Nanostructural Effect on Photocurrent Multiplication in Semiconducting Molecular Crystals

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Abstract

A photocurrent multiplication (PCM) effect of large internal gain has been recently reported in films of semiconducting molecular crystals. We have developed a basic technique to control the nanoscale morphology and crystal structure of the films of semiconducting molecular crystals using an ionized cluster beam (ICB) system. We have prepared both Me-PTC and Cu-Pc film specimens on indium tin oxide (ITO) coated glass substrates with optimized crystal structure and surface morphology using this technique. The optimum crystallinity was obtained at an acceleration voltage of 300 V in both materials. The growth plane of the films of Me-PTC was (102) at 298K and (002) at 473K. In the Cu-Pc, only the (002) growth plane was observed. We have also studied the fundamental characteristics of the PCM effect. Photoconductivity was measured at temperatures between 223K and 295K using monochromated light. The observed maximum quantum efficiency of PCM in Me-PTC films was greater than 3,000 at 223K, and greater than 5000 at 298K. The PCM effect has been also observed in Cu-Pc films. The mechanisms of the PCM effect are also discussed.

1. Introduction

A photocurrent multiplication (PCM) effect of large internal gain up to 100,000 has been reported recently in films of semiconducting molecular crystals, and is expected to apply to very sensitive photo-sensing devices [1]. Although details of the multiplication mechanism have not yet been elucidated, the PCM mechanism is correlated with the nanostructure of the films, and the interface between the film and the electrode.

We have developed an ionized cluster beam (ICB) technique to control the crystallinity and growth morphology of thin films of semiconducting molecular crystals, which play a crucial role in determining the performance of these films in optoelectronic applications [2].

In this study, we used thin films of semiconducting molecular crystals of N,N'-Dimethylperylene-3,4:9,10-bis-dicarboximide (Me-PTC), and copper phthalocyanine (Cu-Pc). Me-PTC is known as an electron transporter or n-type semiconducting organic material, and Cu-Pc as a hole transporter or p-type material. We have studied the effects of deposition conditions using an ICB system on crystal structures and on growth morphology of films of these materials. We also studied the fundamental characteristics of PCM in these materials using films prepared under optimized conditions. We have discussed the mechanisms of the PCM based on the current-voltage relations observed with the PCM phenomena.

2. Experimental Procedure

Thin films of both Me-PTC (made by Dainichiseika Color & Chemicals Manufacturing Co. Ltd.) and Cu-Pc (Eastman Kodak Corporation) were deposited in a vacuum of 7x10^{-5} Pa using an ICB technique on a glass substrate coated with indium tin oxide (ITO). The powder of these organic materials was heated to about 673K for 30 min in the vacuum before deposition in order to reduce volatile impurities. An ICB system designed for the deposition of organic materials was used [3]. Both Me-PTC and Cu-Pc were sublimed from a graphite crucible with a nozzle diameter of 0.5 mm, ionized by electron bombardment (Ve=50 V, Ie=60 mA), and accelerated at various voltages ranging from 0 to 2,000 V. The deposition rate, typically 0.2 nm/s, was monitored using an oscillating quartz thickness monitor. The substrate temperature was kept between 298 and 473K. Crystal structures of the films were examined by an X-ray diffraction (XRD) technique, and the

