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Photovoltaic effect in CuTCNQ organic thin films

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Abstract

An experimental study was carried out of photovoltaic effects occurring in the structure Cu/CuTCNQ/ITO(Al). Prototype devices were fabricated by growing CuTCNQ organic thin films directly on a copper substrate and then laying the semitransparent electrodes (glass/ITO or glass/Al) on the CuTCNQ/Cu. By choosing appropriate conditions for formation of the film in the liquid phase, for example solution temperature, growth time and so on, we obtained an open-circuit voltage V_{oc} as high as 2.6 mV, a short-circuit current density J_{sc} of 0.2 $\mu A\,cm^{-2}$, and a fill factor FF of 0.25 for an area of 1.0 cm^2 under 0.7 W illumination by a laser wavelength 488 nm. The photovoltaic effect increased when the structural resistance was raised by decreasing the contact pressure. There were indications that these effects are mainly due to the characteristics of the CuTCNQ thin films.

1. Introduction

The central idea which Carter introduced [1] is that molecular devices could be constructed, usually of organic and polymeric molecules, or of simple aggregations of molecules, using specific techniques which differ from those used until now in producing typical semiconductor devices entirely using photoetching processes. To meet the requirements of developments in molecular electronics, more and more organic and polymeric materials are being tested as functional thin films for fabricating molecular devices. The use of CuTCNQ organic thin films in optical information memories and electrical switches has been reported [2, 3]. In this paper, the photovoltaic effect in CuTCNQ thin films was investigated in the structure Cu/CuTCNQ/ITO(Al), and the conditions of film preparation such as the solution temperature, growth time, etc. were optimized to give better results. This is not only interesting as a scientific curiosity, but also as an attempt to fabricate an optoelectronic information convertible element directly in a device.

2. Experimental details

7,7′,8,8′-tetracyanoquinodimethane(TCNQ) was purchased from Tokyo Chem. & Industrial Ltd. in Japan. A purple copper substrate was chosen as 1 cm × 1 cm copper sheet, and treated by a special process. The selected acetonitrile (CH_3CN) was of spectral purity. Following the method of "spontaneous electrolysis" [3], we placed the Cu sheet horizontally in the vessel containing the CH_3CN solvent with supersaturated TCNQ. The temperature of the TCNQ–CH_3CN solution and the reaction (growth) time could be varied. After the CuTCNQ organic thin films had started to grow directly on the Cu substrates, the CuTCNQ/Cu specimens were removed and then washed with pure CH_3CN solvent. The chemical reaction on the surface of the Cu sheet is [3]

$$\mathrm{Cu + TCNQ \xrightarrow{CH_3CN} CuTCNQ} \tag{1}$$

A semitransparent electrode (ITO or Al)/glass was placed in contact with the CuTCNQ/Cu which had been dried in a vacuum. This cell was then pressed using a pressure block to form the ITO(Al)/CuTCNQ/Cu structure, as shown in Fig. 1. The transmission was about 70% for ITO/glass and 40% for Al/glass at a

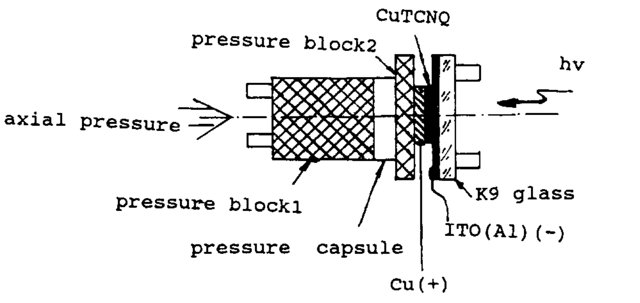

Fig. 1. Schematic diagram of the Cu/CuTCNQ/ITO structure used for photovoltaic measurements.

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wavelength of 488 nm for good electric conductivity. The light source was an Innvova 20 Ar ion laser, and a wavelength of 488 nm was mainly used in our experiments. The photovoltaic voltages were measured with an UJ-59 potentiometer, PZ-89 digital voltmeter, and the currents were measured with an AZ-15 galvanometer, DT-890 DVM. The recorder was a YEW-3600. All photovoltaic measurements were taken at a temperature ranging from 293 to 298 K. The morphology of CuTCNQ thin films was observed by scanning electron microscopy (SEM, S-450, Hitachi Co.).

