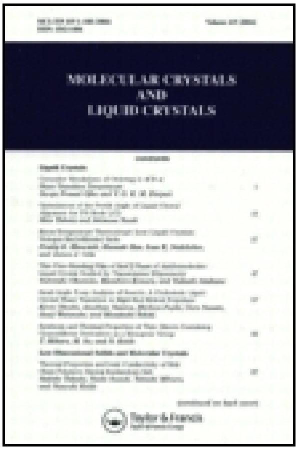

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Photoconductivity in Sandwich Cells with Langmuir-Blodgett Films of Phthalocyaninato-Polysiloxanes

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PHOTOCONDUCTIVITY IN SANDWICH CELLS WITH LANGMUIR-BLODGETT FILMS OF PHTHALOCYANINATO-POLYSILOXANES

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Abstract Charge carrier photogeneration in sandwich cells containing Lagmuir-Blodgett multiassemblies of tetramethoxy-tetra(octyloxy)phthalocyaninato-polysiloxane (PcPS) has been investigated with respect to the spectral response and light flux dependence. The films were contacted using Au or Pt bottom electrodes and Bi or Al top electrodes. The gain factors showed the largest value, close to 1%, at 325nm. The DC current-voltage curves of the cells with Al-electrode show rectification behavior. The rectification ratio (forward- *vers.* reverse-bias current) was typically higher than 40 for the ±0.5V applied. Under illumination, the devices worked like photocells giving open circuit voltage ~0.25V (Al-electrode negative) and a fill factor value 0.43. A mechanism of the charge carrier photogeneration process is proposed that includes free electron generation from ionized PcPS - oxygen complexes at the Al/PcPS interface, electron transfer to the Al-electrode and relaxation of the Schottky space-charge region with subsequent oxidation of the Al-electrode.

Keywords: Langmuir-Blodgett films, photoconductivity, phthalocyanines, charge generation, Schottky

INTRODUCTION

Photogeneration phenomena in phthalocyanine (Pc) and related compounds has been subjected to extensive investigations for several decades. Because of the efficient light absorption in visible region, semiconductor-like electronic structure, high chemical stability and relatively easy and efficient way of chemical syntheses Pc's were believed to be a promising class of materials for construction of cheap photonic and electrical devices, such as photocells, photodetectors and selective gas sensors.

In most cases vacuum sublimation has been used for the preparation of thin Pc layers. Photogeneration action spectra observed on such films (see e.g. monographs[1,2] for further reference) typically followed the linear optical absorption. However, the top gain factor (the number of electrons generated in an external circuit per one absorbed photon[3]) was always less then 2%. Moreover, a strong correlation was observed between photogeneration efficiency and the stacking of the molecules in the different phases. These investigations also revealed that oxygen plays substantial role in determining the electric and photo-electric properties of Pc's. The type of structural order and central cation were found to have predominant effect on the concentration of oxygen in films[3,4].

The Langmuir-Blodgett (LB) technique allows the preparation of ultra-thin layers with a uniform thickness in nanometer range and highly organized structure relatively free of uncontrolled structural defects. These features would act in two ways: (i) to increase photogeneration efficiency by increasing the gradient of attainable effective electric field and by minimizing a 'dead' region of sample volume and, (ii) to make the systems more suitable for systematic investigation, with a high regularity of films expected.

Regardless of the general interest in the Pc derivatives suitable for the LB processing, only a few were found to form stable layer at air/water interface that can be uniformly transferred to a solid substrate. Pc moieties interacting face-to-face through weak van der Waals interactions are typically difficult to deposit in multilayer assemblies thicker than 30-40 molecular layers (ML). Furthermore, these films contain many structural defects, making electrical behavior unreliable, especially in sandwich configuration.

