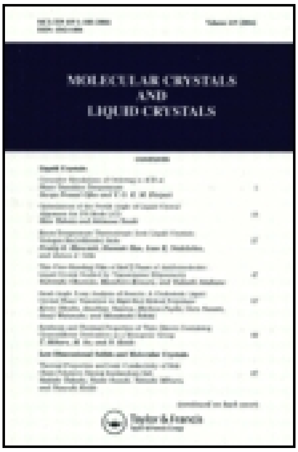

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Charge Carrier Photogeneration and Transport in Phthalocyanine/Perylene Thin Film Solar Cells

Stefan Günster [a], Susanne Siebentritt [a] & Dieter Meissner [a]

[a] Institute for Solar Energy Research (ISFH), Sokelantstr. 5, 3000, Hannover 1, FRG

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CHARGE CARRIER PHOTOGENERATION AND TRANSPORT IN PHTHALOCYANINE/PERYLENE THIN FILM SOLAR CELLS

STEFAN GÜNSTER, SUSANNE SIEBENTRITT and DIETER MEISSNER
Institute for Solar Energy Research (ISFH), Sokelantstr.5, 3000 Hannover 1, FRG

Abstract: Photoeffects in Phthalocyanine and Perylene thin films and Phthalocyanine/Perylene hetero-p/n- and Perylene/Au Schottky-cells were investigated in wavelength, temperature and intensity dependent measurements. It is concluded that the charge carrier generation occurs only in a small region near or at a p/n- or Schottky type contact whereas the photoconductivity is a true bulk effect. Both type of photoeffects experience their own recombination processes leading to different intensity dependences.

INTRODUCTION

Many investigations have been performed on thin films of polycrystalline organic semiconducting materials. Tang[1] reported in 1986 a solar cell made from Cu-Phthalocyanine (CuPc) and perylene with a solar efficiency of 1%. In the following we report on investigations of cells based on Zinc-phthalocyanine (ZnPc) and N,N´-Dimethyl-3,4,:9,10-perylenbis(carboximid) (M-PP). These materials have a good thermal stability, very high absorption coefficients (>10^5 1/cm) in the visible spectral region and they show the electrical properties of n- (M-PP) and p-conducting (ZnPc) materials[2].

EXPERIMENTAL

"p/n"-sandwich cells were produced by sucsessive evaporation of the dyes M-PP and ZnPc on ITO substrates. The evaporation rate was kept constant at a value of 0,4-0,6 nm/sec for ZnPc and of 0,5-0,8 nm/sec for M-PP. The pressure was always below $4 \cdot 10^{-6}$mbar. As top electrode a 40 to 50 nm thick gold film was evaporated onto the ZnPc film. Ohmic ZnPc sandwich samples and Perylene Schottky cells were produced the same way. However, for ohmic ZnPc samples gold was used as a bottom electrode. The evaporation was performed without breaking the vacuum. All following investigations were done in an air ambient.

The spectral dependence of the short-circuit current, open circuit voltage and photocurrent were taken with monochromatic light held at constant photon flux for all wavelengths. Intensity dependent spectra were taken by using greyfilters. The spectral characteristics of the greyfilters have been considered. For temperature dependent measurements a cryostat was mounted into the spectrometer.