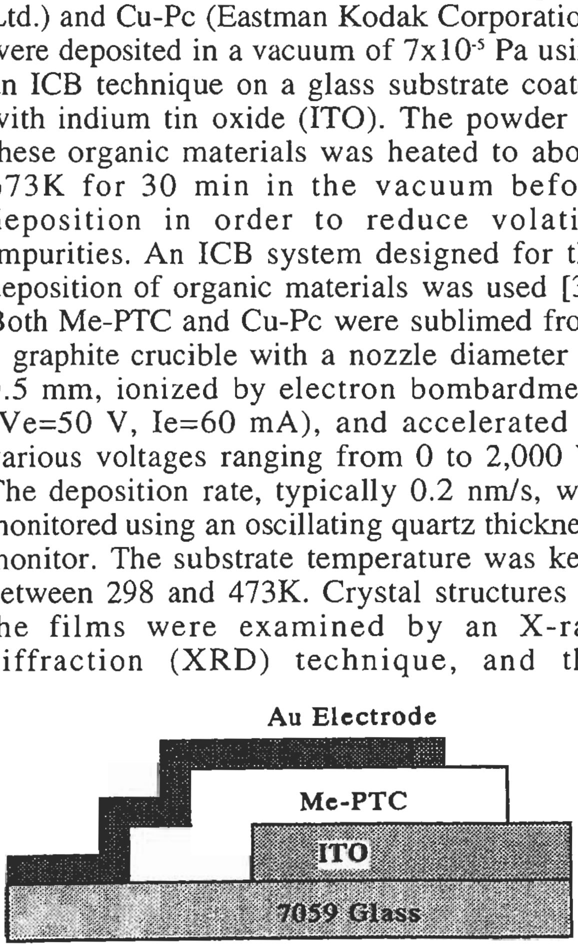

Fig.1 Illustration of a specimen used for the measurement of photoconductivity..

morphology was observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques.

A sandwich-type specimen, illustrated in Fig. 1, was used for the measurement of photoconductivity. The typical thickness of the film was 500 nm. Au electrodes were deposited onto the film surfaces. The photoconductivity of the film was measured at temperatures between 223 and 298K using an optical cryostat and monochromated light.

3. Results and Discussion

3.1 Nanostructure

The crystal structure of Me-PTC films was found to be identical to that of the powder specimen previously reported [4]. The crystal structure was monoclinic with a space group of P2$_1$/c, and lattice constants of a=0.3874, b=1.5580, c=1.4597 nm and β=97.65°. The crystal structure of the Cu-Pc films was of the α form [5]: monoclinic with a space group of C2$_1$/c, and lattice constants of a=2.592, b=0.3720, c=2.392 nm and β=90.4°. Figure 2 shows the XRD peak height of the (102) plane of the Me-PTC films deposited at 298 K plotted as a function of the acceleration voltage. Optimum crystallinity was obtained at an acceleration voltage of 300 V, but degraded at higher acceleration voltages, forming an amorphous structure at voltages higher than 1 kV. We have observed similar ion beam effects in Cu-Pc films [2,6].

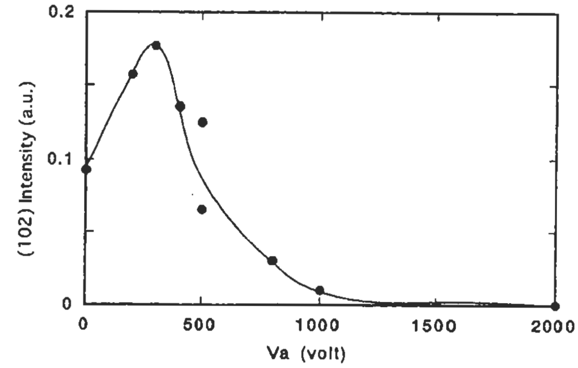

Fig.2 The XRD peak intensities of the (102) plane in Me-PTC films as a function of the acceleration voltage of the ICB.

The crystallographic growth plane of films of Me-PTC changed according to the deposition temperature. The dominant XRD peak at 295 K corresponded to the (102) plane and at 423K to (002). The Me-PTC molecule has a planar configuration, and the molecular plane lies nearly parallel to (102). The (102) and (002) growth planes therefore correspond to the parallel and standing orientations of the molecules, respectively. The perspective views of the molecules in both the (102) and (002) planes are illustrated in Fig. 3.

