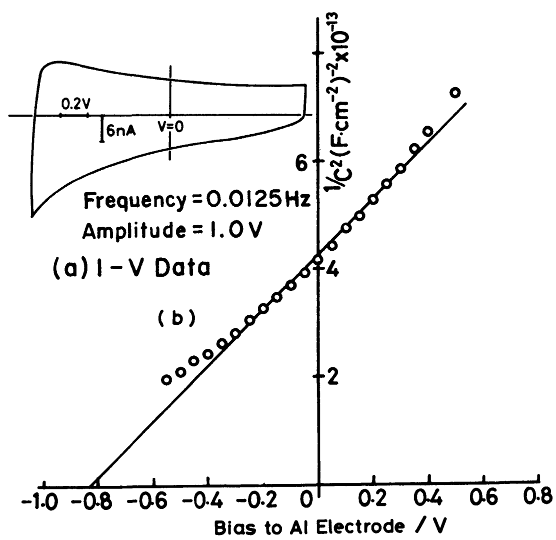


Fig. 6. (a)I-V curve for the triangular voltage sweep, and (b)Mott-Schottky plot.

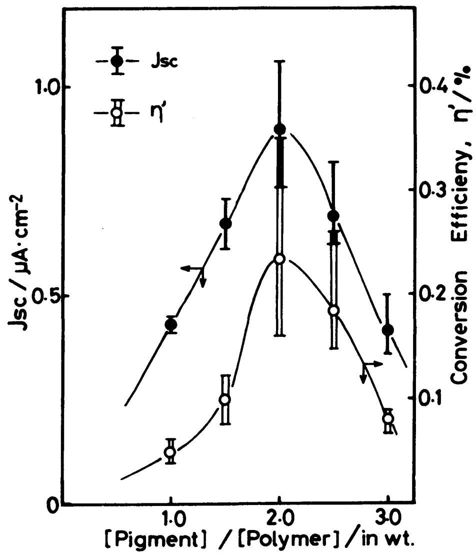
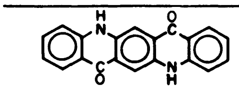
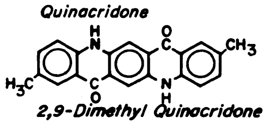
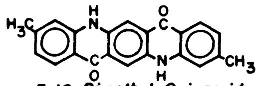
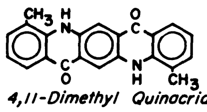
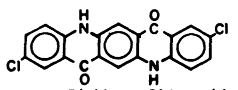
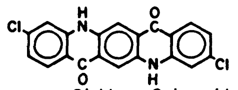


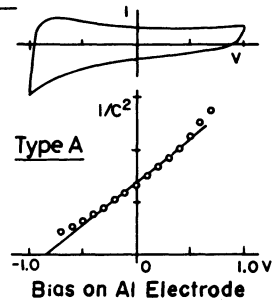
Fig. 7. J_{sc} and η' as a function of the dispersion ratio of the pigment. Front illumination at 550 nm, 1.5 $mW \cdot cm^{-2}$, $T_{Al}(\%)_{a.v}$=10.

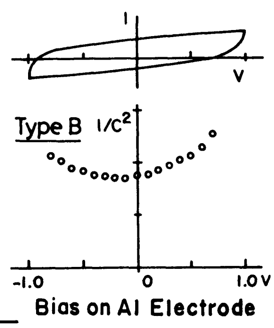
of the cell performance for several kinds of the quinacridone derivatives. Two groups were found in the cell performance depending on the substituents and their positions. Non-, 2,9-dimethyl, and 3,10-dimethyl substituted quinacridones exhibited the relatively high performance, each giving a linear relation as Type A in the Mott-Schottky plot. On the other hand, 2,9- and 3,10-dichloro or 4,11-dimethyl substituted quinacridones were in another group, in which no straight line suggesting the Schottky barrier formation was obtained as Type B, and the low power conversion efficiency was obtained. At present, 2,9-dimethyl qunacridone seems to be fairly good by all accounts.

Thus, the result that the quinacridone pigments attained the relatively high performance will provide a new material group in organic photovoltaic materials.

Table 1. The cell performance for several quinacridone derivatives

Pigment	$\eta'(\%)_{a.v.}$	Capacitance Measurement	Peformance
 Quinacridone	0.05 – 0.1	Type A	Good
 2,9-Dimethyl Quinacridone	0.2 – 0.4	Type A	Good
 3,10-Dimethyl Quinacridone	0.1 – 0.2	Type A	Good
 4,11-Dimethyl Quinacridone	0.01 – 0.05	Type B	Poor
 2,9-Dichloro Quinacridone	≈ 0.0	Type B	Poor
 3,10-Dichloro Quinacridone	≈ 0.01	Type B	Poor





Measured on front illumination at 550 nm, 1.5 mW·cm^{-2}, $T_{Al}(\%)_{a.v}$ = 10.

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References

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6) A.J. Twarowski and A.C. Albrecht, J. Chem. Phys., 70, 2255(1979).
7) Assumed from the value of ε = 4.55 in the metal-free phthalocyanine pigment.

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