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폴리아닐린 MIS 소자의 광기전력 성질

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Photovoltaic Properties of Polyaniline MIS Cells

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요 약 : 아닐린을 전기화학적으로 산화시켜 폴리 아닐린 필름을 제조하고 폴리아닐린과 금속사이에 프라즈마 중합된 폴리(*N,N'*-디페닐-p-페닐렌디아민) (PDP) 박막을 두어 M / PDP / 환원상태의 폴리아닐린 (PA) / Au MIS 소자(여기서, M은 알루미늄 혹은 금)를 제조했다. MIS소자의 광기전력 특성은 출력밀도가 13mW / cm^2인 Xe램프를 광원으로 사용해서 조사했다 : Al / PDP / PA / Au 소자는 에너지 변환효율 0.2퍼센트, 개방단전압 0.42V, 단락광 전류밀도 1.9×10^{-7}A / cm^2, 곡선인자 0.32 그리고 이상인자 3.0의 값들을 얻었다. MIS 소자는 Al / PA / Au MS 소자에 비해 안정된 광기전력 특성을 나타내었다 : Al / PA / Au MS 소자는 6시간 공기중에 노출시킨 결과 광기전력 효과가 소멸되었으나 Al / PDP / PA/Au MIS 소자는 17시간 공기중에 노출시켜도 정류비 55(노출전 99)와 에너지 변환효율 0.07%를 유지했다.

Abstract : Polyaniline film was prepared by electrochemical oxidation of aniline and M / PDP / reduced polyaniline (PA) / Au MIS cells (where, M is either Al or Au) were fabricated by inserting a thin plasma-polymerized poly(*N,N'*-diphenyl-p-phenylene diamine) (PDP) film between polyaniline and a metal. The photovoltaic properties of MIS cells were investigated by using a Xe lamp with an output power density of 13mW / cm^2 as a light source ; a power conversion efficiency of 0.2 percent, a open-circuit voltage of 0.42 V, a short-circuit current density of 1.9×10^{-7} A / cm^2, a fill factor of 0.32 and as ideality factor of 3.0 were estimated for Al / PDP / PA / Au cell. The stability of photovoltaic properties of MIS cell was improved compared with Al / PA / Au MS cells : the photovoltaic effect disappeared after 6 hours of exposure in air for Al / PA / Au MS cell but a rectifying ratio of 55, initially about 99, and a conversion efficiency of 0.07 percent were held even after 17 hours of exposure for Al / PDP / PA / Au MIS cell.

INTRODUCTION

Inorganic materials such as GaAs, InP, Si, and Ge are being used for commercial solar cells because they show the high power conversion efficiency. However, inorganic solar cells did not find a great demand because of high material cost and difficult material processing for cell fabrication. Organic materials such as anthrancene,[1] tetracene,[2,3] copper phthalocyanine,[4,5] magnesium phthalocyanine,[6] zinc phthalocyanine,[7~10] nickel phthalocyanine,[11] metal free phthalocyanine,[9,10,12~14] chlorophyll,[15,16] and merocyanine[17] have received considerable attention for organic solar cells in spite of their low power conversion efficiency because of their material cost, the availability of large film area, and the simple fabrication of photovoltaic device.

Shiozaki et al.[18] have investigated the photovoltaic properties of electrochemically polymerized polyaniline using the MS cell and pointed out the unstability of photovoltaic propertis in ambient conditions.

The present work has been done on the basis that by coating very uniform thin plasma-polymerized film on the polyaniline surface the penetration of oxygen and / or moisture into polyaniline film can be prohibited or delayed, and consequently the long-term stability of photovoltaic properties of polyaniline in ambient conditions be obtained.

EXPERIMENTAL

Visible Absorption Spectra

The visible absorption spectra of PA films which were electrodeposited on NESA(tin oxide) quartz glass were recorded with a Hitachi 557 visible spectrometer.

Photovoltaic Measurements

Photo current-voltage characteristics were measured using an electrometer and a DC voltage supply or a function generator as in the preceding article. The light source was a Xe lamp(Using Denki, UXL-500D) with an output power density of 13mW / cm^2. The weaker light intensties were obtained by using a set of filters (Toshiba ND Filter). Transmittance of each filter of the set was 1%, 10%, and 30%, respectively. The light intensity was measured with a powermeter (model 360001, Scientech Co.) and a microelectrometer (AM 1001, Okura Electric Co.). The spectral response was investigated by using a Nikon G 250 monochromator.

Fabrication of Sandwich Cells

The details on the experimental procedure of cell fabrication and the configuration of sandwich cell were reported by the authors in the preceding paper.