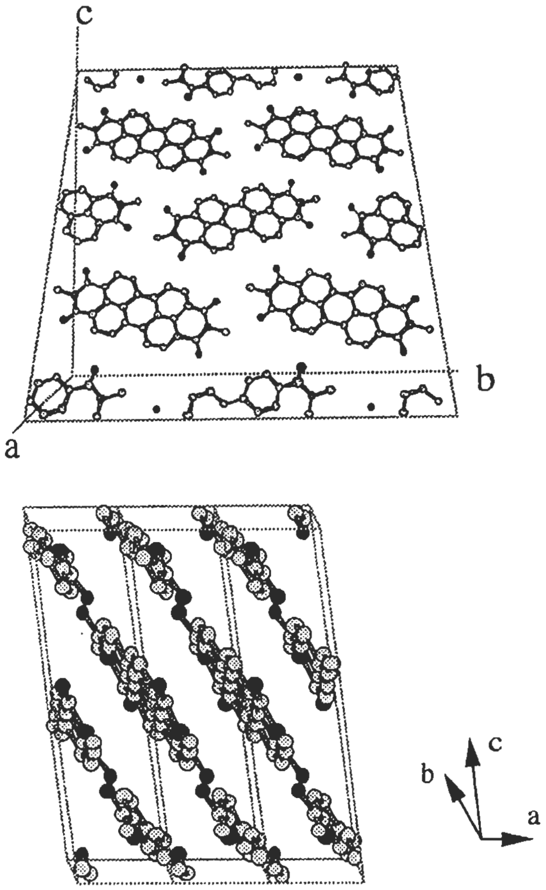

Fig.3 Illustration of the molecular arrangements of Me-PTC.(a) The (102) growth plane of a film deposited at 298 K. (b) The (002) growth plane of a film deposited at 423 K

With the Cu-Pc films deposited onto ITO, only the (002) growth plane was observed corresponding to the standing orientation. Both (200) and (002) growth planes were observed when deposited on mica (muscovite) substrates [2].

The growth morphology of both Me-PTC and Cu-Pc changed drastically from equiaxial crystallites to elongated whisker-like ones depending on the deposition temperature and also on the ICB condition.

3.2 Photoconductivity

Preliminary results of the PCM effect will be described in this section. The films used in the evaluation of photoconductivity were deposited at 298K, with the acceleration voltage of the ICB at 200 V. Films with good crystallinity and a smooth surface consisting of equiaxial small crystallites were obtained in Me-PTC as well as in Cu-Pc.

A photocurrent was measured using the following procedure. The dark current was monitored for 60s after the application of a bias voltage, then the light shutter was opened to irradiate a specimen for 60s while the light current was being monitored. The bias voltage was held for another 60s after the shutter was closed to measure the dark current. The result obtained shows the transient responses of dark current to the bias voltage, the transient responses of the light current to the light irradiation, and of the irradiation after effect in the dark current.

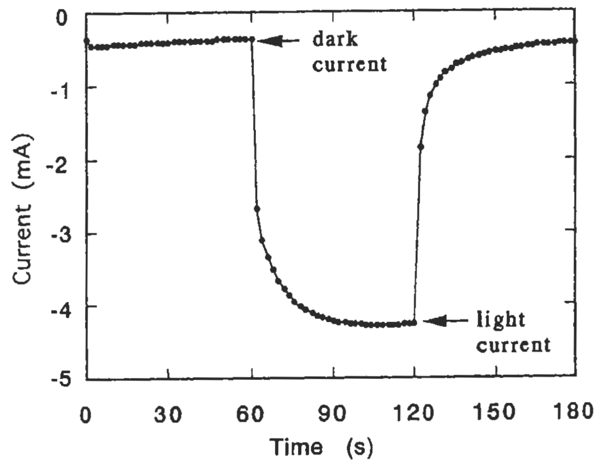

Fig.4 An example of the photocurrent measurement in an Me-PTC specimen irradiated by a 540 nm light of $432\mu W/cm^2$ at 298 K. Bias voltage was -11 V. The characteristic dark and light currents are designated by arrows.