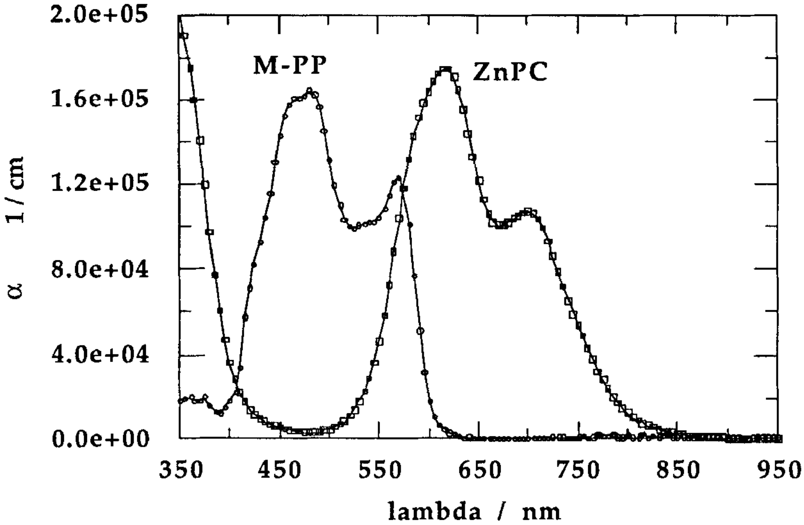

FIGURE 1 Absorption coefficients of ZnPc and M-PP thin films

RESULTS

Current voltage curves of ohmic samples in the dark show an ohmic behaviour for low voltages and space charge limited characteristics for higher voltages. The current voltage characteristics of the hetero-p/n- and Schottky-cells have a rectifying behaviour in the dark and under illumination they show a power plot influenced by the series resistances of the dye layers[4].

The photocurrent spectra of ohmic samples (Fig.2) have maximum contributions at

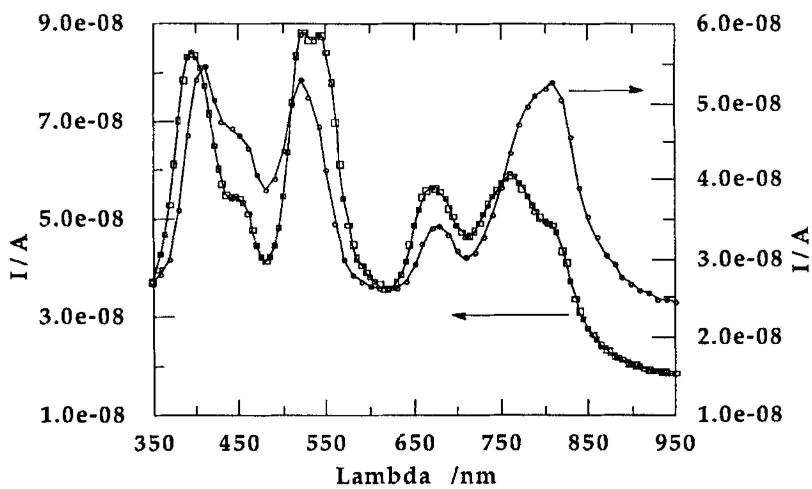

FIGURE 2 Photoconductivity spectra of a Au/ZnPc/Au sample (0.1 V) illuminated through the bottom (right scale) and the top (left scale) electrode

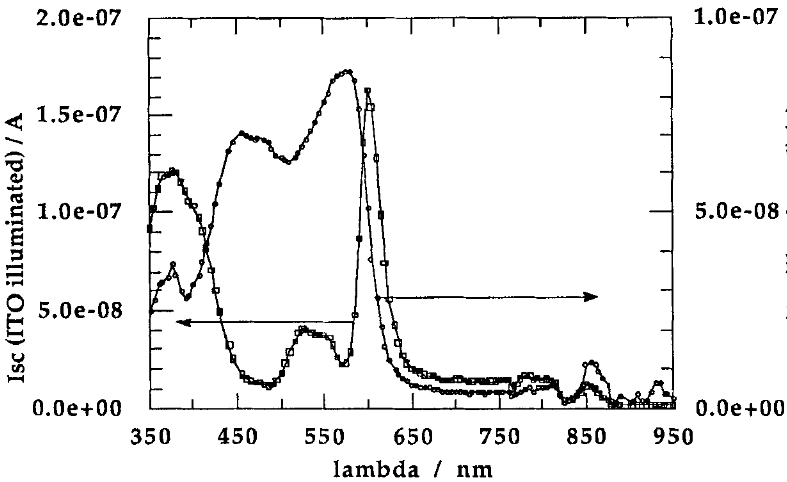

FIGURE 3 Short circuit current spectra of the cell ITO/M-PP(600nm)/Au

wavelengths with medium absorption of the dyes (Fig1.). The photoconductivity spectra are dominated by the region with the minimum concentration of generated photocarriers. However, the short circuit current spectrum of the M-PP Schottky cell shows the M-PP absorption characteristic for illumination of the Schottky-contact, the Au/M-PP interface, and the inverse absorption spectrum for ITO irradiation (Fig 3.). A hetero-p/n-cell shows the absorption characteristics of the backward dye if the first layer is thick compared to the penetration depth of the light. In figure 4 the short circuit current spectra for a M-PP (240nm)/ZnPc(300nm) cell illuminated from both sides are given. It is obvious that the short circuit current generating region is in the vicinity of the p/n respectively the Schottky

