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Studies on phase transformation and molecular orientation in nanostructured zinc phthalocyanine thin films annealed at different temperatures

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ABSTRACT

Studies on the electronic and optical properties of thin films of organometallic compounds such as phthalocyanine are very important for the development of devices based on these compounds. The nucleation and grain growth mechanism play an important role for the final electronic as well as optoelectronic properties of the organic and organometallic thin films. The present article deals with the change in the film morphology, grain orientation of nanocrystallites and optical properties of zinc phthalocyanines (ZnPc) thin films as a function of the post deposition annealing temperature. The effect of annealing temperature on the optical and structural property of vacuum evaporated ZnPc thin films deposited at room temperature (30 °C) on quartz glass and Si(100) substrates has been investigated. The thin films have been characterized by the UV–vis optical absorption spectra, X-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy. From the studies of UV–vis absorption spectra and XRD data, a metastable α to β-phase transformation has been observed when the thin films were annealed at a temperature greater than about 250 °C. The FESEM images have shown the particlelike structure at room temperature and the structure became rodlike when the films were annealed at high temperatures. TEM image of ZnPc film dissolved in ethanol has shown spectacular rod-shaped crystallites. High resolution transmission electron microscopy image of a single nanorod has shown beautiful "honey-comb" like structure. Particle size and root mean square roughness were calculated from AFM images. The changes in band gap energy with increase in annealing temperature have been evaluated.

1. Introduction

Metal phthalocyanines (MPcs) are dye pigments [1] consisting of a central metallic atom bound to a π-conjugated ligand and the chemical structure of these materials has a similarity with biological molecules chlorophyll and hemoglobin. MPcs are well-known for their interesting properties such as high thermal and chemical stabilities [2,3], catalytic activity, [4] semiconductivity [5,6] and photoconductivity [7]. Researchers have attempted to use thin films of MPcs as molecular components in various electronic and optoelectronic devices [7–9]. Most of the MPcs can easily form ordered thin films and high vacuum evaporation technique has become the most widely used technique [10–12] for the deposition of MPc films. It has been observed that structure, morphology, electronic and optical properties of the films are crucial for their technological applications [13]. In our research laboratory growth of nanoparticles, nanoflowers, nanocabbages, nanorods, nanoribbons in copper phthalocyanine (CuPc) [14,15] and other MPcs [16], effects of annealing [17] on the morphology and optical property of CuPc thin film, power spectral analysis [18] and photoconductivity behavior [18] in CuPc nanostructured thin films, nanostructured organic–inorganic photodiodes [19], persistent photoconductivity [20] etc. in nanostructured CuPc have been studied. Louis et al. [21] have studied molecular orientation and optical properties of zinc phthalocyanine (ZnPc) grown under different pressure conditions. Effects of thickness and temperature on the structural and electric-optical properties of ZnPc thin-films have been studied by Zanfolim et al. [22]. Other reported works on ZnPc include the effects of phase change on dielectric properties of ZnPc thin films [23], studies on infrared and Raman spectra from density functional theory calculations [24], gas sensing property [25] of different phases of ZnPc, studies of incident photon to current efficiency in organic solar cell [26] containing ZnPc, crystal behavior of ZnPc thin films in alcohols [27], nanostructure formation in vacuum evaporated ZnPc thin films deposited at different temperatures [28], effects of temperature on the molecular orientation of ZnPc films [29] etc. Based on the Fourier transform infrared (FTIR) data of only one annealed (at 200 °C) ZnPc sample it was suggested by Gaffo et al. [29] that a phase transition from α- to β-polymorphs occurs through metastable *x*-form with a flat-on preferential orientation of macrocycle plane on the substrate.

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It has been reported [30] that for application in various devices, the nucleation, grain growth and orientation of grain play an important role in determining the final electronic as well as optical properties of organic thin films. The understanding and control of the orientation of the grains or crystallites in the film and roughness of film surface would allow regulating many important properties that depend on grain boundaries, grain size and film roughness [30]. Considering the importance of the ZnPc thin films in future nanotechnology, it was thought worthwhile to study systematically the morphology and molecular orientation in ZnPc thin films after annealing at a wide range of temperatures from room temperature to temperatures much higher than 200 °C. In the present experiment ZnPc thin films were annealed at different temperatures. Then the change in film morphology, molecular orientation and optical properties were studied at room temperature. The change in Davydov splitting, of the absorption band of ZnPc thin film in the visible range, with annealing temperature was studied to check the effects of structural changes and its correlation with the interplanar spacing. Transmission electron microscopy (TEM) image of ZnPc film dissolved in ethanol has shown spectacular rod-shaped (few micro meters) crystallites. High resolution transmission electron microscopy (HRTEM) image of a single nanorod has shown beautiful "honey-comb" like structure. Thin film of ZnPc grown on carbon coated grid has shown elongated crystallites and the interplanar spacing calculated from selected area electron diffraction (SAED) pattern exactly matches with the interplanar spacing calculated from X-ray diffraction (XRD) analysis of ZnPc thin films. Our results from the FTIR studies do not agree with the reported results by Gaffo et al. [29] regarding the preferential orientation of macrocycle plane of ZnPc on the substrate surface. The results are discussed in this article.

