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LANGMUIR–BLODGETT AND RELATED FILMS

SUBSTITUTED SILICON PHTHALOCYANINE LANGMUIR–BLODGETT FILM AND ITS POSSIBLE USE IN ELECTRONIC DEVICES

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This paper summarizes the preparation of Langmuir–Blodgett (LB) films of a substituted silicon phthalocyanine, namely tetra-4-*tert.*-butyl-phthalocyaninato-silicon dichloride (ttb-PcSiCl$_2$), and its possible use in electronic devices. We describe how high quality ttb-PcSiCl$_2$ LB films which exhibit mechanical and thermal stability can be successfully deposited. The aggregation in the floating film is much reduced and the molecules are stacked edge on to the substrate with a preferred orientation perpendicular to the dipping direction. There are two distinct types of possible use for this film in electronic devices whose performance is enhanced by the incorporation of a few monolayers of ttb-PcSiCl$_2$: (1) the phthalocyanine layers take an "active" part in photovoltaic devices and gas-sensitive structures; (2) the layers play a "passive" role in metal–organic chemical-vapour-deposited (MOCVD) ZnSe/LB film and MOCVD InP/LB film metal insulator/semiconductor structures.

1. INTRODUCTION

Langmuir–Blodgett (LB) films have been widely used as model systems in fundamental research. During the past decade their extensive application potential has also been recognized. For stability reasons, traditional materials have limited practical applicability and therefore it is important to produce more robust LB film assemblies.

Phthalocyanine has been shown to display excellent characteristics. It is an inexpensive, non-toxic dye and is very stable relative to other organic compounds. Most phthalocyanine materials can be heated to 400 °C before sublimation. A range of phthalocyanine compounds can be successfully deposited using a Langmuir trough[1], but even after careful optimization of the solvent and subphase condition there is still evidence of aggregation in the floating films and a tilted monolayer

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configuration on the substrate. For some applications it may be impossible to accept reduced crystalline order.

In a recent publication[2] we described the deposition of high quality LB films of a substituted silicon phthalocyanine, namely tetra-4-*tert*-butyl-phthalocyaninato-silicon dichloride (ttb-PcSiCl$_2$). What is encouraging is that aggregation is much reduced and that, even with a simple solvent, film deposition is relatively straightforward. The uniformity of the films was reflected in their ability to sustain relatively high electric fields (more than 10^8 V m^{-1}) in a sandwich geometry between conducting electrodes. We have described how ttb-PcSiCl$_2$ LB films also possess interesting photoelectrical characteristics and are promising materials for the development of organic photovoltaic cells and electroluminescent devices[3,4]. In this paper we summarize the preparation of the ttb-PcSiCl$_2$ LB film and its possible use in electronic devices. We also describe the fabrication of electronic devices based on ttb-PcSiCl$_2$ and discuss the electrical and photoelectrical properties of the resulting structures.

2. PREPARATION OF ttb-PcSiCl$_2$ LB FILM

The introduction of bulky butyl groups renders ttb-PcSiCl$_2$ soluble in chloroform. Figure 1 shows a typical curve of surface pressure *vs.* area with a sharply rising condensed phase region. The calculated area per molecule of approximately 62 Å^2 is consistent with the faces of the molecule being edge on to the water surface (4.5 × 13.8 = 62 Å^2). The modern Langmuir trough used in our investigation possesses the required control facilities. The phthalocyanine monolayers were removed from the subphase under the following dipping conditions: surface pressure, 25 mN m^{-1}; pH value, 8.5; dipping speed, 5 mm min^{-1}. The Z-type deposition observed was monitored using the useful method of plotting the dipping head position *vs.* surface area.