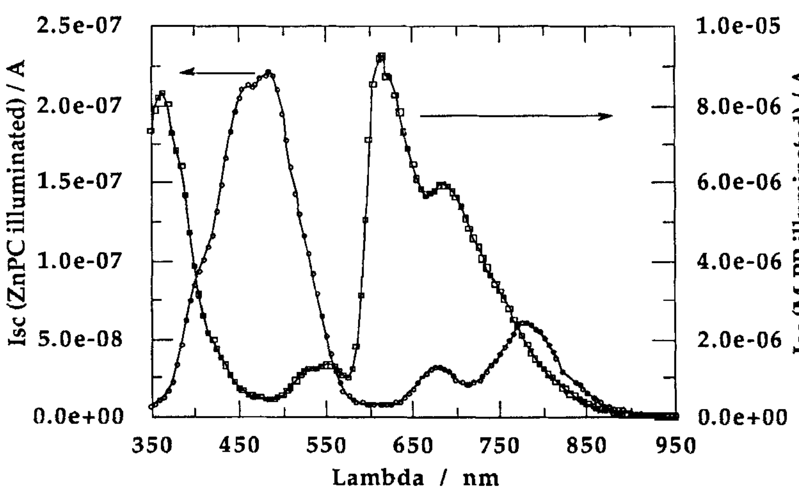

FIGURE 4 Short circuit current spectra of the cell ITO/M-PP(240nm)/ZnPc(300)/Au

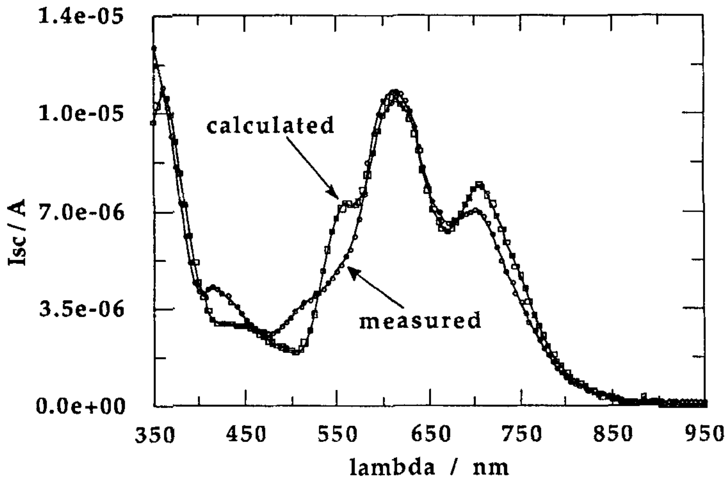

FIGURE 5 Measured and calculated short circuit current spectrum for an ITO/M-PP(78 nm)/ZnPc(164 nm)/Au cell (illuminated throught ITO)

interface. If photons throughout the cell contributed to the current we would expect a current spectrum following the absorption spectrum of the M-PP or double layer, and the short circuit current spectrum should be equal for all illumination directions.

Using the absorption of the film as given by the Lambert-Beer law and neglecting reflection and interference effects, we can estimate regions of carrier production around the interface of the p/n cell:

$$I_{sc,theo} = G \{ N_0 \exp(-2\alpha_1 (d_1 - L_1)) (1 - \exp(-\alpha_1 L_1)) + N_0 \exp(-\alpha_1 d_1) (1 - \exp(-\alpha_2 L_2)) \} \quad (1)$$

The first part gives the number of absorbed photons in a sheet with thickness L_1 near to the interface within the first layer and the second the number of photons absorbed in a sheet with thickness L_2 in the second layer. N_0 is the number of incident photons, α_1 and α_2 the absorption coefficients of the two dyes, d_1 and d_2 the thicknesses of the two layers (Fig. 6). G is the quantum efficiency. Assuming for all wavelengths a value of unity for G, $L_1 = 20$ nm and $L_2 = 10$ nm, one can calculate a spectrum which reproduces the main features of the short circuit current spetrum (Fig.5)[4]. The best agreement is found in the regions of ZnPc absorption. A more quantitative evaluation needs a careful treatment of reflections and interference between the dye films, the substrate and

