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Conductometric gas sensing studies of tert-butyl silicon-[bis ethyloxy]-phthalocyanine LB films

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Abstract Ultrathin Langmuir-Blodgett film properties of tert-butyl silicon-[bis ethyloxy]-phthalocyanine (tbPcSi $(OC_2H_5)_2$) have been studied and characterised. Surface pressure–area isotherms reveal an area per molecule of around 0.85 nm^2, and that a compact 'solid' phase occurs in the region 10–30 $m\,N\,m^{-1}$. LB films of different thicknesses were deposited onto gold interdigitated electrodes on glass in order to facilitate I–V measurements and assess the conductometric sensing properties in response to 5 ppm NO_2. The I–V characteristic is Ohmic and yields conductivity in the range comparable to that obtained for other phthalocyanine monomers. The gas sensing behaviour of these films in response to NO_2 was investigated and modelled using a double exponential model. Preliminary UV–visible spectroscopic investigations indicate that the film also responds optically.

Introduction

Phthalocyanines (Pc) are artificially synthesised macrocycles, which are related to porphyrins. They are brightly coloured materials used in dyes and inks [1]. They are simple to synthesise, highly stable and have strong $\pi - \pi^*$ transitions in the visible region. Metal Pcs are organic semiconducting materials, which have measurable electrical conductivities, are considered to be useful chemical sensors [2] and have strong affinity towards electrophilic gases like oxygen and nitrogen dioxide [1]. Phthalocyanine films can be produced by several methods, like spin coating, vacuum sublimation and Langmuir-Blodgett techniques. LB films are highly ordered films and one can make multilayer structures with varying layer composition that can be deposited on a variety of substrates [3].

Little work has been carried out on Silicon Phthalocyanines over the years with respect to Langmuir–Blodgett characterisation and studying properties such as conductivity and gas sensing, according to our knowledge. Series of silicon phthalocyanines are being investigated for their potential as sensitisers for photodynamic tumour therapy [4, 5] due to their intense absorption in the visible region, high efficiency to generate reactive oxygen species (like singlet oxygen) and low dark toxicity [6]. However, studies have been carried out on Langmuir Blodgett films of tetra-4-tert-butyl-phthalocyaninato-silicon dichloride, which could be incorporated as sandwich layers in electronic devices like photo voltaic devices and gas sensitive structures [7]. Extensive work has been performed on other metal Pcs like Copper, Cobalt and Zinc. This has fueled interest in other metal Pcs including the silicon derivative discussed here (Fig. 1). The emphasis of this work is placed on the conductivity behaviour and the variation of conductivity in response to exposure to low concentrations of nitrogen dioxide(NO_2) gas. Tert-butyl Si phthalocyanine, shown in Fig. 1 has been characterised by surface pressure–area isotherms, UV-visible spectrocopy in solution and the solid state. The I–V characteristics of the sample have

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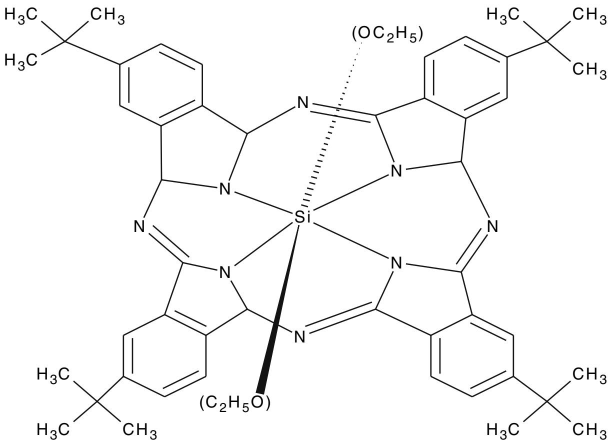

Fig. 1 Tert-butyl silicon phthalocyanine($(OC_2H_5)_2$; (SiPc)

been studied. Furthermore, the ability of the Pc to work as an NO_2 gas sensor has also been investigated.