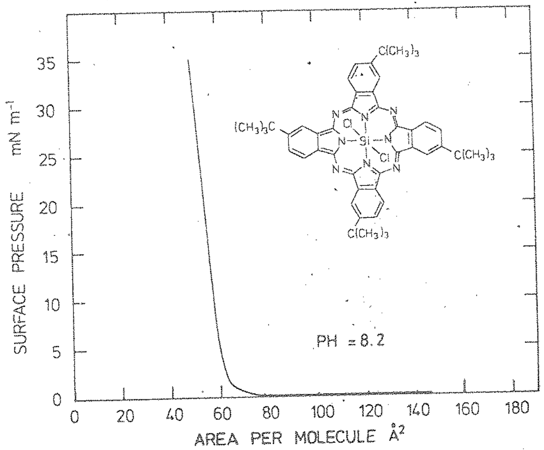

Fig. 1. Surface pressure–area isotherm for ttb-PcSiCl$_2$ molecule whose structure is shown in the inset. The molecular area is estimated to be 62 Å^2.

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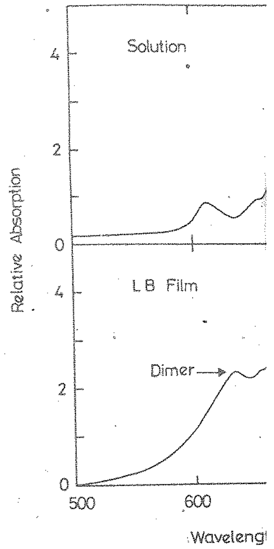

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3. POSSIBLE USE OF ttb-P

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The characteristic absorption peak observed in metal containing phthalocyanine at approximately 690 nm has been assigned to a phthalocyanine π–π^* transition[5]. In general, the spectrum of deposited films tends to be broadened and the dominant peak shifted to higher energies corresponding to the formation of dimers or higher complexes. Aggregation effects are also responsible for broadening the spectra. Figure 2 compares the absorption spectra of ttb-PcSiCl$_2$ in chloroform solution and when deposited as an LB film. It is interesting to note that the dominant peak in both cases is near 690 nm, corresponding to monomer formation. Further investigations with polarized light show that in this film there is a preferred orientation along the dipping direction. These results provide further support for the proposed vertical orientation of these molecules, since a planar orientation would not result in any polarization effect. The uniformity of the films was reflected in their ability to sustain relatively high electric fields in a sandwich geometry between conducting electrodes. The fine control of the LB layer thickness permits the optimization of the characteristics of electronic devices.

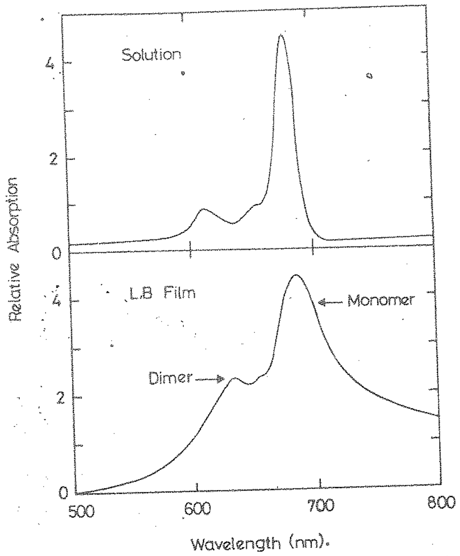

Fig. 2. Optical absorption spectra of ttb-PcSiCl$_2$ in chloroform solution (upper graph) and in LB film form (lower graph).

3. POSSIBLE USE OF ttb-PcSiCl$_2$ LB FILMS IN ELECTRONIC DEVICES

3.1. *Taking an "active" part*

3.1.1. *Photovoltaic devices*

Schottky barrier structures were obtained by depositing the ttb-PcSiCl$_2$ LB layers (as a p-type semiconductor) on conducting indium–tin oxide (ITO) glass; aluminium top electrodes were then thermally evaporated. The rectification characteristics can be obtained for these structures. We have fabricated a series of ITO/ttb-PcSiCl$_2$/Al structures containing different thicknesses of organic layer.

