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Electron beam modified zinc phthalocyanine thin films for radiation dosimeter application

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ABSTRACT

Present study deals with the effect of electron beam irradiation on electrical and gas sensing properties of zinc phthalocyanine (ZnPc) thin film prepared on flexible Biaxially Oriented Polyethylene Terephthalate (BOPET) sheet. The electron beam irradiation of ZnPc films were carried out using a 10 MeV RF Linear accelerator, under different radiation dose levels from 1 kGy to 30 kGy. The pristine and irradiated films were characterized by using X-ray photoelectron spectroscopy, Atomic Force microscopy, UV–vis spectroscopy and X-ray diffraction. Samples irradiated in the dose range of 1–18 kGy exhibit linear enhancement of electrical conductance due to increasing content of adsorbed oxygen. Beyond 18 kGy the sample exhibit saturation in the content of adsorbed oxygen as well as in electrical conductance. The pristine ZnPc films exhibit excellent chemi-resistive response towards H_2S gas in 1–20 ppm range at room temperature. The response of the irradiated films decreases monotonically with increasing electron beam dose due to the strong binding of oxygen at the Zn sites. A plausible mechanism of electron beam induced modification of ZnPc films and its implication on charge transport as well as chemi-resistive gas sensing behavior are discussed. This work highlight the utilization of ZnPc thin films as potential radiation dosimeter based upon linear rise in electrical conductance.

1. Introduction

The electron beam irradiation technology involves modifying the physico-chemical properties of materials using electron beam as a tool. The electron beam irradiation experiments are usually performed using linear accelerators, which generate high dose rates ranging from a few Gy/s to 10^6 Gy/s and also provides a large energy range from 300 keV to 10 MeV [1]. In the last few decades the electron beam has been extensively used to modify the physico-chemical properties of organic materials [2]. The nature of interaction between electrons and organic materials depends on the energy as well as dose of the incident electron beam [3]. One of the most widely studied organic semiconductor material is metal phthalocyanine (MPc) due to its high thermal/environmental stability, low cost and wide range of application including gas sensors [4], organic solar cells [5,6], organic field effect transistors [7] etc. Since intrinsic MPcs are basically insulators and can become p-type semiconductor when exposed even to the atmosphere because of the associated surface modifications. This hints at a possibility of tuning the electrical properties of MPcs by using other means that can introduce surface modifications. In the case of atmospheric exposure, the tailoring of electrical conductivity mainly arises due to the change in electron/hole concentrations because of adsorption of gas molecules at MPc surface [8–11]. In the present work, we have first investigated the modification of ZnPc thin films on irradiation with electron beam of different doses. Further the pristine as well as irradiated films were compared for the electrical and gas sensing studies. We demonstrate that the surface chemistry as well as bulk structure of pristine ZnPc films gets modified on interaction with electron beam resulting in the linear enhancement of electrical conductance with electron beam dose. Such a linear dependence of electrical conductance of ZnPc films on electron beam dose is proposed for the development of radiation dosimeter. The pristine ZnPc films exhibit good sensitivity towards H_2S gas in ppm concentration range at the room temperature. Interestingly in spite of having high electrical conductivity of irradiated ZnPc films, there is systematic lowering of the response towards H_2S gas with increasing electron beam dose. Detailed characterization of pristine as

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well as irradiated ZnPc films has been carried out to explain the observed charge transport and gas sensing behaviors.

2. Experimental

2.1. Synthesis of flexible ZnPc films

Thin films of ZnPc having thickness of ~20 nm were grown on flexible biaxially oriented polyethylene terephthalate (BOPET) substrates by vacuum thermal evaporation technique. The ultrasonically cleaned BOPET polymer sheet (Dupont make) having thickness of ~100 μm was used as flexible substrate. The base pressure of the chamber during the deposition was $\sim 2 \times 10^{-6}$ mbar. The distance between source (ZnPc filled tantalum boat) and the substrate is about 12 cm. High electrical current was passed through the tantalum boat to evaporate the material at a controlled rate (deposition rate ~1 Å/s measured using a Quartz crystal based thickness monitor). The film preparation was concluded by keeping the substrate at room temperature (during deposition) followed by in-situ vacuum annealing at 100° C for 15 min. For electrical and gas sensing measurements, a few pairs of gold electrodes (thickness ~50 nm) of size 3 mm × 3 mm having separation of ~12 μm, were thermally evaporated on the ZnPc thin film using a metal mask.

2.2. Electron beam irradiation of ZnPc films

The electron beam irradiation of ZnPc films has been carried out using a 10 MeV electron beam generated with RF Linear accelerator (Linac) at the Electron Beam Centre (EBC, BARC), Kharghar, Navi Mumbai, India [2]. The 10 MeV electron Linac, indigenously designed and developed by BARC, consists of a series of coupled cavities and electron acceleration takes place with oscillating electric fields which is driven at resonance by a microwave (or RF) power source, klystron. It is operated in pulsed mode and the beam pulses are scanned over a 1 m long titanium exit window with a scan frequency of 1 Hz. The beam pulses generated from the accelerator with a certain repetition frequency and it was set in such a way that the desired uniformity of radiation dose can be realized over the full irradiation area (or scan length) [12]. The output dose rate is around 1 kGy per pass in the dynamic mode of irradiation keeping a product speed at 2 m/min under fixed operating parameters and the dose delivery was done by setting appropriate number of passes [13]. In order to protect from dust the films were kept in a close plastic box of thickness around 2 mm which does not attenuate 10 MeV electron beam significantly. The irradiation experiments were carried out under atmospheric conditions.