Experimental work

The (tert butyl silicon Pc($(OC_2H_5)_2$), (SiPc) was supplied by University of Durham and its synthesis has been published elsewhere [8]. The surface pressure–area isotherms for SiPc were studied in a clean room environment at room temperature of 20 °C using a 102M model Nima trough. Deionised pure water from an Elga Purelab water purifier was used as the subphase. Chloroform (Aldrich) was used as the solvent. The SiPc was dispensed from a 100 μL Hamilton syringe drop by drop onto the water subpase. Deposition was carried out on clean glass slides (which were rendered hydrophobic by pretreating them with HMDS) using the Langmuir–Blodgett method, which involved vertical dipping of the substrate through the monolayer. For electrical measurements, gold electrodes (length = 2.88 mm) were used, which had 28 interdigitated fingers. A Joyce–Loebl model trough (Mini-Trough) was used for deposition. A deposition pressure of 15 m N/m was used and the deposition speed was maintained at 10 mm/min. UV–visible solution spectroscopy for different concentrations was carried out using an Ocean Optics Spectrometer (World Precision Instruments) and similarly, solid state spectra studies were recorded on a Spectromate spectrophotometer (World Precision Instruments) The conductivity chamber was a sealed entity with movable probe wires, which made contact with the electrodes on interdigitated samples. A Keithley 236 source measure unit was used to monitor the flow of the current. Gas sensing was carried out using 5 ppm NO_2 in N_2. Two Tylan FC-260 mass flow controllers (Millipore) enabled the regulation of NO_2 and N_2 in the required ratios.

Results and discussions

Surface-pressure–area isotherms

Figure 2 shows the surface pressure–area isotherms of SiPc using a chloroform solution of concentration 0.326 mg/mL. The area deduced by extrapolating the rectilinear portion of the surface pressure–area isotherm, which is called the "limiting area", is approximately 0.85 nm^2.

The material is stable at the air–water interface. The isotherm shows a gradually rising surface pressure with no abrupt phase transitions and is characteristic of isotherms measured for many other phthalocyanine monomers [9]. The ligands attached to the metal ions are comparatively short, so do not interfere drastically in the packing process during compression unlike ligands composed of long alkyl chains.

Chemical Modelling (Accelrys MS 3.1) has been carried out in order to determine the size of the molecule and consequently the orientation of the SiPc on the glass substrate. Pc rings can have two extreme orientations; namely they can lie parallel on the LB substrate or show an edge-orientation. The width of the molecule is 0.7 nm and and its length is 1.2 nm. The area per molecule is calculated to be 0.84 and 1.44 nm^2 for edge-on and flat orientation, respectively. So it is suggested that the molecules are tilted edge-on in the water with the oxyethyl chains attached to the central silicon atom protruding upwards and overlapping with the neighbouring molecules. This value obtained for edge-on orientation is similar to that obtained by the surface-pressure–area plot, being approximately 0.85 nm^2. But it should be borne in mind that this alone does not provide conclusive evidence of the orientation of the molecules [10, 11].

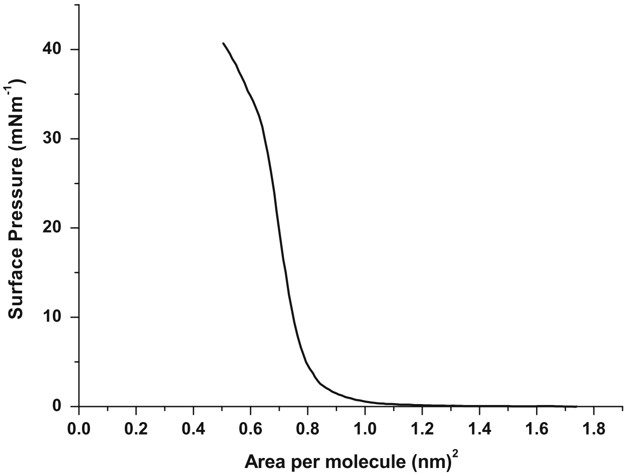

Fig. 2 Surface pressure–area isotherm

UV–visible spectroscopy

The SiPc was dissolved in chloroform and the optical absorbance was studied as shown in Fig. 3. Phthalocyanine macrocycle behaviour in solution is dependant on the nature of solvent, dilution and the strength of molecule–molecule interaction. There are two peaks visible at 618 and 325 nm, and a shoulder at 283 nm. There is no evidence of dimerisation seen. Figure 4 indicates no dimerisation for the specific concentration range taken, and that the Beer–Lambert law is obeyed.