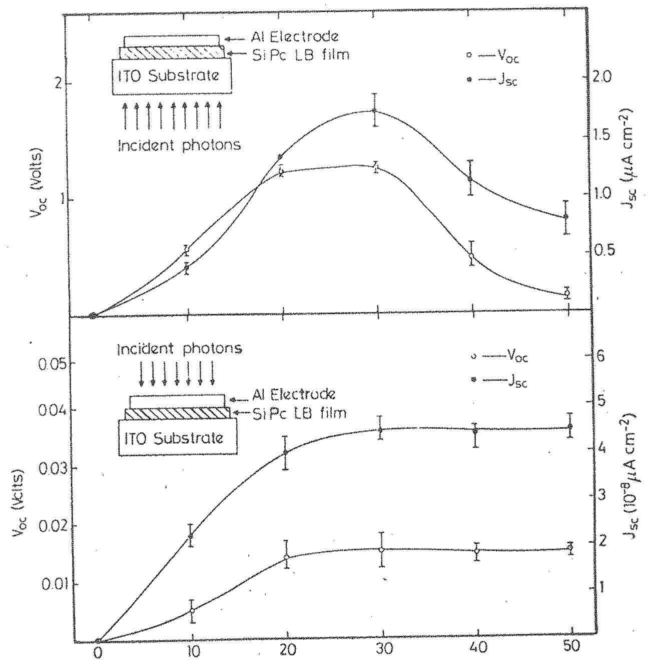

Fig. 3. Open-circuit photovoltage (V_{oc}) and short-circuit photocurrent density (J_{sc}) for Al/ttb-PcSiCl$_2$/ITO structures under approximately AM1 illumination *vs* number of LB layers, for illumination through ITO layer (upper graph) and aluminium electrode (lower graph).

Figure 3 shows how V_{oc} and J_{sc} depend on the number of LB layers when the devices are illuminated through the transparent ITO substrate or the aluminium electrode. The results clearly indicate an optimum thickness for the organic film of approximately 30 layers (450 Å), corresponding to values of $V_{oc} = 1.3$ V and $J_{sc} = 1.7\ \mu\text{A cm}^{-2}$. When the same devices were illuminated through the aluminium electrode, the much smaller values for V_{oc} and J_{sc} are due to the lower transmittance of the metal electrode. In this case no maximum in either the current or voltage curve is observed. From the data shown in Fig. 3 we estimate a value of the Schottky barrier depletion width plus the exciton diffusion length of approximately 450 Å. Phthalocyanine generally possesses very high absorption coefficients. Thus, when the devices are illuminated through the ITO (back) contact, both V_{oc} and J_{sc} will begin to decrease when the film thickness becomes greater than 450 Å. In contrast, once the organic layer is thick enough to support the depletion region of the Schottky barrier, the corresponding values obtained with illumination through the aluminium (Schottky) contact are relatively unaffected by the film thickness. This result indicates that if suitable material combinations can be found, the LB process may offer an alternative technique for the production of high efficiency and low cost photovoltaic devices.

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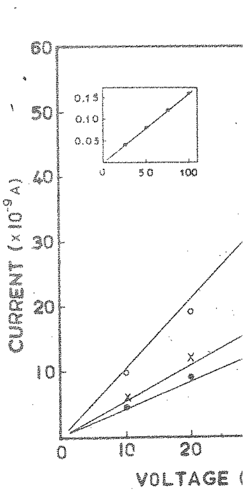

Fig. 4. Current–voltage cha
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3.1.2. Gas-sensitive structures

The main advantage of gas-sensitive structures incorporating LB films are the simple technology, high sensitivity and very short response and recovery times. Wohltjen *et al.* reported the gas-sensitive characteristics of substituted copper phthalocyanine LB film on a planar interdigital microelectrode and considered that the central metal atom has a profound effect on the conductivity of the crystal and its selectivity to various gases[6]. We have fabricated a series of gas-sensitive structures with different layers of ttb-$PcSiCl_2$ deposited on an aluminium interdigital microelectrode (50 finger pairs of electrodes, width 100 μm, spaced 100 μm apart) and investigated the gas-sensitive performance of the ttb-$PcSiCl_2$ LB film on exposure to NO_2. Figure 4 shows the current–voltage characteristics for a gas–sensitive structure incorporating 30 layers of ttb-$PcSiCl_2$ in different environments. These curves show that after injecting 200 ppm of NO_2 in vacuum and in the atmosphere, the conductivity value for the LB film shows a large increase (by 100 and 1.5 times respectively). This result indicates that the LB films of both central non-metal (silicon) substituted phthalocyanine and central metal (copper) substituted phthalocyanine are very sensitive on exposure to some gases, but the effect of NO_2 alone on the conductivity of ttb-$PcSiCl_2$ LB film is much larger than the joint effect of NO_2 and the atmosphere. This differs from the substituted copper phthalocyanine that we have studied. The joint effect of NH_3 and the atmosphere on the conductivity of substituted copper phthalocyanine is much larger than the effect of NH_3 alone. The result that both metal and non-metal substituted phthalocyanines are very sensitive to the presence of certain gases indicates that the conductivity increase is not only effected by the central metal atom. We think it is possible that the increase in conductivity for the central non-metal substituted phthalocyanine is the result of electrophilic attack of the extensive π orbital system of the phthalocyanine molecules by certain gases.