2. Experimental details

The ZnPc powder (dye content ~ 97%, obtained from Aldrich, USA) was used for the preparation of the thin films on quartz glass and Si(100) substrates. The molecular structure of a ZnPc molecule is shown in Fig. 1. Before coating, rectangular quartz glass substrates were first cleaned with a liquid detergent and water. Then they were placed in dilute nitric acid for 30 min and then they were washed with distilled water and agitated ultrasonically in alcohol. Finally, the substrates were rinsed in acetone and dried in an oven. Then the residual amount of adsorbed species was removed from the substrates by high-tension discharge cleaning available in the high vacuum coating unit. The film deposition technique was similar as reported earlier [14–20]. The ZnPc source contained in a molybdenum boat was resistively heated in a high vacuum chamber by using a Hind Hivac coating unit (model 12A4D; Hind Hivac, Bangalore, India). Repeated degassing of the ZnPc source prior to deposition was carried out. Deposition was done when the chamber pressure could no longer reduce to the base pressure and the current (~1.9 A) through the molybdenum boat was kept constant. ZnPc films were deposited at a substrate temperature of 30 °C (room temperature) and at chamber pressure of $\sim 1.333 \times 10^{-4}$ Pa. The thickness of the deposited ZnPc film and the rate of deposition were maintained at 300 nm and 0.06–0.1 nm s^{-1}, respectively. Previously, Zanfolim et al. [22] have reported that the temperature of the source reached about 410 °C by passing 2.2 A current through a Ta boat containing ZnPc powders. As ZnPc remains stable upto ~447 °C in nitrogen atmosphere, it is understood that this material was stable during deposition under high vacuum. After deposition, the ZnPc films were annealed at different temperatures (ranging from 30 to 350 °C) under normal atmosphere for 1 h. It has been reported by Bayliss et al. [31] that metal free phthalocyanine (H_2Pc) remains stable upon annealing for 2 h under open air at a temperature of 330 °C. From the observed systematic changes in UV–vis spectra of ZnPc upon annealing upto 350 °C in air, we believe that ZnPc remains stable under annealing. The thin films have been characterized by UV–vis absorption spectra, XRD, FESEM, AFM, FTIR and TEM. ZnPc thin films were analyzed by XRD using a Bruker axs, (D8 advance) diffractometer supported by LynXEye super-speed detector and Ni-filtered Cu-Kα ($\lambda = 0.15418$ nm) radiation generated at 40 kV/40 mA. The diffractometer has been operated with a scan speed of 0.5 s for steps of 0.02° in 2θ. An UV–vis Scanning Spectrophotometer (UV-2401 PC, Shimadzu, Japan) was used to record the electronic absorption spectra of the films at room temperature. FESEM (model: JSM-6700F, JEOL, Japan, operating voltage 5 kV) was used to record the scanning electron micrograph images of the ZnPc thin films. To estimate the surface roughness of the thin films, the semi contact mode AFM images were taken using NT-MDT (Solver PRO-M), Moscow, Russia. TEM images were taken by using TEM (Model: JEM-2010, JEOL, Japan, operating voltage 200 kV).

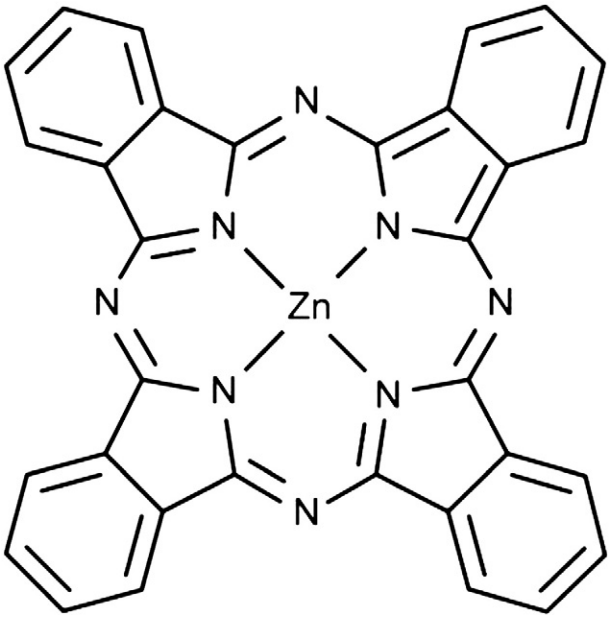

Fig. 1. Structure of a ZnPc molecule.

3. Results and discussion

3.1. FESEM images of ZnPc thin films

FESEM images of ZnPc thin films deposited on a quartz substrate at room temperature and annealed at different temperatures after deposition are shown in Fig. 2. Fig. 2a shows the densely packed nanoparticles at room temperature (30 °C). The particles are almost spherical in shape and the average diameters of the particles are in the range 50–70 nm. Few particles having larger diameter are also observed (inset of Fig. 2a) in the as deposited thin film and these particles arise due to the coagulation of smaller particles. For the film annealed at 100 °C, the average size of the particles increases as seen from Fig. 2(b). This is due to the enhancement in the coagulation of particles (inset of Fig. 2b shows the coagulation in the magnified scale). The films annealed at a temperature of 200 °C show an average diameter of particles about 100 nm (Fig. 2c) and the particles are almost uniformly distributed throughout the whole regions. When the annealing temperature of the ZnPc thin films increases to 250 °C, the shape of the particles changes from spherical nanoparticles to cylindrical nanorods, as shown in Fig. 2d. The average length of the nanorods is in the range of 150–200 nm and the diameter is around 70 nm. Some changes in alignment of the nanorods are also noticed. It is clearly observed from Fig. 2d that the nanorods have a tendency