RESULTS AND DISCUSSION

The photovoltaic action spectrum with the incident radiation through semitransparent aluminum electrode for an Al / PA / Au cell along with the visible absorption spectra of polyaniline films was shown in Fig. 1. The reduced (dedoped) polyaniline film has two current peaks at 336 and 645 nm as shown in Fig. 1-a. The reduced film (Fig. 1-b) has an absorption peak at 336 nm, while the oxidized film (Fig. 1-c) has a broad absorption peak at 686 nm. Ideally the action spectrum of the polymer should resemble the absortion spectrum. However, the action spectrum does not closely match either of both absorption spectra (b) and (c). The strong current peak at 336 nm matched well with the absorption peak of the reduced film, but the weak current

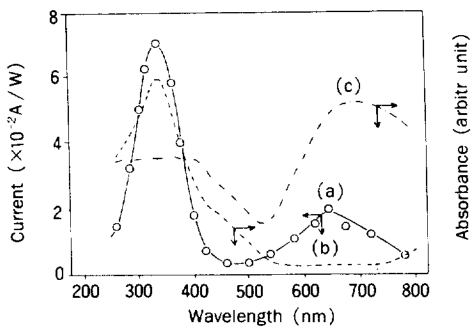

Fig. 1. Action spectrum of the short-circuit photocurrent for Al / PA / Au cell(a), absorption spectra for reduced polyaniline (b) and oxidized polyaniline (c) films.

peak at 645 nm did not. The weak current peak, however, was located close to the absorption peak of the oxidized film. This disagreement between the action spectrum and the absorption spectrum can not be explained explicitly at the present. When the incident radiation was directed through the gold electrode and it was done even through the aluminum electrode for Al / oxidized polyaniline / Au cell, the photocurrent was not observed. From these results it is suggested that the Schottky barrier is formed between aluminum and reduced polyaniline and polyaniline behaves as a p-type semiconductor.

A photocurrent density-voltage characteristic was shown in Fig. 2. The white light of Xe arc was illuminated through semitransparent aluminum. Photocurrent is defined as an increase of current upon illumination and indicates the presence of free carriers generated by the absorbed photons. The phenomenon of photocurrent involves the processes of absorption of photons within the depletion layer, photogeneration of charge carriers, their separation, diffusion and drift in an applied electric field which sweeps out the electrons and holes in opposite directions. Several fundamental parameters such as the open-circuit voltage, the short-circuit current density, the fill factor(defined as the maximum power output of the cell devided by the product of the open-circuit voltage and the short-circuit current), and the power conversion efficiency are extracted from Fig. 2. They are 0.42 V, $1.9\times10^{-7}A/cm^2$, 0.32, and 0.20 percent, respectively. Since the incident light must pass through the aluminum electrode, which has a transmittance of about 0.1% for the cells discussed here, the power conversion efficiency was calculated using the transmitted light power instead of P_{in} in the following equation[19]:

$$\eta = I_{sc}V_{oc}FF / P_{in}$$

The photovoltaic properties are strongly dependent on the light intensity. Figures 3, 4, and 5 show log-log plots of the short-circuit current density, the open circuit voltage, and the conversion efficiency versus the light intensity, respectively. The short-circuit current density is proportional to the light intensity, while the open-circuit voltage and the conversion efficiency increase linearly

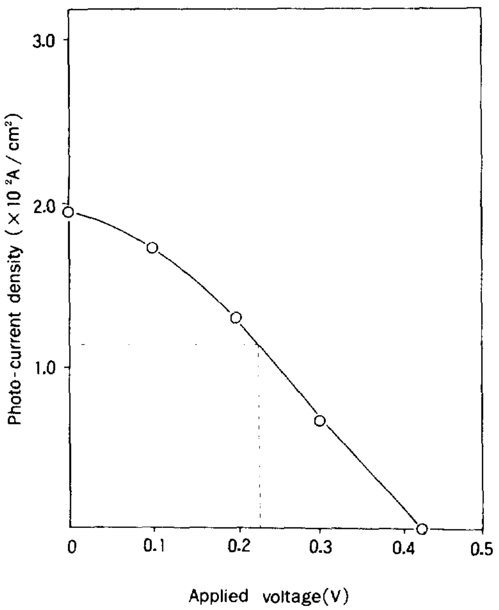

Fig. 2. Photocurrent density-voltage characteristic for Al / PDP / PA / Au cell.

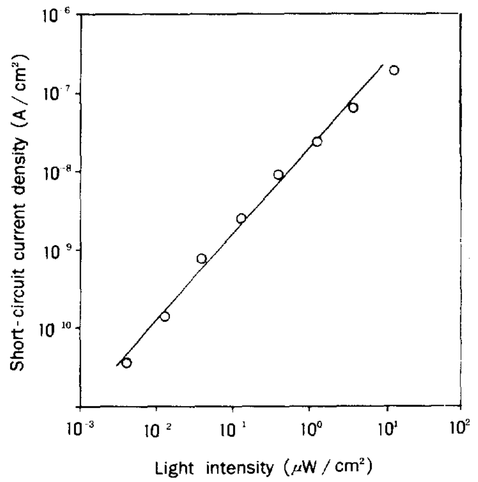

Fig. 3. Log-log plot of short-circuit current density vs. light intensity for Al / PDP / PA / Au cell.