Introduction of phthalocyaninato-polysiloxane (PcPS) as a material for LB technology meant significant improvement in this respect. This material belongs to the family of 'hairy-rod' molecules recently developed for use with LB technique[5,6]. Homogenous films of excellent quality can be formed with number of layers exceeding 100. In particular, PcPS films show a high level of structural organization[7,8] (dichroic ratio >2.5 for light propagated normally to the LB plane and wavelength 545 nm, regular stacking of the molecular layers with period ~2.0nm in the normal direction). The very low level of structural defects in the PcPS films has been confirmed by the long term stability achieved with an electrolyte/insulator/silicon device containing PcPS LB-film as the ion-sensitive membrane[9], and by remarkable rectification behavior observed in ITO/PcPS/Hg and Pt/PcPS/Hg sandwich cells[10]. The typical blue shift and broadening of the Q-band in the polymer absorption spectrum relative to the monomer spectrum[6] is a remarkable feature when one considers the possible use of the PcPS films in broad-band photocells. On the other hand, results obtained with unsubstituted phthalocyaninato-polysiloxane films prepared by solid-state polymerization of Cl-Pc(Si)-Cl monomer on glass substrate suggest significant lack of effective charge carrier photogeneration in the PcPS compound[11].

The aim of this article is to present preliminary photoconductivity measurements obtained with metal-contacted sandwich cells containing PcPS LB multiassemblies as an active layer.

EXPERIMENTAL

PcPS was synthesized as described previously[12,13]. An average polymerization degree of about 150 was estimated from light scattering experiments. The LB-films were built up using a Lauda FW-1 film balance under the conditions described in reference 14. The films were transferred onto glass substrates hydrophobized with dimethyl-dichlorosilane and partially covered with Pt (20nm, sputtered) or Au (15nm, vacuum evaporated) electrodes. The LB deposition was Y-type with the transfer ratio close to 1, independent of the number of layers. A relative high dipping speed of 2cm^2/min was possible with the transfer pressure 25 mN/m corresponding to the area per repeating unit of PcPS of about 0.8 nm^2. The subsequent Bi and Al top electrodes were evaporated at rates less then 0.1nm/s. Top and bottom electrodes were then connected to thin wires using silver paint. Finally the samples were covered with another glass plate to prevent any mechanical damage during manipulation.

The electrical and photo-electrical experiments were carried out in a home-made multi-functional measuring chamber equipped with a vacuum system, a broad-range heating and cooling system (100-500K), sample illumination optics (300W Xe-lamp, Bentham monochromator with wavelength adjustable over 250-900nm, optional full Xe-lamp white beam), light detection (Si-diodes for registration of the reference and transmitting beam respectively, Newport 835 power meter) and electrical measuring circuits (Keithley 610C electrometer with A/D converter, Prema 5000 multimeter, DS 6705 calibrated power source).

RESULTS AND DISCUSSION

The current-voltage curves of 20 LB-layers of PcPS measured under ambient conditions are shown in Fig.1. The samples with Al top electrode showed rectification behavior, especially outstanding for the Au/PcPS/Al cell (Fig.1a). Bi-contacted cells (Fig.1b) showed a rather linear dependence followed by a superlinear increase at higher applied voltage. Further experiments published elsewhere could prove the rectifying behavior of the Bi-PcPS contact[15].

The specific conductivity (σ) value of the entire sandwiches estimated from the linear region reached about 10^{-8} S/cm for both Pt and Au substrates and Bi top electrode. With the Al top electrode, the σ-value was typically several order of magnitude less (in Fig.2, $\sigma \approx 0.07$ nS/cm and 0.03 nS/cm for the Au/PcPS/Al and Pt/PcPS/Al cell respectively, at 300kV/cm applied electric field), very likely because of an uncontrollable Al-oxide layer growing at the Al/PcPS interface. The observed difference in the rectification behavior cannot be explained solely by a simple model of metal/semiconductor junction, because the reported work function values for Al and Bi are quite similar (4.28 eV for Al, 4.22 eV for Bi[16]). It is well known that rectification observed with thin films of Pc's can be essentially governed by an anisotropy in 'oxygen-doping' which is strongly dependent on sample preparation. For example the different evaporation temperature of the Bi and Al electrodes could lead to different oxygen concentration profile. This effect might also explain the observed increase in rectification ratio of a Pt/PcPS/Hg cell after annealing[17]. Thus, the influence of a controlled annealing treatment on the rectification ratio, with simultaneous control of the oxygen distribution, should be a subject for further investigation. The presence of structural defects (pinholes) could also be influenced by such annealing treatment.