Electrical measurements

The material follows Ohm's law. The I–V characteristics for four different layers on independent glass slides, of SiPc are shown in Fig. 5. It can be seen that 15 and 20 layer conductivities are in between that of 5 and 10 layers. The I–V behaviour for each film thickness shows that Ohm's Law is obeyed, but the dependance of the level of current does not appear to follow the expected increasing trend. This is most likely owing to the unpredictable reproducibility of the transfer quality of the SiPc layers beyond around 10 layers.

The conductivity (five layers) is calculated to be $2.57 \times 10^{-6}\ \Omega\ \mathrm{cm}^{-1}$ for parallel orientation and $1.50 \times 10^{-6}\ \Omega\ \mathrm{cm}^{-1}$ for edge-on orientation on the substrate. These values compare well with conductivities obtained by other researchers such as $5.7 \times 10^{-7}\ \Omega\ \mathrm{cm}^{-1}$ for Co tetra-amine Pc hydrate, $1.3 \times 10^{-6}\ \Omega\ \mathrm{cm}^{-1}$ for Ni tetra-amine Pc Hydrate to $7.6 \times 10^{-7}\ \Omega\ \mathrm{cm}^{-1}$ for Cu tetra-amine Pc Hydrate [12].

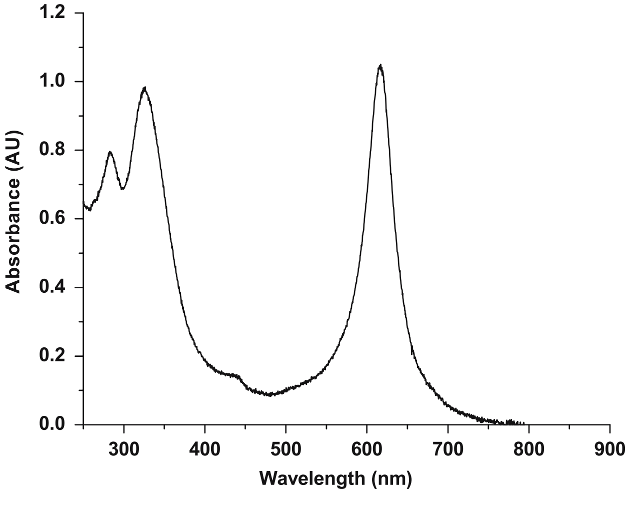

Fig. 3 Solution UV–visible spectra of SiPc

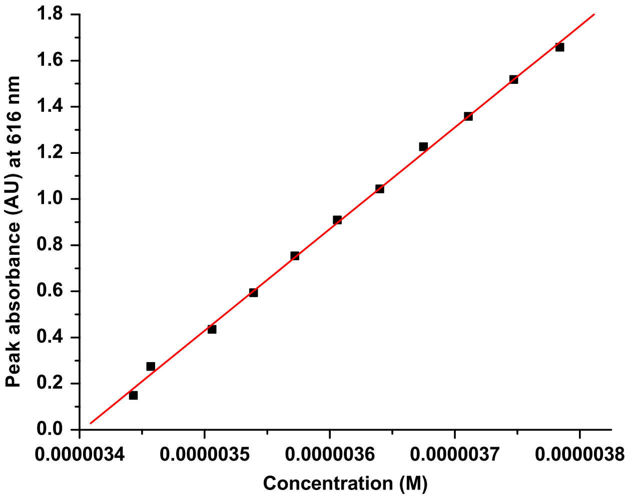

Fig. 4 Beer–Lambert Plot of 3.572M SiPc

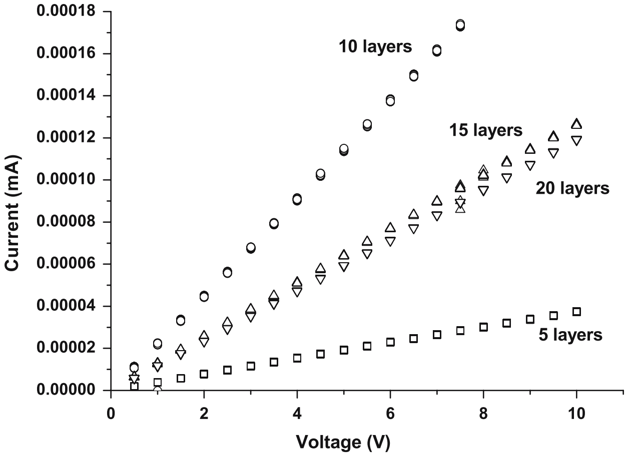

Fig. 5 I–V Characteristics of SiPc

Gas sensing characteristics