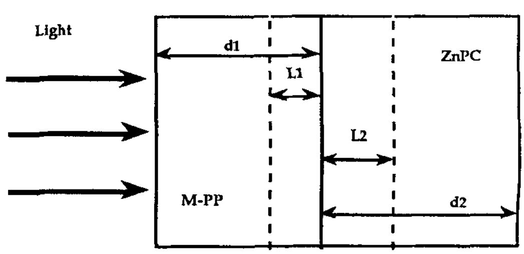

FIGURE 6 Cell configuration

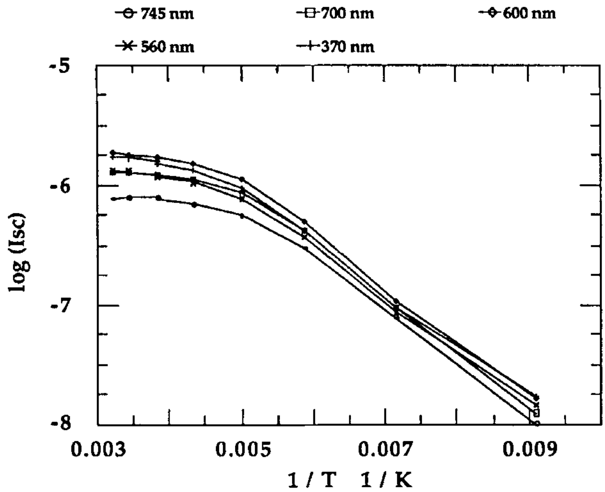

FIGURE 7 Short circuit current of M-PP/ZnPc cell in dependence of T

the gold electrode.

Intensity dependent mesurements of the photocurrent and the short circuit photocurrent (I_{sc}) provide informations about the mechanisms of carrier generation and carrier transport. In our measurements we variied the light intensity over three orders of magnitude up to a value of 10^{16} photons per second and square centimeter. The photocurrent measurements of the ohmic samples gave a square root dependence on light intensity for every wavelength, for the short circuit photocurrent we found a linear intensity dependence for all wavelengths and both illumination sides.

The temperature dependence of the short circuit photocurrent was measured in the temperature range from 100 K to 380 K. The illumination was performed through the ITO electrode. In figure 7 we show the Ahrreniusplot of I_{sc} for different wavelengths of high absorption. Only for low temperatures we can assume an activated behaviour. For higher temperatures the short circuit photocurrent saturates. It should be mentioned that the characteristic is the same for all absorption regions.

DISCUSSION

From the intensity measurements we conclude that the photoconduction is limited by a bimolecular recombination process. However, for I_{sc} we found a linear dependence on the light intensity . Thus the process of carrier generation is not governed by a two particle recombination process. It can be seen also from the I_{sc} characteristics under additional bias light illumination, that the short circuit current is not influenced by recombination effects [3]. We found, that the whole current level rises without a pronounced decrease of the photoeffects. Increased recombination effects at higher light intensities as found for the photoconductivity would have diminished the photocurrent spectra under additional bias light illumination.

The region of charge carrier generation can be extracted from the short circuit current spectra of different illumination sides and cells with different thicknesses. We can estimate, that the region of carrier production is really the region near to the interface, i.e. it is smaller than the whole cell. But we have to investigate the other extrem case: All carriers are only generated in a monomolecular layer at the interface. If we assume a monolayer thickness of 2nm[5] and an absorption value of $2 \cdot 10^5$ 1/cm (ZnPC at 350 nm), we calculate an absorption of nearly 4%. From the short circuit current spectra we can compute the quantum efficiency for our cells. For the cell shown in figure 3 we measured at the wavelength 350 nm with $I_{sc}=7.4\,\mu A$ a quantum efficiency of about 10% for a illumination intensity of $5.03 \cdot 10^{14}$ photons per second onto the sample. This corresponds to the 2.5 fold value of absorption in one monolayer.

The temperature dependent measurements of the conductivity of single layer samples of ZnPC and M-PP show activated behaviour, with two different activation energies[6,7]. The short circuit photocurrent of a hetero-p/n-cell saturates for higher temperatures and shows an activated behaviour only for low temperatures. Therefore the short circuit photocurrent seems not to be restricted by the conductivity of the materials as concluded also from the contradicting intensity dependences of the photoconductivity and short circuit current.

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