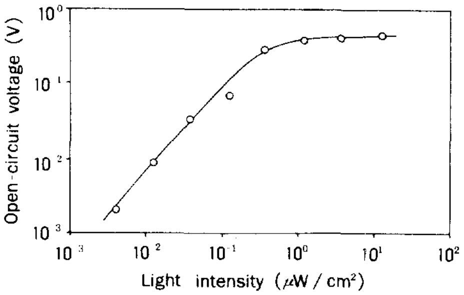

Fig. 4. Log-log plot of open-circuit voltage vs. light intensity for Al / PDP / PA / Au cell.

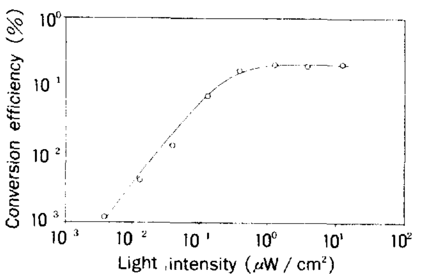

Fig. 5. Log-log plot of conversion efficiency vs. light intensity for Al / PDP / PA / Au cell.

upto a light intensity of $0.39 \mu W / cm^2$ and have the limitting values of about 0.40 V and 0.20 percent, respectively.

In contrast with the other conducting polymers, the electroactive properties of polyaniline are not destroyed upon exposure in air. However, the photovoltaic properties change for the worse. The rectification ratio versus the air exposure time for MS (Al / PA / Au) and MIS (Al / PDP / PA / Au) cells was shown in Fig. 6. The rectification ratio was obtained by deviding the forward biased current with the reverse biased current at the bias voltage of 2.0 V.

Fig. 7 shows the power conversion efficiency vs. the exposure time in air for MS and MIS cells.

As shown in Figures 6 and 7, in the case of MS cell the photovoltaic properties have disappeared after 6 hours of exposure, while in the case of MIS cell a rectification ratio of about 55 and a conversion efficiency of 0.07 percent, initially about 99 and 0.2 percent, respectively, are maintained

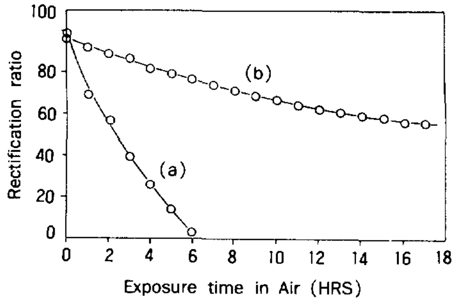

Fig. 6. Rectification ratio vs. exposure time in air for Al / PA / Au (a) and Al / PDP / PA / Au (b) cells.

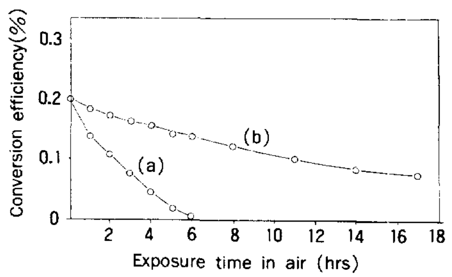

Fig. 7. Power conversion efficiency vs. exposure time in air for Al / PA / Au (a) and Al / PDP / PA / Au cell.

even after 17 hours of exposure. The stability of the electrochemically polymerized films in ambient conditions depends very much on the oxidation state. The films are sensitive to the oxygen in the air and the reduced films are particularly unstable. Reduced polythiophene films prepared by electrochemical polymerization became increasingly oxidized and showed a decrease in the contact angle with water.[20] The reduced (dedoped) polyaniline film is also susceptible to oxidation by the air and the polyaniline film containing even a trace amount of residual dopant can absorb the moisture from the atmosphere due to the hydrophilic property of polyaniline and sulfuric acid. From these results it is strongly suggested that by placing thin PDP film between polyaniline and aluminum layers the oxidation and / or moisture absorption of polyaniline (especially in the reduced state) film are / is delayed and consequently the photovoltaic effects are kept relatively insensitive to exposure to ambient conditions. It, therefore, appears that the careful encapsulation and handling of polyaniline in the extremely dry and oxygen-free atmosphere may reduce the instability and keep the electrical and the photovoltaic properties for a long term.

CONCLUSION

From the results of the photovoltaic properties of electrochemically polymerized polyaniline, the following conclusion can be drawn :

1) The photovoltaic action spectrum with the incident radiation through semitransparent Al electrode for the Al / PA / Au cell did not match the absorption spectrum.

2) A open-circuit voltage of 0.42 V, a short-circuit current density of 1.9×10^{-7}A / cm^2, a fill factor of 0.32, and a power conversion efficiency of 0.20 percent are estimated from a photocurrent density-voltage characteristic.

3) The short-circuit current density is propor tional to the light intensity but the open-circuit voltage and the conversion efficiency show the saturation values of 0.40 V and 0.20 percent at a light intensity of 0.30μW / cm^2.

4) The photovoltaic properties of Al / Pa / Au cell disappear after 6 hours of exposure to the air but the Al / PDP / PA / Au cell maintained a rectification ratio of 55, initially about 99, and a conversion efficiency of 0.07 percent even after 17 hours of exposure.

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