3. Results and discussion

Cu/CuTCNQ/ITO(Al) prototype devices were constructed by applying pressure to maintain contact between the ITO/(Al) and /CuTCNQ/Cu. The open-circuit voltage V_{oc} *vs.* laser power for values of structural resistance R_1 is shown in Fig. 2, and seems to show that V_{oc} is affected by R_1. The change in structural resistance R_1 was due to changing pressure. R_1 was raised when the contact pressure was decreased. A SEM image of a CuTCNQ thin film is shown in Fig. 3 and from this we can suggest that the semitransparent electrode is only connected to some of the microcrystals. This means that R_1 comprises mainly the electrode resistance R_e, the CuTCNQ film resistance R_f, and the contact resistance R_c, etc. and the cell structure can be described by the equivalent circuit shown in Fig. 4 where R_2 is the leak resistance. R_e was very small and can be ignored. It was apparent that R_f and R_c would both change as a result of pressure and affect the V_{oc} of devices *vs.* laser power. From the equivalent circuit in Fig. 4(b), we can derive a relationship between V_{oc} and R_1 ($R_1 = R_f + R_c$):

$$V_{oc} = V_0 R_2/(R_f + R_c + R_2) \quad (2)$$

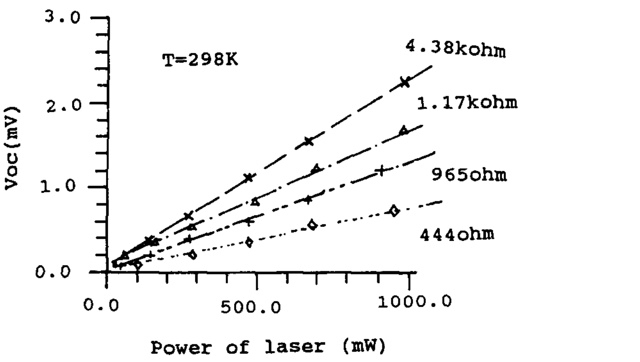


Fig. 2. Characteristics of open-circuit voltage V_{oc} *vs.* laser power in Cu/CuTCNQ/ITO devices with different values of structural resistance.

Fig. 3. SEM image of a CuTCNQ thin film prepared at 298 K for a growth time of 0.5 h.

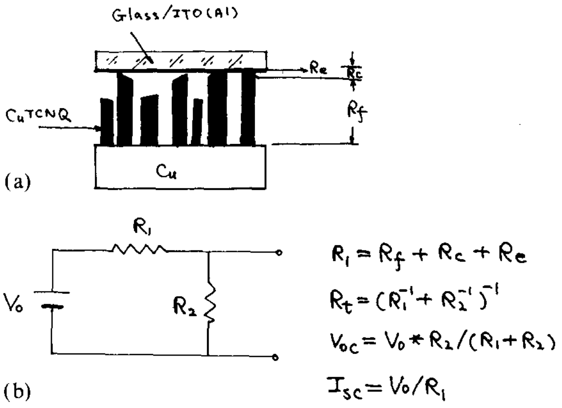


Fig. 4. (a) Diagram of the glass/ITO(Al) connected with the CuTCNQ/Cu, and (b) the equivalent circuit of the cell structure.

In usual cases, R_2 is negligibly larger than R_1 and is a constant. In Fig. 4(a), we see that R_c is increased when the pressure is decreased. Although there is no way of estimating R_f and R_c separately, we can compare the influence of R_c or R_f on V_{oc}. In Fig. 2, it is seen that the V_{oc} is higher when R_1 is increased (when the pressure is decreased). The CuTCNQ film contained lots of microcrystals and an increase in R_c meant that there were fewer microcrystals connected to the ITO(Al) electrode. A decrease in contact pressure caused an increase in R_c and a decrease in V_{oc}, from eqn. (2). However, the results of Fig. 2 do not agree with this explanation. This indicates that the increase in V_{oc} is not due to R_c but is due mainly to a decrease in R_f. The plots of short-circuit current I_{sc} *vs.* laser power for variations in R_1 are similar to Fig. 2. This shows that the change in the photovoltaic effect is intrinsic. Yoshikawa *et al.* reported that pressure in the direction of growth of

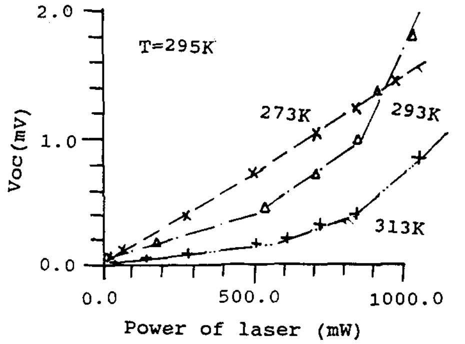
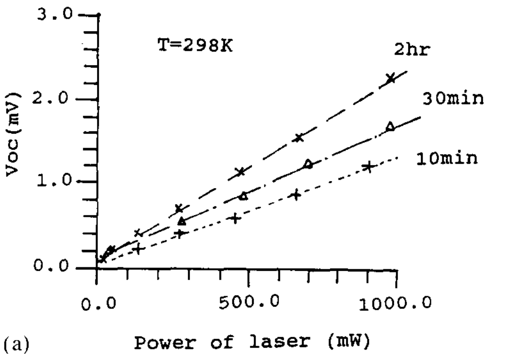
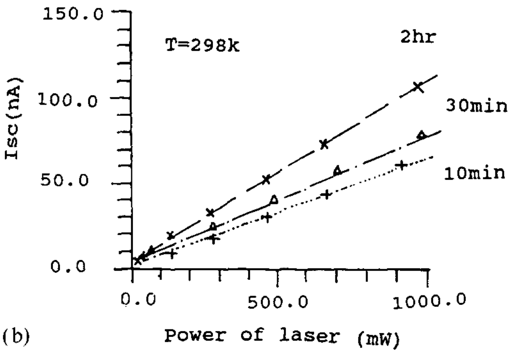