The gas sensing response has been recorded for a five-layer SiPc film. Initially gas sensing effects on the material were studied optically, as seen in Fig. 6. There is a decrease in intensity of the 618 nm peak over the time period of the NO_2 gas flow. The corresponding recovery is very slow (several hours). Hence, it was decided to test whether the film would work more favourably as a conductometric gas sensor. The gas sensing response of five layers Pc has been studied for 5 ppm NO_2 at constant voltage of 5 V, as shown in Fig. 7. The gas response kinetics was studied for around 7,000 s at a constant voltage of 5 V using a five layer LB film. The conductivity increases over the time as NO_2 adsorbs onto the film.

The sensitivity, S, is a very versatile indicator, which relates the size of response to the original signal. In case of conducting gas sensors, the sensitivity is given by: $S = \frac{\mathrm{d}I}{I_\mathrm{o}} \times 100\%$ where $\mathrm{d}I = I - I_\mathrm{o}$, where I is the final

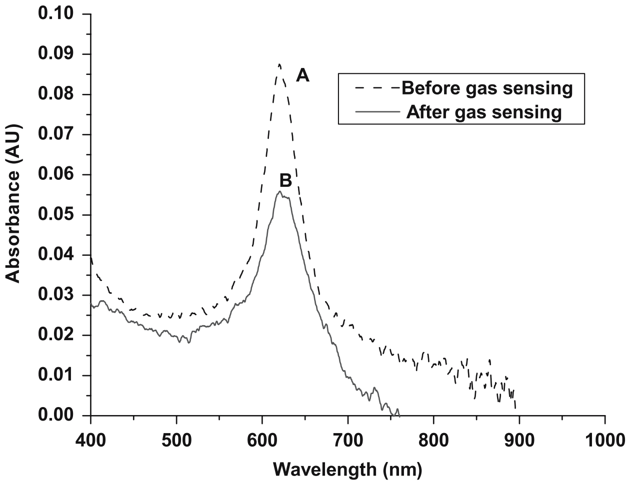

Fig. 6 UV–visible spectra of SiPc and optical gas sensing activity of SiPc

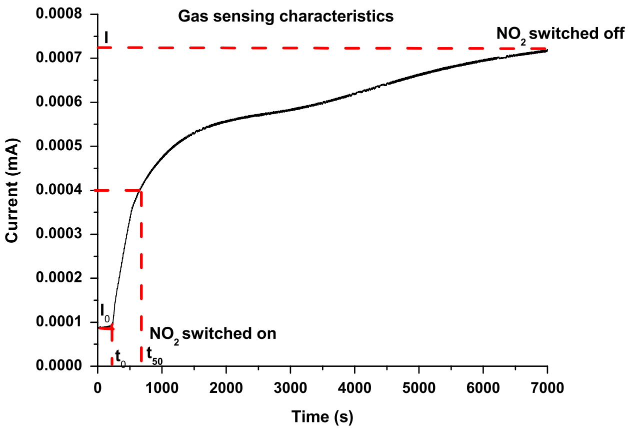

Fig. 7 NO_2 gas sensing behaviour of SiPc

current when the toxic gas is switched off and I_o is the initial current when the toxic gas is switched on. One of the gas sensing parameters to characterise the speed of response and recovery is the t_{50}. It is defined as the time taken for the conductivity curve to reach 50% of its final saturated value.