Figure 4 shows an example of the result in an Me-PTC specimen 500 nm thick. The bias voltage was -11 V. The wavelength and the intensity of the light was 540 nm and $432\mu W/cm^2$, respectively. The specimen was irradiated from the ITO side. The dark and light currents are plotted as functions of time. The dark current decreased slightly with time. The light current increased rapidly, was saturated 30 s after the shutter was opened and trailed off about 30 s after the shutter was closed. The response of light and dark current varied widely depending on the temperature, the bias voltage, and the intensity of light. In order to characterize these responses, the dark current is defined as the current observed just before the shutter is opened, the light current as that just before the shutter is closed, and the photocurrent as the difference between the light and dark currents. The arrows in Fig. 4 illustrate this definition.

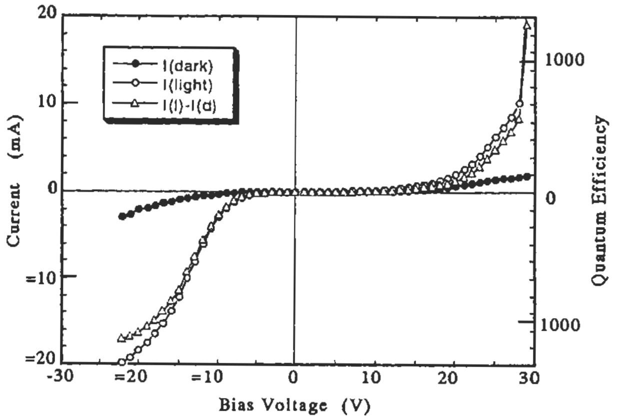

Fig.5 Dark, light, and photocurrents are plotted as functions of the bias voltage in Me-PTC specimen at 298 K. The irradiation conditions are the same as in Fig.4.

Figure 5 shows an example of the dark, light, and photocurrents plotted as functions of bias voltage in the same specimen. The irradiation conditions and the temperature were the same as those in Fig. 4. These currents showed the polarity to the bias voltage. In the negatively biased condition, the photocurrent became apparent at the bias voltage of -6 V, while in the positively biased condition, it became apparent at +15 V. At a bias voltage smaller than 1 V, the I-V curve showed the same characteristic as a photodiode with a positive Au electrode. The photocurrent at a bias voltage of 0 V was 1.2 x 10^{-9} A, and the electromotive force without external current was +0.2 V. These results suggest that a Schottky barrier diode is formed at the interface between the Au electrode and the Me-PTC film. Although the hysteresys effect was observed, the specimen did not break after a maximum current density of 250 mA/cm^2. The maximum allowable current density depended on temperature, bias voltage, and specimens. The observed maximum was 625 mA/cm^2.

The quantum efficiency of the PCM effect is defined here as the ratio of the number of electrons in the photo-induced current to the number of photons irradiated. This is given on the right-hand scale in Fig. 5. The maximum quantum efficiency observed in this figure was approximately 1250. The quantum efficiency of the PCM increased monotonically with the bias voltage, but was limited by the maximum allowable current density of individual specimens. The observed maximum quantum efficiency was 5000 at 295K and 3000 at 223K.

Although a large PCM quantum efficiency of up to 100,000 has been reported in Me-PTC when the specimen was cooled to 223 K, such a large quantum efficiency has not been attained at room temperature [1]. It is interesting that a moderately large quantum efficiency has been observed at room temperature as well as at 223K in the present study.

The current-voltage relation in PCM, especially the correlation between the light and dark currents, has not been fully discussed in the literature. We have tried to examine I-V relations of PCM in some detail to understand the mechanism of PCM effect. The dark, light, and photocurrents shown in Fig. 5 are replotted using a logarithmic scale in Fig. 6. When a negative bias voltage was applied, the I-V curves were approximately parallel and varied proportionately to the 3rd to 4th power of the bias voltage, and saturated at a bias voltage lower than -10 V. The ratio of light and dark currents was approximately 10:1. When a positive bias voltage was applied, the I-V curves were also approximately parallel and varied proportionately to the increasing 1.5th to 4th power of the bias voltage. The light and dark current ratio was approximately 3:1. The parallel nature of dark, light, and photocurrents suggests that these currents are controlled by an identical mechanism.