Fig. 5. Plot of V_{oc} *vs.* laser power for different temperatures of CuTCNQ film preparation.



(a)



(b)

Fig. 6. Variation of (a) V_{oc} *vs.* laser power, and (b) short-circuit current I_{sc} *vs.* laser power for different growth times.

TCNQ radical ion salts would redistribute the electronic charge in the realm of the C–C wing bond of TCNQ molecules [4]. It is suggested that variation in R_f could change the properties of the Cu/CuTCNQ/ITO(Al) structure.

In experiments, we found that the preparation of CuTCNQ thin films was affected by the solution temperature, concentration of TCNQ–CH_3CN and growth time, etc. The film was formed of tightly packed individual microcrystals oriented almost along the direction of Cu–TCNQ growth for solution temperatures in the range 273–303 K, whereas microcrystals formed on a Cu substrate at solution temperatures above 303 K were disarranged and even broken. This could explain the preliminary results shown in Fig. 5, and reveals that a temperature in the range 273–303 K is suitable for preparing CuTCNQ with as high a value of V_{oc} as possible. The following films were prepared at 294 K.

For different film growth times, plots of V_{oc} and the short-circuit current I_{sc} *vs.* laser power are presented respectively in Figs. 6(a) and 6(b). With increasing growth time, we obtained thicker CuTCNQ films. Values of 6–7 μm per 2 h, 4–5 μm per 30 min, and 3.5–4 μm per 10 min at 293 K were detected by a surface profile measuring system (Dektak IIA). These facts illustrate that V_{oc} and I_{sc} are increased for thicker CuTCNQ thin films. This is evidence that the photovoltaic effect is due to the CuTCNQ film itself. The photovoltaic phenomenon occurring in both the Cu/CuTCNQ/ITO and Cu/CuTCNQ/Al structures also confirms this. Long-term measurements, *e.g.* exposure for 8 h, did not reveal any variation in current or voltage with measuring time. From these experimental results, we found $V_{oc} = 2.6$ mV, $I_{sc} = 0.2$ μA, and fill factor FF = 0.25. In addition, although instability has often been cited as a major problem for organic materials under exposure, it appeared that the CuTCNQ thin films were very stable under strong irradiation since repeated measurements of the same sample in multiple measurement processes gave very good results.

We tried to give a qualitative explanation of this photovoltaic effect, based on the ionic structure in the ground state of the CuTCNQ molecular aggregation. CuTCNQ is an quasi-one-dimensional system in which the donor Cu and acceptor TCNQ are arranged in separate stacks, determined from X-ray diffraction data for CuTCNQ compared with data for AgTCNQ [5]. When the stacking axis of TCNQ is not parallel to the direction of growth of the thin film (the direction of growth of most microcrystals), CuTCNQ demonstrates weak electret characteristics revealing polarizable phenomena, *i.e.* expression of Cu[+]/CuTCNQ/ITO(Al)[−]. The same polarization under exposure was found in all experiments. This explanation has been borne out by the above facts, *i.e.* the photovoltaic effect increased when the structural resistance was raised by decreasing the contact pressure or by increasing the thickness of the CuTCNQ thin film.

4. Conclusion

We fabricated the sandwich structure Cu/CuTCNQ/ITO(Al) and then observed the photovoltaic characteristics of these structures. It was found that V_{oc} and I_{sc} are affected by several parameters, such as the solution temperature, growth time and so on. A preliminary explanation of this phenomena was given.

Acknowledgments

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References

1 F. L. Carter, *Molecular Electronic Devices*, M. Dekker, New York, 1983.
2 R. S. Potember, R. C. Hoffman, S. H. Kim, K. R. Speck and K. A. Stetyick, *J. Mol. Electron.*, *45* (1988) 15.
3 R. S. Potember, T. O. Poehler and D. O. Cowan, *J. Appl. Phys. Lett.*, *34* (1979) 405.
4 M. Yoshikawa, S. Nakashima and A. Mitsuishi, *Solid State Commun.*, *48* (1983) 13.
5 Z. Z. Gu, J. Z. Liu and Y. Wei, *J. Phys. Chem.*, *97* (1993) 2543.