The next remarkable feature is considerable hysteresis in the current-voltage curves exhibiting non-linear behavior. This hysteresis became more pronounced as the sweep rate decreased. This was believed to be an effect of keeping the sample under voltage for large periods of time. After some relaxation time (typically hours) the conductivity returned to the original level or, in the case of Al top electrodes, to levels slightly below the original value. In the same way, the rectification ratio was increasing. Keeping the sample under voltage with the Al-electrode positively biased resulted in faster conductivity decrease followed by complete conductivity breakdown after about 10 hours. Keeping the sample under vacuum resulted in an overall reversible decrease in conductivity for the Au/PcPS/Al sandwich (Fig.2 compared to Fig.1a). Strong reduction of the conductivity under vacuum has been observed[18] e.g. in single crystals of PcCu and is considered to be characteristic of semiconductors with holes as the majority carriers.

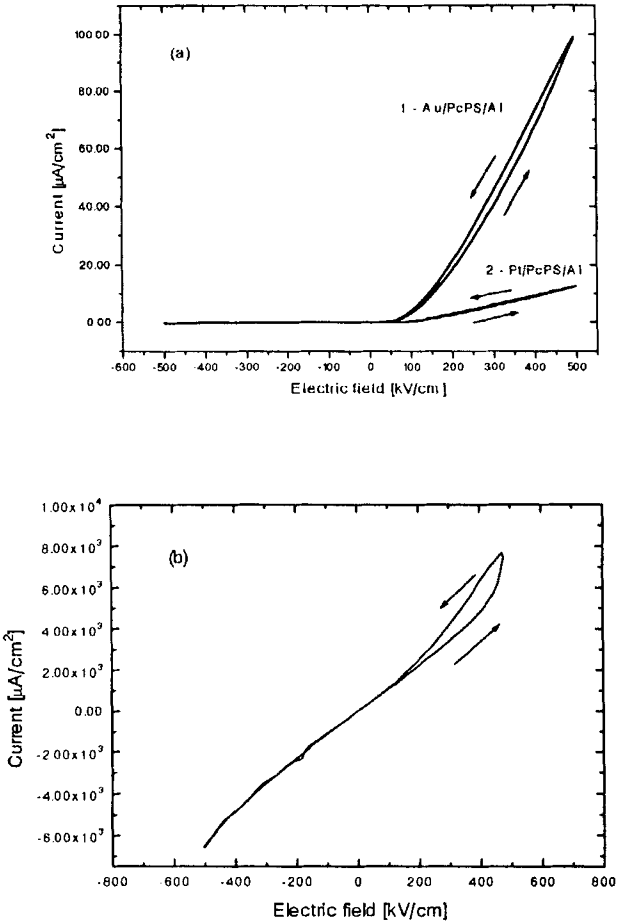

FIGURE 1: Dark current-voltage characteristics of 20 LB layers of PcPS in different sandwich cells under ambient conditions, positive bias corresponds to the Au- or Pt-electrode positive: (a) 1- Au/PcPS/Al, 2- Pt/PcPS/Al, (b) Au/PcPS/Bi.

Under near-UV-light illumination, the Al-contacted samples showed non-zero values of short circuit current (I^{SC}) and open circuit voltage (U^{OC}) (Fig.3). The values were sensitive to voltage cycling, as a result of the above mentioned hysteresis effect. The rather rectangular shape of the current-voltage curve of the Pt/PcPS/Al sample resulted in the relatively high fill-factor value 0.43. This suggests that some change in the internal resistance of the cell should take place[19]. The difference between the dark current and current under illumination was insensitive to external electric field under reverse bias up to relative high external field values 500 kV/cm.

