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Diffusion Behaviour of Charge Carriers in Thin Films of Phthalocyanines

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ABSTRACT

Phthalocyanine (Pc) thin films were prepared by the vacuum-evaporating method. The diffusion behaviour of the charge carriers in these films was investigated by means of transient photovoltage (Dember effect) measurements. The experiments imply that the dominant charge carriers in phthalocyanines are electrons which diffuse from the surface closest to the light to the internal bulk. As a comparative system, photovoltic cells of Pc were also investigated. There was a close relationship between the short-circuit photocurrent (I_{sc}) of the devices and the maximum transient Dember photovoltage (V_{max}).

INTRODUCTION

Recent interest in phthalocyanine (Pc) derivatives has been expressed in terms of their use in materials for optical data recording and charge generation, because of their thermal and chemical stability.[1] Knowledge concerning the diffusion direction of photoelectrons and positive holes is very important for an understanding of charge generation in recording media. The diffusion behaviour of the free charge carriers in phthalocyanine thin films has been investigated by many scientists,[2] e.g. samples of 1–10 μm thick films of α-CuPc were irradiated with a Hg or W lamp filtered through a monochromator, to study the internal photoeffect. The results can be explained quantitatively by assuming an exponential distribution of electron traps.[3] For Al/MgPc/Ag sandwich

cells, there is a Schottky barrier at the Al/MgPc interface.[4] The electron diffusion length is estimated to be about $1{\cdot}5 \times 10^{-6}$ cm, the quantum efficiency $1{\cdot}5 \times 10^{-3}$, the lifetime about 10^{-9} s, and the mobility about $0{\cdot}1$ cm^2 s^{-1}.

Under non-homogeneous exposure, the product of the number and diffusion length of free electrons is not equal to that of the number and diffusion length of free holes. Therefore, the net charge length difference results in a Dember photovoltage. In this paper, the Dember effect measurement has been employed to obtain information on the diffusion of free charge carriers in some phthalocyanine vacuum-evaporated thin films and films based on a AgBr single-crystal, under non-homogeneous exposure without an external field. It was expected that the microsecond-resolved signal of the Dember effect on the phthalocyanine would give information on the initial excitation step of the systems. For comparison, a photovoltic cell consisting of a phthalocyanine vacuum-evaporated thin film was also investigated.

MATERIALS AND EXPERIMENTAL

Materials

Phthalocyanines, H_2Pc and MPc (M = Zn, Mg, Cu, AlCl, Co), were prepared in our laboratory. The structures and their purity were confirmed by elemental analysis, mass spectra and IR spectra.

The AgBr single-crystal used in the study was obtained by the crucible-dropping method, and then treated by polishing and chemical etching. It was cut to a thickness of 2 mm to expose the (422) face. The crystallographic orientation was checked by X-ray diffraction (Model D/max-IIIA, diffraction angle 81·4°, $d(422) = 1{\cdot}18$ Å). All thin films of Pc were formed by evaporating the dyes thermally at a vacuum of $1{\cdot}33 \times 10^{-3}$ Pa. The Pc film thickness was about 30 nm and it exhibited uniform amorphous aggregation using scanning electron microphotography (SEM).

Dember effect measurements

A block diagram of the Dember effect instruments is given in detail in Ref. 5. The light source used in the experiments consists of a specially shielded Xenon 437A Nanopulser, which gives a uniform noise-free exposure of $0{\cdot}02$ μJ cm^{-2} on the sample plane. The photovoltage data were stored on a Hewlett–Packard HP 9825 computer and transferred to an HP 9872B plotter.

Photovoltic cell measurements

The 'sandwich' configuration devices (Nesa glass/Pc/Ag) were prepared using a vacuum of $1{\cdot}33 \times 10^{-3}$ Pa.[6] The light (1000 W tungsten bromide, 15·7 mW cm^{-2} exposure intensity on the samples) was incident from the Nesa glass face; the exposure area was 0·2–0·3 cm^2. The short-circuit photocurrent and open-circuit photovoltage of the devices were measured using an automatic test system.[7]

RESULTS AND DISCUSSION

Charge carriers in phthalocyanine thin films

In the light-induced initial process, the separation of charge carriers in Pcs is a very important step. The diffusion behaviour of the free carriers in Pc thin films can be observed by the transient photovoltage (Dember effect). For instance, a MgPc thin film vacuum-evaporated on a polyethylene terephthalate film exhibits a Dember effect as shown in Fig. 1(a). The results for ZnPc are similar to those for MgPc, and are different to those for H_2Pc, CuPc and AlClPc [as shown in Fig. 1(b)]. The peak values of the positive signal (V_{max}) are listed in Table 1. As seen in the figure, the rise time of the positive signal is very short and the time for the positive signal to decay to half peak height is about 1 μs. This positive signal is caused by the diffusion of photoelectrons, since the product of the number of free electrons and their diffusion length is much larger than that of the number of free holes and their diffusion length at the initial responding time. There is a net electron diffusion current moving from the surface closest to the internal bulk due to the surface potential. However, there are electron-traps in the Pc thin films; electrons will be captured by these traps and recombine with free holes. The lifetime of free electrons is shortened, and the number of free electrons is decreased.

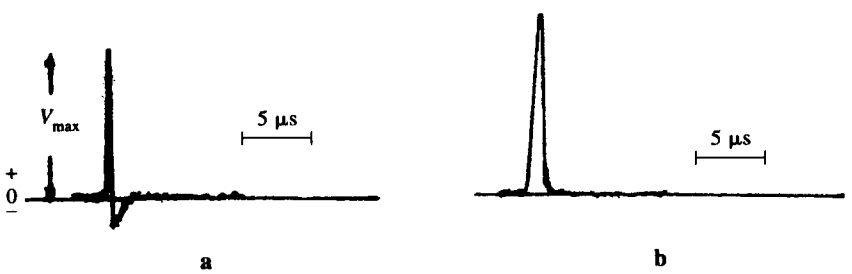

Fig. 1. Transient photovoltage for (a) ZnPc or MgPc: (b) H_2Pc, CuPc, AlClPc.