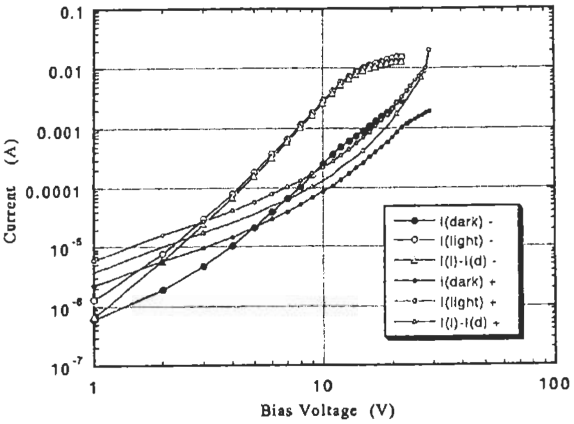

Fig.6 Dark, light, and photocurrents in Fig. 5 are replotted using a logarithmic scale.

Possible mechanisms that may control the I-V relation in the dark current are as follows: an ohmic law current, a space charge limited (SCL) current with or without traps, carrier injection into the film through a Schottky type barrier electrode, or tunneling injection of carriers through an insulating film. The linear I-V relation which would suggest an ohmic law was hardly observed at all. As described previously, a diode type I-V relation was observed at a bias voltage lower than 1 V. This suggests the formation of a Schottky barrier diode between the Me-PTC film and the Au electrode. However, the polarity of the dark current at higher bias voltages is not consistent with this. The power law I-V relation suggests the dominance of the SCL current with (n=4) or without (n=2) traps. At a positive bias voltage, electrons are injected through the ITO electrode. Both the I-V relation and the low dark current at positive bias voltages compared with those at negative bias voltages may be attributed to the tunneling injection through the thin insulating oxide film formed on the surface of ITO.

It has been shown that the quantum efficiency can be higher than unity when the effective lifetime of the carrier is longer than the transit time for carriers to travel across the specimen [7]. It is necessary, however , to examine this model more closely in order to explain the large quantum efficiency observed in the present study.

A quantum efficiency higher than unity has been observed in experiments on the photoconductivity of organic semiconductor films [8.9]. The quantum efficiency varied according to the bias voltage, and increased rapidly at high voltage to exceed unity. This has been attributed to the secondary multiplication of carriers in the local high electric field region. Specific multiplication mechanisms have yet to be suggested. The extensive operation of the avalanche mechanism observed in inorganic semiconductors [10], may not occur in organic semiconductors, such as used in the present study. This is due to the extremely low mobility of carriers. Such a low mobility makes it difficult to explain the large quantum efficiency in the present results.

An injection control mechanism has been proposed to explain a large quantum efficiency in the PCM effect observed in organic semiconductors [1]. In this model, photo-generated minority carriers are assumed to be trapped and accumulated at the interface between the film and the electrode to form a strong dipole like field of the order of 10^7

V/cm. This dipole like field causes the localized band bending to allow the tunneling injection of majority carriers across the barrier. The barrier height is determined by the difference between the work function of the metal electrode and the electron affinity of the lowest unoccupied molecular orbit (LUMO) of the film. In this model, an extra photocurrent is introduced, superimposed over the dark current.

The close correlation between the dark and the light currents observed in the present results can be qualitatively explained by this model. The observed PCM effect is induced by increasing the injection efficiency of majority carriers at the electrode through the accumulation of photo-generated minority carriers at the interface. In this model, however, a specific structure for the traps has not been established, and neither has the detailed quantitative mechanism, which is necessary for further analysis.

The PCM effect has been also observed in Cu-Pc films. Further examination of the results, including discussion of the nanostructural effect on the PCM are in progress.

Acknowledgments

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