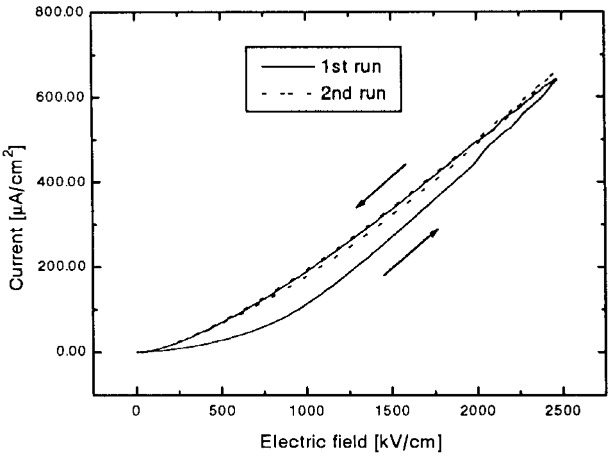

FIGURE 2: Dark current-voltage characteristics of Au/PcPS (20ML)/Al under vacuum (5 mPa), positive bias corresponds to the Au-electrode positive.

The spectral response of the I^{sc} was used to calculate spectral dependence of the photogeneration gain factor (an example is given in Fig.4). These action spectra exhibited several interesting features: (i) The general shape followed the absorption spectrum, but with a dominant effect in the near-UV region. The top gain factor value reached about 1% for a Pt/PcPS/Al sandwich with 10 LB layers. (ii) For all tested samples, the maximum was shifted to shorter wavelength relative to the principle maximum of absorption B-band. The drop on the high-energy side essentially followed the absorption edge of the glass cover. (iii) The observed spectral shape was found to be sensitive to the kinetics of measurement: if a shorter time *per* point was used in data acquisition process (with the increasing wavelength), the principal near-UV maximum was followed by a faster decrease in the gain factor value and a subsequent (intermediate) change in polarity of the generated voltage and orientation of the current flow (at the maximum, the Al-electrode was steadily negative). (iv) Under vacuum, there was no significant difference in the top gain factor value relative to the value measured under atmospheric pressure, but the spectral shape showed faster decrease and the intermediate reverse current was about twice stronger. (v) The transmittance of Al-electrode was found to change with exposure time, resulting in complete removal of the metal layer 15 nm thick after 3 days of exposition with 325 mn light beam (5mW/cm^2).

Fig.5 shows response curve of the short circuit current under a white light source illumination observed with a Au/PcPS(20ML)/Al sandwich cell after switching the light on and off. Before the current reached a stabilized value, transient effects could be observed. The change of the current flow direction after turning the lamp off suggests similarity with the kinematical effect already mentioned in context with the action spectra.

