NOTES

Photo-Current Characteristics of Two-Layered Organic Thin Films Prepared by Plasma Polymerization

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Organic thin film devices attract special attention for potential to replace inorganic semiconductors in the development of large-area, lightweight, and inexpensive light-electricity conversion devices.^{1–3} Plasma polymerization is a unique technique for forming polymer thin films from almost all organic gas vapors. Extensive investigation of the electrical properties of plasma polymerized films using a wide variety of organic^{4–9} and metal containing^{10–13} monomers has been carried out and interesting results have been achieved. Studies on the photo conduction of plasma polymeric films have also extensively been carried out.^{14,15}

Tetracyanoquinodimethane (TCNQ) and its derivatives are strong electron acceptors, and investigation of their properties is of interest since a number of stable charge transfer complex crystals with high electrical conductivity can be formed from them by combining with a variety of electron donors.

We previously reported that TCNQ can be polymerized by plasma polymerization at 13.56 Hz to give polymeric films^{16,17} with conductivity from 10^{-10} to 10^{-6} S cm⁻¹. Infrared, ultraviolet, and X-ray photoelectron spectroscopy were used to characterize structure, and the results as well as those from electrical measurements confirmed that a

conjugated structure with delocalized π -electrons is formed in the films.

This paper reports the photo-current characteristics of two-layered organic thin films composed of plasma-polymerized TCNQ (p.p.TCNQ), copper phthalocyanine (CuPc) (p.p.CuPc), *N*-[3-(dimethylamino)propyl] acrylamid (DMAPAA) (p.p.DMAPAA), and 2-vinylpyridine (VP) (p.p.VP) or solution-casted polyethyleneimine (PEI) film (c.PEI). A two-layered polymeric cell shows rectification phenomena and sensitive photo responses presumably due to the formation of depletion layer at the interface of the two layers.

EXPERIMENTAL

TCNQ (courtesy from Osaka Organic Chemical Industry Ltd.,) was recrystallized at 60°C in acetonitrile. DMAPAA was distilled at 120°C under reduced pressure (532 Pa) before use. PEI (approximate molecular weight 70×10^3 mol g⁻¹ with branches, Nippon Shokubai Kagaku Kogyo) was reagent grade and used without further purification. Purified CuPc was provided by Toyo Ink Co., Ltd.

Plasma polymerization of TCNQ, CuPc, DMAPAA, and VP were carried out using plasma apparatus with a radio-frequency generator operating at 13.56 MHz. During

polymerization, the system was kept under a pressure of 0.7 Pa, TCNQ and CuPc were heated to 380°C in order to obtain an organic vapor. TCNQ and CuPc were polymerized with a discharge power of 50 W and discharge duration of 45 min. The polymerization of DMAPAA was carried out at room temperature with a discharge power of 100 W and discharge duration of 15 min. PEI film was prepared by casting 10% aqueous solution onto ITO or glass substrate and drying *in vacuo* at about 140°C for 24 h. Film thickness was 0.2–1.4 μm .

Opto-electrical properties were measured by a sandwich cell interposed between ITO and Au electrodes. Photo response was examined by irradiating 750 W tungsten lamp through an IR cut-off filter from a distance of 15 cm and illuminance on the surface of sample was 600 lux from ITO side. Film conductivity was measured with coplanar cells.

RESULTS AND DISCUSSION

Plasma polymerized films prepared from TCNQ and DMAPAA were brownish yellow and smooth with a thickness of 130–200 nm. Electrical conductivities of p.p.TCNQ, p.p.DMAPAA monolayer films, and the conductivity of p.p.DMAPAA/p.p.TCNQ and c.PEI/p.p.TCNQ two-layer films are summarized in Table I.

Cells fabricated by the procedure in the experimental section exhibited rectifying and photo response effects. Figure 1 shows typical current-voltage characteristics for the ITO/c.PEI/p.p.TCNQ/Au cell with an Au electrode

positive for the cell. As seen in the figure, the cell has rectifying behavior and the rectification ratio at 5 V was 32. A similar study was also made using the ITO/p.p.TCNQ/Au monolayer but showed no rectification.

Thus, the observed rectifying behavior of the two-layer cell is not due to the formation of

Figure 1. Dark current-voltage characteristics of c.PEI/p.p.TCNQ bilayer film. Au is the positive electrode for the cell.

Figure 2. Short circuit photocurrent of ITO/p.p.-DMAPAA/p.p.TCNQ/Au (a), ITO/c.PEI/p.p.TCNQ/Au (b), and ITO/p.p.TCNQ/Au (c) film. Au is the positive electrode for the cell.

Table I. Electric conductivity for monolayer and two-layer films

Sample	Conductivity/ Scm^{-1}
p.p.TCNQ	6×10^{-7}
p.p.DMAPAA	4×10^{-5}
p.p.DMAPAA/p.p.TCNQ	3×10^{-6}
c.PEI/p.p.TCNQ	7×10^{-5}

an organic-metal junction at the p.p.TCNQ/Au interface, but to the formation of an organic donor/organic acceptor heterojunction at the interface of c.PEI/p.p.TCNQ.