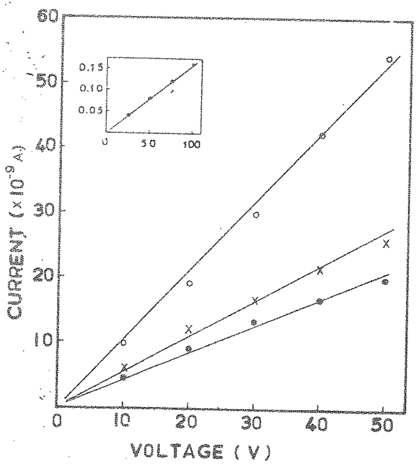

Fig. 4. Current–voltage characteristics for gas–sensitive structure incorporating 30 layers of ttb-$PcSiCl_2$ in the atmosphere (●), after injecting 200 ppm NO_2 in the atmosphere (×) and after injecting 200 ppm NO_2 in vacuum (○). Inset: current–voltage characteristics in vacuum in an expanded form.

3.2. *Playing a "passive" role*

3.2.1. *Au/ttb-PcSiCl$_2$ LB film metal–organic chemical-vapour-deposited (MOCVD) ZnSe metal/insulator/semiconductor (MIS) electroluminescent (EL) devices*

In order to obtain a low voltage, high efficiency blue d.c. EL device which has an MIS structure, the insulator must be coated over relatively large areas and be of high quality, *i.e.* it must be mechanically and thermally stable, able to pass the currents required for electroluminescence and of precisely defined thickness. This last requirement suggests an application for ttb-PcSiCl$_2$ LB films. In our work, 7 layers of ttb-PcSiCl$_2$ were deposited on epitaxial n-type ZnSe films grown on single-crystal GaAs substrates by atmospheric pressure metal–organic chemical vapour deposition. Good rectification characteristics were exhibited by the Au/ttb-PcSiCl$_2$ LB film/MOCVD ZnSe MIS devices. Under a forward bias greater than 2.8 V the MIS devices emitted a blue–white light from beneath the gold top electrode at room temperature. It should be noted that no such effect was observed for structures which did not include the LB layer (*i.e.* simple Schottky diodes). The spectrum of the emission is shown in Fig. 5. There are two distinct peaks shown in the electroluminescence spectrum, at approximately 460 and 500 nm. The former peak is almost certainly associated with band-to-band recombination in the ZnSe. It is thought that the presence of the LB layer causes an increase in the minority carrier injection ratio in the II–VI semiconductor.

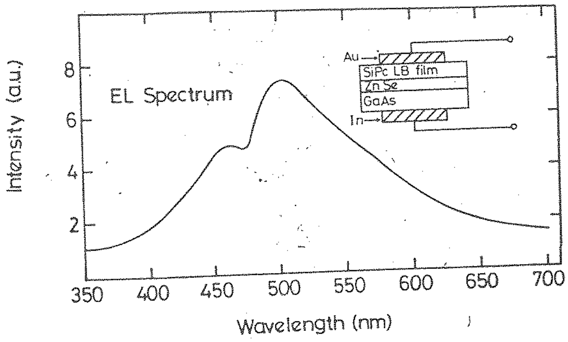

Fig. 5. Electroluminescence spectrum obtained for an Au/ttb-PcSiCl$_2$/ZnSe MIS diode operated under pulsed condition in forward bias.