A ideal gas sensor would exhibit a large and quick response on exposure to the gas, which would result in a large sensitivity and a small t_{50}, respectively. The t_{50} for the five layers sample was also calculated and found to be 457 s. Gas sensing studies were also conducted on 2 and 10 layer samples in identical conditions and similarly, the t_{50}s for the corresponding 2 and 10 layer samples were found to be 755 and 773 s, respectively. The sensitivities for the 2, 5 and 10 layer films are calculated to be 181.10, 706.3 and 635.3, respectively. These sensitivity values are in tandem with vacuum sublimed films exposed to 0.5 ppm nitrogen dioxide at 170 °C, which included PbPc, CoPc, NiPc, FePc, CuPc and MgPc showed sensitivities (Percentage conduction change) ranging approximately between 1,500, averages of 536, 463, 444, 1,200, 325 and 0. The authors conclude that some of these are relative sensitivities and can vary with conditions. Besides this, no data were available for MnPc, Na_2Pc and AgPc either because they were difficult to deposit or showed no measurable conductances. Also though ZnPc did show gas sensing ability, the sensitivity values were not widely reproducible [13]. Armand et al. who deposited MPcs (M = Co, Cu, Zn and Ni) as Langmuir Blodgett films on interdigitated gold electrodes and exposed them to 28 ppm NO_2, observed conductometric response, but the metal sensitivity values did not correlate to the metal sensitivity values obtained by Bott et al. Phthalocyanine do make good gas sensors as Armand et al. further conclude that all MPcs tested did detect NO_2 even at concentrations as low as 2 ppm [14]. These above studies indicated that MPcs are electrically very stable and make good gas sensors although they do not seem to follow a specific trend and not very strongly influenced by specific parameters like the central ions. In the case of SiPc as well, though the sensitivities were not reproducible at a large extent, the conductivity trend was largely stable and its gas sensing properties were intact. However, further work is in progress with respect to reproducibility of the gas sensing characteristics.

There is a rapid increase in current once the NO_2 gas stream is switched on. This can be attributed to the p-type carrier activity of the Pc. The NO_2, being an electron acceptor, withdraws electrons from the Pc resulting in increased conduction. Furthermore, we hypothesise that the relatively short alkyl chains substituted onto this SiPc derivative means that the tunneling barrier between adjacent Pc molecules is small, and that this leads to relatively high conductivity. Also the four tert butyl groups are weak electron donor groups; hence they can enhance the electron donor power of a Pc macrocycle to an electron acceptor molecule like NO_2, as a result of which, the conductivity of the Pc film is elevated [15]. As soon as the NO_2 is switched off, the current begins to decrease since the NO_2 begins to desorb, but recovery is very slow (taking several hours at room temperature).

Gas adsorption modelling

We have tried to understand and model the gas sensing response.The measure of t_{50} is less meaningful when the response does not reach full saturation. The standard Langmuir gas adsorption model and the Elovich model could not be fitted for this material. So an associative exponential was modelled onto the graph, as shown in Fig. 8. This model was also used to explain the gas sensing response of Phthalocyanine Langmuir Blodgett films by

Lando et al. namely for $[(C_6H_{13})_3SiOSiPcOGePcOH]$ phthalocyanine [16]. The theoretical discussion is carried out in the subsequent section.

Theoretical background-gas sensing mechanism

Experimentally, the interactions of gases with solid Pc film surfaces are complex. Basically, the morphology of thin films of phthalocyanines depends on several factors: material, substrate, deposition conditions and subsequent treatment of the deposited film. Ideally, with respect to gas sensing, there will be a range of different adsorption sites available corresponding to the different crystal faces, edges, corners and a range of structural defect sites [17].

According to Weaver et al., the long time scales taken to achieve saturation or full conductivity change suggests that migration of the adsorbed gas to more effective carrier production sites is a slow process, as seen in Fig. 8 (so that if reaction is not initiated during the initial adsorption phase, a considerable delay may be expected before the reactive sites are populated) [18]. A proportional correlation would be expected between film thickness and the magnitude, rate or reversal of the response to the gas, if both surface and bulk contributions occurred [19]. In this case, a direct correlation is between film thickness and conductivity has not been observed, though it could be assumed for lower number of layers. As the conductivity is still increasing rapidly after the 1,000s mark has been crossed as seen in Fig. 8, it becomes clear that a secondary slower process must follow the initial gas adsorption before charge carriers are produced [18]. To adsorb on the surface of the film, the NO_2 will have to displace the already adsorbed gas, in this case oxygen, from the surface. The presence of tert-butyl groups in the phthalocyanine rings facilitates the reactivity towards oxidation processes [20]. Oxygen displacement will occur most easily from the weakest adsorption sites on a heterogenous surface, so the initial rate of adsorption will be small, as the NO_2 will have to compete with the excess of oxygen molecules already present. As the volume of NO_2 steadily increases with time in the chamber, and as more NO_2 is adsorbed on the surface, the molecules will begin to compete with the already present oxygen, leading to lateral repulsions with the adsorbed oxygen in the neighbouring sites, gradually causing displacement of more strongly bound oxygen. Now these sites, will have higher sticking coefficients as well, so the NO_2 adsorption increases [19].