Figure 2 shows the short circuit photo current J_{sc} of the two-layer cell, ITO/p.p.DMAPAA/p.p.TCNQ/Au and ITO/c.PEI/p.p.TCNQ/Au. The monolayer cell ITO/p.p.TCNQ/Au is also shown in the same figure. The two-layer cell showed fast and stable photo response compared with the monolayer cell which had a small and unstable photo response. Photo currents of ITO/c.PEI/Au and ITO/p.p.DMAPAA/Au monolayer cell showed no response to light, probably since the ITO electrode and Au electrode each have relatively high work function and make ohmic or almost ohmic contact with organic films. Two-layered cells prepared by vacuum evaporation at 10^{-3} Pa showed no photo response. Similar results were obtained by fabricating cells with structures of ITO/p.p.CuPc/c.PEI/Au and ITO/p.p.CuPc/p.p.VP (Figure 3).

The above results could be explained on the basis of a donor acceptor model. TCNQ is an electron acceptor and amino derivatives are electron donors. At the TCNQ/Amino derivative interface, conduction and valence band edges of the two organic compounds are bent down and a heterojunction barrier similar to

a p-n junction may be formed at the interface corresponding to TCNQ as p- and amino derivatives as n-type semiconductors. When the light was turned on, excitons were generated in the PEI or DMAPAA layer and with the aid of a bending band, excitons can easily be injected into the TCNQ layer and show extensive photo response. Photo voltaic power conversion efficiencies of the two-layer cells were about $10^{-6}\%$. Such low power conversion efficiency presumably results from large internal resistance and high trap density of the present cells. The transient spike-like photo current behavior in Figures 2 and 3 would indicate that the lifetime of an exciton is very short, possibly due to the trapping effect. The fact that only the two layer cells made of p.p.TCNQ showed photoresponse suggests that the energy band of p.p.TCNQ is split into a broad multilevel mini-band due to polymerization. The mini-band functions as an acceptor and makes TCNQ behave as a p-type semiconductor. Vacuum evaporated TCNQ is like an intrinsic semiconductor without acceptor to accept electrons and this may explain why two layer cells made of vacuum evaporated TCNQ do not show a heterojunction similar to p-n junction.

Figure 4 shows the dependence of photo

Figure 3. Short circuit photocurrent of ITO/p.p.CuPc/p.p.VP/Au (a), ITO/p.p.CuPc/c.PEI/Au(b), and ITO/p.p.CuPc/Au (c) films. Au is the positive electrode for the cell.

Figure 4. Dependence of photocurrent density on the thickness of PEI film. Open circles: short circuit photocurrent density (no bias). Closed circles: photocurrent density at bias voltage of -10V. Au is the positive electrode for the cell.

current density of ITO/c.PEI/p.p.TCNQ/Au two-layer cell on the thickness of PEI film at constant thickness of TCNQ film. The Au electrode is positive for the cell in the measurement. As seen in the figure, photo voltaic current density without bias and photo current density with bias of -10 V increased with decrease of thickness, and when the thickness of PEI decreased to zero, corresponding to the TCNQ monolayer cell, it showed extremely small photo response compared to the two-layer cell. The same was observed for the ITO/p.p.DMAPAA/p.p.TCNQ/Au cell but the value of the photo current of this film was smaller than that of the ITO/c.PEI/p.p.TCNQ/Au cell. This might be the direct evidence that the polymeric donor-polymeric acceptor interface dominates the electrical and photoelectric characteristics of the two-layered film.

REFERENCES

1. C. W. Tang, *Appl. Phys. Lett.*, **48**, 183 (1986).
2. M. Inoue, H. Morita, Y. Takai, T. Mizutani, and M. Ieda, *Jpn. J. Appl. Phys.*, **27**, 1059 (1988).
3. K. Uehara, K. Takagishi, and M. Tanaka, *J. Appl. Polym. Sci.*, **35**, 1759 (1988).
4. A. Bradley and J. P. Hammes, *J. Electrochem. Soc.*, **110**, 15 (1963).
5. J. Boonthanom and M. White, *Thin Solid Films*, **24**, 295 (1974).
6. A. Bradley, *Trans. Faraday Soc.*, **61**, 773 (1965).
7. W. A. Pliskin, *J. Vac. Sci. Technol.*, **14**, 1064 (1977).
8. D. Ristow, *J. Mater. Sci.*, **12**, 1411 (1977).
9. M. Yamada, S. Hattori, and S. Morita, *Jpn. J. Appl. Phys.*, **21**, 10 (1982).
10. Y. Osada and K. Yamada, *Thin Solid Films*, **151**, 71 (1987).
11. J. P. Gong, Y. Kagami, K. Yamada, and Y. Osada, *Bull. Chem. Soc. Jpn.*, **63**, 1578 (1990).
12. A. Mizumoto and Y. Osada, *J. Appl. Phys.*, **59**, 1776 (1986).
13. Y. Osada, Q. S. Yu, H. Yasunaga, F. S. Wang, and J. Chen, *J. Appl. Phys.*, **64**, 1476 (1988).
14. Y. Takai, Y. Hayse, T. Mizutani, and M. Ieda, *J. Phys. D*, **17**, 399 (1984).
15. J. Guastavino and H. C. Bui, *Thin Solid Films*, **27**, 225 (1975).
16. Y. Osada, Q. S. Yu, H. Yasunaga, F. S. Wang, and J. Chen, *J. Appl. Phys.*, **64**, 1476 (1988).
17. Y. Osada, Q. S. Yu, H. Yasunaga, and Y. Kagami, *J. Polym. Sci., Polym. Chem.*, **27**, 3799 (1989).