3.2.2. *Au/ttb-PcSiCl$_2$ LB film/MOCVD InP MIS structures*

The application of MOCVD InP emerges as an encouraging prospect in field effect transistor (FET) integrated systems[7]. The first metal semiconductor field effect transistor fabricated with MOCVD InP was made by preparing a thin oxidic film on the InP surface. The barrier height of the Schottky gate was increased from 0.48 to 0.66 eV and better parameters for the FETs were obtained. However, the oxidization technique is difficult to master.

Since the Langmuir–Blodgett technique has advantages compared with common methods for making insulating layers, ttb-PcSiCl$_2$ LB films were used in the MIS structure instead of oxidic layers.

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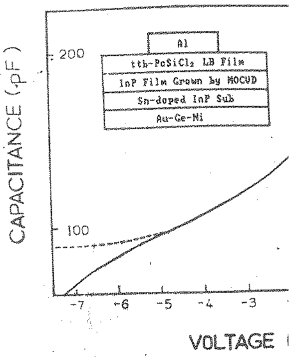

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TABLE I

BARRIER HEIGHTS Φ_B AND IDEALI
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δ (Å)	*Numb*
27.6	2
55.2	4
82.8	6
110	8

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A schematic diagram of the MIS structure fabricated is shown in the inset of Fig. 6. The ttb-PcSiCl$_2$ LB films were deposited on the surface of MOCVD InP with different layers, and over them the gold electrode was deposited.

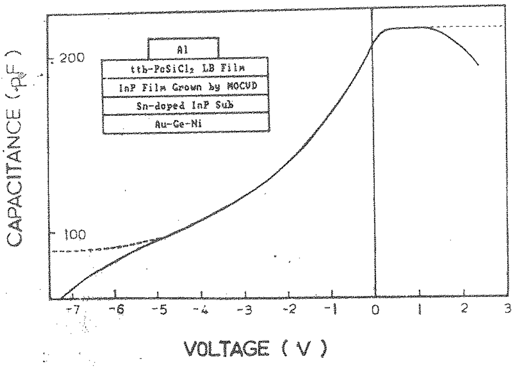

Fig. 6. Typical C–V characteristic ($f = 1$ Mhz) of Au/LB/MOCVD InP structure. The schematic diagram of the structure is shown in the inset.

From the current–voltage characteristics we calculated the relevant barrier heights and ideality factors corresponding to different thicknesses of LB film, these are listed in Table I. It is found that the barrier height is increased to 0.8 eV in the presence of LB film and there is an optimized thickness range of LB film, 50–80 Å, in which the structure has a relatively high barrier height but a relatively small ideality factor.

TABLE I

BARRIER HEIGHTS ϕ_B AND IDEALITY FACTORS n CORRESPONDING TO DIFFERENT THICKNESSES δ OF ttb-PcSiCl$_2$ LB FILM

δ (Å)	*Number of ttb-PcSiCl$_2$ layers*	ϕ_B (eV)	n
27.6	2	0.53	1.15
55.2	4	0.68	1.20
82.8	6	0.76	1.30
110	8	0.80	1.42

Figure 6 is a typical C–V characteristic curve at high frequency of these structures. It shows a consistent character with MIS devices and does not exhibit any hysteresis. The higher stability of the structures was demonstrated by a series of repeatable tests such as deep level transient spectroscopy measurements of the structures. Some excellent characteristics were displayed because of the suppression of surface defects during the deposition of the LB films, *i.e.* because of the passivation of the InP surface which was caused by the LB film.

4. SUMMARY

We have investigated the preparation of ttb-PcSiCl$_2$ LB film and its possible use in electronic devices. All the optical and electrical measurements are consistent with the molecules being stacked edge on to the substrate with a preferred orientation perpendicular to the dipping direction, and the aggregation in the floating film is much reduced. We have also illustrated the role of ttb-PcSiCl$_2$ films as both passive and active layers in a range of electronic devices. Results indicate that the organic layers can be reliably introduced into these devices. The use of the layers to precisely define the thickness enables the optical and electrical performance of these devices to be optimized.

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LANGMUIR–BLODGETT

THE DEPOSITION
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1. INTRODUCTION

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