2.3. Characterization techniques

The X-ray photoelectron spectroscopy (XPS) of samples was carried out using Mg K_α (1253.6 eV) radiation and the recorded data were calibrated using C-1s peak from the adventitious carbon-based contaminant with the binding energy of 284.6 eV. The base pressure of the chamber during the XPS measurement was $\sim 2 \times 10^{-8}$ mbar. The analyzer was operated at 40 eV and 100 eV pass energy values for the narrow regions and survey spectra, respectively. Elemental atomic concentrations were calculated from areas under the XPS peaks and the corresponding Scofield sensitivity factors corrected for the analyzer transmission work function. The UV–vis spectroscopy was done using a double beam spectrophotometer (Jasco, V 530). Bruker (CA, USA) make Dimension Icon Atomic force Microscope (AFM) was used to image the surface morphology of the samples. Scanasyst-air cantilever of 2 nm tip size and having 0.4 N/m force constant has been used in Scanasyst mode (tapping mode). The X-ray diffraction (XRD) was done in the powder diffraction mode with a PANanalytical instrument (model EMPYREAN) using a Cu-Kα source (λ ~ 1.5418 Å) with an emission current of 15 mA and voltage at 30 kV. Scans were collected over the 2θ range from 5.5° to 8° in a step size of 0.01° and count time of 0.5 s/step.

2.4. Electrical conductivity and chemiresistive gas sensing measurements

The electrical conductivity of the films was measured using conventional two probe technique. Electrical connections on the sample were made using silver wire of diameter ~100 μm and silver paint (Electrolube make) was used to attach the wire with the gold electrodes prepared on films. Electrical and gas sensing properties of the samples were measured using a voltage source/picoammeter (Model: Keithley 6487). The measurements were carried out using a personal computer equipped with the software. The Current-Voltage (*I–V*) curve was plotted by varying bias voltage in range of ± 50 V (in steps of 1 V) and measuring the current. It may be noted that in the present work two probe method was applied to measure the electrical properties of the zinc phthalocyanine films due to their very high electrical resistance (~1000 MΩ). Since films (ZnPc) and electrode (gold) has nearly matching work function of ~5.1 eV, hence films/electrode interface is ohmic in nature (also revealed by the linear current-voltage characteristics shown in Fig. 8(a)) with contact resistance ≪films resistance. In addition for four probe measurement of electrical property for such highly resistivity films is extremely difficult due to the fact that constant current (for measurement of resistance) cannot be sent through the sample from current source due to its low internal impedance. For gas sensing experiments the response curves (current versus time data) were recorded for ZnPc films using a static gas testing setup and applying a fixed voltage to the sample. Briefly, the films were mounted in a leak tight stainless steel chamber having net volume of about 1000 cm^3. The schematic of gas sensing set up is shown in Fig. 1. A desired concentration of the test gas in the chamber was introduced by injecting a known quantity of gas using a micro-syringe. Once a steady state was achieved, recovery of films was recorded by exposing the sensor films to atmosphere by opening the lid of the chamber. The response (%) of the sensors was calculated from the response curves using the relation:

$$\text{Response (\%)} = \frac{|R_g - R_a|}{R_a} \times 100 \quad (1)$$

where R_g and R_a stand for the resistance values of the sensor films in test gas and fresh air respectively.

3. Results and discussions

3.1. X-ray photoelectron spectroscopy

The survey XPS spectra of pristine and irradiated ZnPc films (Fig. 2) exhibiting the presence of C1s, N1s, Zn2p and O1s peaks in the spectrum. The spectrum is in conformity with other MPcs [14].

High resolution C1s, N1s, Zn2p and O1s XPS spectra are shown in Fig. 3(a–d). Using the area under curve for high resolution C1s, N1s and Zn2p XPS peaks and corresponding elemental sensitivity factors, for pristine films the atomic ratios C/Zn and N/Zn were found to be 31.6 and 7.7 respectively. It indicates that the pristine ZnPc films have the same chemical composition ($C_{32}H_{16}ZnN_8$) as that of the source ZnPc material. The high resolution C1s peak shown in Fig. 3a consists of three main components. The features at binding energies of 284.6 eV and 286 eV are attributed to aromatic carbon of the benzene rings and to pyrole carbon linked to nitrogen, respectively. The area ratio of both peaks (number of C atoms in benzene ring to the number of C atoms in pyrrole ring) is ~3, which is in agreement with chemical structure of ZnPc. The broad lower intensity components (at ~288.2 eV) is attributed to the shake-up satellite due to $\pi - \pi^*$ transitions [15]. As for other PCs, the N1s spectra [Fig. 3b] for pristine films consist of two peaks centered at about 398 eV and 399.8 eV respectively representing the two chemically slightly different N atoms in ZnPc. One of the N