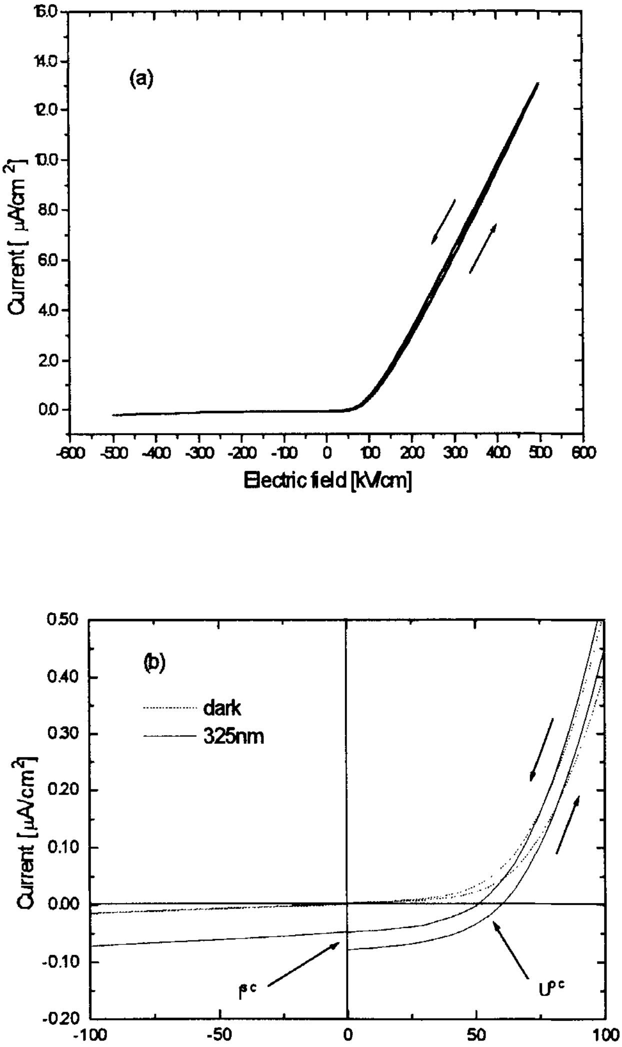

FIGURE 3: Current-voltage curves for Pt/PcPS/Al cell, 20 LB layers, 325nm light, incident photon flux 5mW/cm^2, Al-electrode illuminated, positive bias for the Pt-electrode positive, full scale (a), expanded view (b); the dark current-voltage curve is added for comparison.

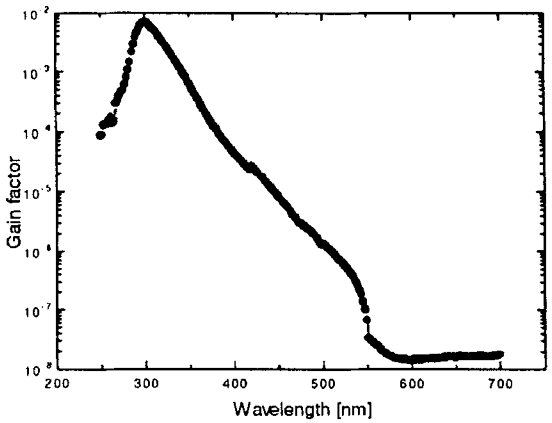

FIGURE 4: Observed spectral dependence of the gain factor for Pt/PcPS/Al sandwich sample, 20 LB layers of PcPS, Al-electrode illuminated, atmospheric pressure, room temperature, wavelength increment 2nm, time *per* point 20 sec.

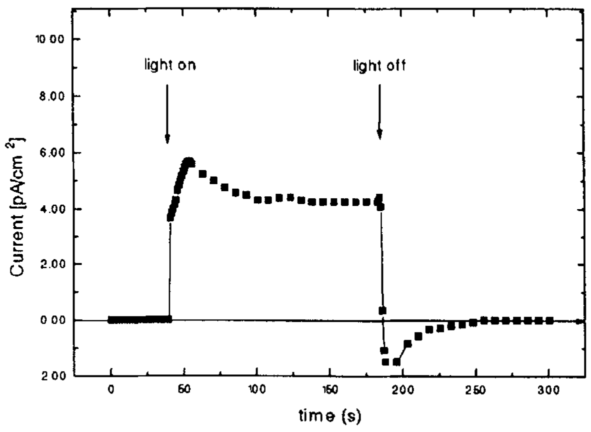

FIGURE 5: Course of the short circuit current after switching the light source on and off; Au/PcPS/Al cell, 20 LB layers, the Al-electrode illuminated, white source (full Xe-lamp spectrum), incident light intensity 96 mW/cm^2, positive current value for the Au-electrode positive.

The dependence of U^{oc} and I^{sc} on the incident light intensity showed a relationship that can be roughly approximated by power laws $U^{oc} \approx P^{1.0}$ and $I^{sc} \approx P^{0.3}$ (Table 1). The exponent value 0.3 in the latter relation has already been observed with single crystal samples of PcH_2 and can be described by a model of free charge generation taking place preferentially on the Al/PcPS interface and including a desensitization process due to a diffusion-dependent bulk recombination[20]. This model requires that the average dark concentration of free charge carriers be very low compared to the concentration of photogenerated carriers. In our case, the desensitization process can likely originate in a modification of the interfacial blocking space charge. The observed independence of the I^{sc} values on the reverse bias voltage already mentioned suggests that the internal electric field in the active charge carrier generation region is significantly higher then MV/cm.

The photo-effects observed in this system may be explained in part by involving a model similar to that described by Simon and Andre[3] for metallophthalocyanine sandwich cells. The model assumes a fundamental role of oxygen molecules in the photogeneration process. The presence of oxygen in the PcPS LB films used in experiments was suggested by ESCA measurements. The obtained average oxygen concentration in 20 PcPS LB layers deposited on gold was approximately 1 O_2 molecule *per* 1 monomer unit.