Two different values of t_1 and t_2 can be seen in this case, with reference to Table 1; one is a fast process and the other a slow process. The fast process could be attributed to the receptive adsorption sites, where oxygen is displaced easily. But the longer process will be the result of displacement of more strongly bound oxygen molecules by the NO_2. There is clearly more than one process involved in the contribution to the overall gas response [21]. This feature can probably be due to the different processes occurring on the surface and the bulk of the film, or the presence of two types of adsorption centres [22].

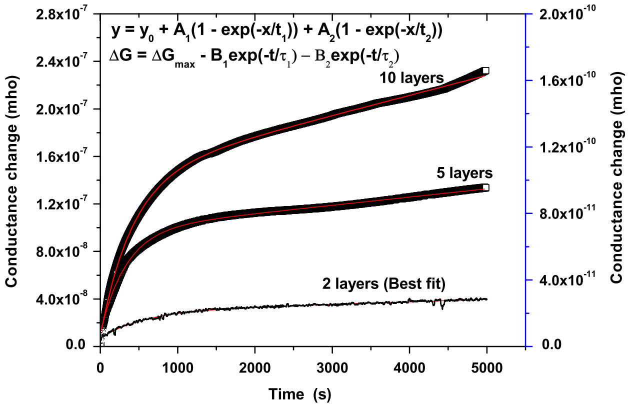

Fig. 8 Electrical gas sensing activity of SiPc

It is to be noted that alkyl substituent chain lengths can influence molecular packing and reorganisation in LB films and hence, can influence properties of phthalocyanines like photoconductivity, modulation of conductivity on exposure to gases and also not the least, optical absorption [23]. Monolayer behaviour and film deposition are highly sensitive to the type of alkoxy group attached to the ring and whether the compounds have been rendered amphiphilic through the modification of side chains. Similarly, metallated derivatives show consistently better behaviour than metal free derivatives [24]. To sum up, shortening the chain has two effects: the more obvious is the reduction of the insulating aliphatic component of the molecule, the less obvious is a change in the molecular packing within the LB

Table 1 NO_2 gas response of t-butyl Si Pc-with reference to Fig. 8

Layers	$\Delta G\ (\Omega^{-1})$	t_1 (s)	t_2 (s)	A_1	A_2
2	4.97×10^{-12}	558.8	9.92×10^{10}	1.6×10^{-11}	1.4×10^{-4}
5	9.98×10^{-9}	418.9	1.16×10^{12}	1.3×10^{-7}	19.7
10	1.2×10^{-8}	333.7	2.8×10^{14}	8.6×10^{-8}	1951.1

With respect to the inset equation in Fig. 8 [16], t_1 and t_2 are the two time constants, ΔG is the conductance change and A_1 and A_2 are constants film [25]. Future work will continue to try to understand the response of gases to the SiPc with respect to its dependance on alkyl chain substituents and presence of metal ions.

Conclusions

Measurements of I–V characteristics of the SiPc have shown Ohmic behaviour for 0.1–10 V. The SiPc is sensitive to 5 ppm NO_2 since the conductivities increased over the gassing time period. The reason for this is that the gas being an electron acceptor interacts with the SiPc, thereby increasing the number of charge carriers. The conductivities obtained are in the similar range as obtained for other metal Phthalocyanines. A double-exponential model has been fitted with the gas sensing kinetics and revealed a fast initial response followed by a very slow contribution. Future work will focus on studying a range of silicon phthalocyanines containing axial ligands composed of alkyl substituents of different lengths in order to establish the relationship between ligand length, orientation within the Langmuir layer and film conductivity.

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