TABLE 1

Samples	V_{max} *(mV)*	I_{sc} *($\mu A\ cm^{-2}$)*	V_{oc} *(V)*	η *(%)*
AlClPc	1·6	16·8	0·95	0·46
CuPc	1·4	6·8	0·94	0·18
H_2Pc	1·08	5·0	0·75	0·11
ZnPc	0·86	2·6	0·71	0·05
MgPc	0·69	2·6	0·41	0·03
CoPc		0·12	0·92	0·003

V_{max} is the transient peak photovoltage measured by the Dember effect: I_{sc} and V_{oc} are the maximum short-circuit current and open-circuit voltages measured in the 'sandwich' thin film photovoltic cell, respectively; and η is the photoelectric converting efficiency of the cells

Corresponding to this case, the positive transient photovoltage rapidly decays to the base line [Fig. 1(b)].

Except for the recombination with free electrons, in some cases (e.g. for ZnPc and MgPc) there will be a net hole diffusion current moving along the original direction, catching up with the electrons and developing. From this time, the product of the number of free holes and their diffusion length is larger than that of the number of free electrons and their diffusion length. This results in a negative Dember signal [Fig. 1(a)]. For the same reason, free holes are captured by hole-traps which exist in the film, and the negative signal indicates that the diffusion of free holes also decays rapidly to the base line. The experiments imply that the dominant charge carriers in these Pcs are electrons. It is necessary to explain here that the excitons in the Pc thin solid films used in this study do not dissociate at impurity sites in the bulk, since the vacuum-evaporation method results in a high purity for the Pc. Therefore, the concentration of free charge carriers at the high light absorption region (surface) is higher than that in the bulk.

Pc/AgBr systems

The Dember signal on a AgBr single-crystal sheet has been investigated as described in Ref. 5. The transient photovoltage on the AlClPc/AgBr system, with white flash exposure incident on different faces, is shown in Fig. 2. The difference in the diffusion of charge carriers due to different incident faces results in the difference of the transient photovoltage. With the AlClPc facing the light source [curve (a) in Fig. 2], the photoelectrons of the AlClPc diffuse to the AgBr crystal, because the lowest vacant level of AlClPc is higher than the conduction band of the AgBr single-crystal (−3·37 eV). The concentration of electrons on the conduction band is

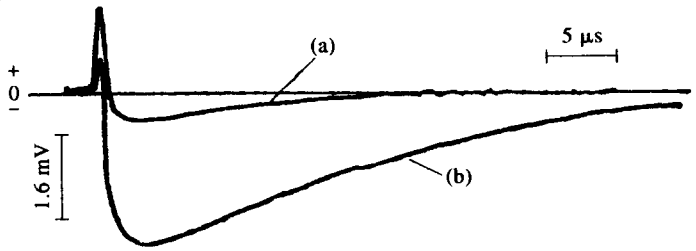

Fig. 2. Transient photovoltage for AlClPc/AgBr system with different light incident faces. Curve (a): AlClPc facing light; curve (b): AgBr facing light.

increased and the diffusion of electrons towards the bulk of the sample results in a positive transient photovoltage. This will quench the excitation of the AgBr single-crystal and sensitize the recombination of conduction band photoelectrons with holes. However, after a certain time, the diffusion length of the free holes is much larger than that of free electrons. Therefore, there is a net hole diffusion current moving in the original direction, and catching up with the electrons going forward. A negative signal, due to the diffusion of free holes, thus appears and then decays slowly. When MPc faces the light, a part of the free holes recombines with electrons and the negative signal becomes smaller. When the AgBr single-crystal faces the light (curve (b) in Fig. 2), the photoelectrons in AgBr (despite their small amount) can diffuse into the Pc phase. These electrons will be immediately entrapped by the MPc, so that the positive signal, due to diffusion of free electrons, is smaller and decays rapidly ($\tau_{1/2} \cong 0{\cdot}35$ μs), whereas holes may diffuse from the AgBr to the MPc phase after a certain time, during which the diffusion rate of free holes is affected. The decay time of the negative signal is longer. Results of the experiments on H_2Pc/AgBr and MPc/AgBr (M = Zn, Mg, Cu) were similar to those shown in Fig. 2.

Photovoltic cells of Pc

The short-circuit photocurrent (I_{sc}) and open-circuit photovoltage (V_{oc}) of the Pc thin solid film are listed in Table 1. The 'sandwich' devices comprising these Pcs have a converting efficiency (η) of about 0·03–0·46%. As is shown in Table 1, the order of the photoelectric converting efficiency (η) for a Pc thin film in the device is the same as that of the transient photovoltages, which were measured by the Dember effect for a Pc thin solid film. A previous study on Al/MgPc/Ag sandwich cells showed rectification and photovoltaic response due to a Schottky barrier at the Al/MgPc interface. The barrier width is narrow, but it is not due to high

carrier density. The photovoltaic action spectra can be explained by considering that only those carriers that reach the barrier contribute to the short-circuit photocurrent.[4] Because the short-circuit current (I_{sc}) is determined by the product of the number of charge carriers and their diffusion rate, there is a close correlation between I_{sc} and the maximum transient photovoltage (V_{max}), as seen in Table 1. For Pc films, the positive transient photovoltage is due to the diffusion of free photoelectrons. The larger the peak value of the signal, the larger the value of I_{sc} in the devices.

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