TABLE 1: Dependence of open circuit voltage (U^{oc}) and short circuit current (I^{sc}) on incident light power observed with Au/PcPS/Al cell (20 LB layers) under a white source illumination (full Xe-lamp spectrum), with the Al-electrode as the front one, Al-electrode steadily negative.

Light flux (mW/cm^2)	I^{sc}(pA)	U^{oc}(mV)
30.0	1.20	1.9
51.2	1.38	3.1
66.7	-	4.4
96.0	1.68	6.4

Specifically, the photogeneration is influenced by the following two processes. The process (1) maintains a single effective Fermi level equilibrium. Electrons flow from the Al-electrode to the PcPS film containing O_2 molecules (relaxation current) and the space-charge depletion region is formed (1a). The Al^+ ions can interact with the oxygen molecules at interface Al/PcPS and an aluminium oxide layer is growing (1b).

$$\text{Al-electrode}/(\text{PcPS}^{+\delta},\text{O}_2^{-\delta}) \ \text{->}\ \text{Al-electrode}^{+1}/(\text{PcPS}^{+\delta},\ \text{O}_2^{-(1+\delta)}) \quad (1a)$$

$$\text{O}_2,\text{Al-electrode}^{+1} \ \text{->}\ \text{Al-oxide},\ \text{Al-electrode}^{+1} \quad (1b)$$

The parameter δ represents average charge transfer equilibrium between PcPS and O_2 molecules. Under illumination, the second process (2) is initiated. Free electrons and holes are generated and the charge carriers are accelerated by the internal electric field of depletion region (2a). Electrons flow to the Al-electrode, holes drift in the opposite direction. Some portion of the holes can annihilate with the electrons trapped in the depletion region (2b). Furthermore, direct ionization of the trapped electron can be also considered (2c):

$$\text{PcPS}^{+\delta},\ \text{O}_2^{-\delta} \ \text{-- h}\nu\text{-->}\ \text{PcPS},\ \text{O}_2 + \text{h}^+ + \text{e}^- \quad (2a)$$

$$\text{PcPS}^{+\delta},\ \text{O}_2^{-(1+\delta)} + \text{h}^+ \ \text{->}\ \text{PcPS}^{+\delta},\ \text{O}_2^{-\delta} \quad (2b)$$

$$\text{PcPS}^{+\delta},\ \text{O}_2^{-(1+\delta)} \ \text{-- h}\nu\text{-->}\ \text{PcPS}^{+\delta},\ \text{O}_2^{-\delta} + \text{e}^- \quad (2c)$$

Both the processes (2b) and (2c) decrease the concentration of the interfacial space charge and stimulate the process (1). The resulting photocurrent is proportional to the dynamic balance between the processes (1) and (2). When a faster decrease in the photogeneration process (2) occurs the relaxation current prevails and the Al-electrode changes polarity as observed in the action spectra and Fig.5. Under constant illumination, change in the total current flowing through the cell could be related to a change of the interfacial blocking space charge and in this way to a subsequent change of internal resistance. This type of behavior is consistent with the observed high fill-factor value. The observed hysteresis in current/voltage cycling suggests that the space charge region can also be modified by the applied voltage. A hole trapping process with average lifetime of the order of hours could be postulated.

CONCLUSION

The reported data show that a photoelectric effect with a gain factor close to 1% can be achieved with PcPS LB films as a sensitive layer using Al as the top electrode material. The photogeneration process is strongly dependent on the measurement kinetics. The suggested model is able to describe qualitatively the main effects observed. A more detailed analysis regarding particular features such as charge carrier transport in PcPS (average charge carrier concentration and mobility) is necessary to understand fully the interfacial space charge distribution.

The complexity of the devices based on Pc influenced by uncontrolled oxygen content and the instability of the contacting Al-electrodes suggest that further experiments with controlled donor or acceptor doping and more stable contacting metals may be helpful. The LB films of hairy-rod macromolecules provide an excellent construction basis for such multilayer assemblies.

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