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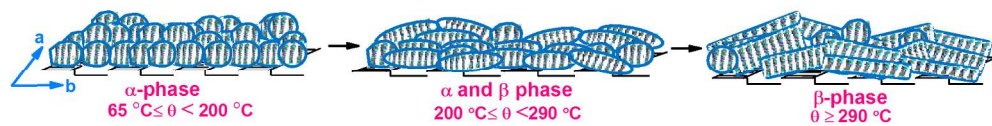


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Model representing growth mechanism in the LB thin film during phase transformation from α to β -phase on annealing.
179x23mm (300 x 300 DPI)

Comparative optical, structural and electrical property study of Zinc Phthalocyanine Langmuir Blodgett Thin Film on annealing

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The Zinc Phthalocyanine (ZnPc) in mixture of N-Methyl Pyrroldione (NMP) and Chloroform CHCl_3 [1:10(v/v)] spreading solvent observed to have only monomeric absorption peak while on processing the solution into thin film using Langmuir-Blodgett (LB) technique, it shows absorption peaks corresponding to H, J and monomer aggregates as confirmed from UV-Vis absorption spectroscopy. The Q-band absorption spectra of ZnPc LB thin film observed to have a sharp change on annealing at 65 °C indicating a change of aggregation configuration of molecules over the surface. The annealed ZnPc LB thin film is found to be having H and monomer aggregates only, which indicates that ZnPc molecules are arranged in an edge on face-to-face conformation. The ZnPc LB thin film remains in this aggregation till higher annealing temperature. The ZnPc LB thin film shows α -phase characteristic when annealed at 65 °C and it remains intact in this phase till 200 °C. The α — β phase transformation starts taking place from 200 °C and it gets completed at 290 °C. The large increase in crystallite size as obtained from the XRD study and change of shape of the ZnPc nanoparticle from spherical to nanorod structure as observe from FESEM and AFM images confirms the transformation of ZnPc film from metastable α phase to stable β phase. The electrical conductivity is found to enhance greatly for β -phase with respect to α -phase in dark and under photoexcitation because of better charge carrier transport.

Introduction

In organic electronic devices, the structural integrity and uniformity of the organic active layer on different interfaces is highly desirable for optimum device performance [1]. The control of the preferential orientation of the π -stacking direction in a thin film, i.e. the direction of favorable charge transport in conjugated materials is essential in order to improve the transport performances in devices such as organic field effect transistors (OFETs) and organic solar cells [2]. Among the organic semiconductors, the metallophthalocyanines (MPcs) have attracted much interest because of their high thermal, chemical stability, high molecular symmetry, and favorable optical properties [3] combined with unique electronic properties. MPcs consisting of a central metallic atom bound to π conjugated ligand and the chemical structure of these materials has a similarity with biological molecules chlorophyll and hemoglobin. Among the MPcs molecules the Zinc Phthalocyanine (ZnPc) has been used largely because of its semiconductor property and high absorption coefficient (peak value of $1.5 \times 10^5 \text{ cm}^{-1}$) in the wavelength range of 600–750 nm and is hence a popular candidate for small molecule organic solar cells [4-6].

In order to tailor these materials for application in efficient devices, it is important to have a proper knowledge of the crystallinity and morphology of their in thin films, their optical property and transport properties. This makes it necessary to understand the emergence of aggregation behavior of the molecules and the polymorphism in thin films of these macrocyclic π -conjugated materials since it impacts directly the device performances. The growth of organic molecules depends on the interaction of the molecules with different types of surfaces [7]. The weakly interacting substrates have small surface free energy (mainly oxides such as SiO_2 , glass, Al_2O_3 and polymeric substrate), preferentially favor the upright standing growth of planar and nearly linear extended molecules for thin film deposition because the van der Waals and π - π interaction with neighbours is energetically preferred over the molecule-substrate interaction [8]. Similarly on strongly interacting metallic surfaces the organic molecules adopt a flat lying molecular orientation.[9].

Supramolecular self-assembly is a very useful technique to fabricate molecular materials [10] to investigate properties including electrical conductivity and sensing. Phthalocyanine molecules have tendency of forming self-aggregation to form

dimers and higher order aggregates in solution and at the solid-liquid interface [11], owing to π -stacking, hydrogen bond and electrostatic attractive forces between the molecules. The spectral shift in the absorption spectrum takes place due to their self assembly as explained by the molecular exciton theory proposed by Kasha [12-14]. The bathochromically shift (red shift) corresponds to the J-aggregates having edge to edge stacking of the molecules and the hypsochromically shift (blue shift) corresponds to the H-aggregates having face to face stacking of the molecules, are explained in terms of molecular exciton coupling theory i.e. coupling of the transition moments of the constituent dye molecules.

It is well-known that Pcs containing divalent first-transition metal exhibit different polymorphic forms, especially α and β forms when deposited on weakly interacting substrate, both characterized by herringbone structure with molecules stacked along b axis [15]. The α - β phase transformation is achieved in thin films by thermal annealing, by solvent vapor annealing, or by controlling the substrate temperature during deposition [16-19]. α phase is differentiated from the β phase by their structure, surface morphology, optical properties and electronic properties. Here we have opted Langmuir Blodgett (LB) Technique for preparation of ZnPc thin film. Langmuir-Blodgett Technique offers excellent method for constructing supramolecular assemblies or ultrathin organized molecular films of functional materials. Using this technique not only the molecular orientation but also the molecular arrangement and the aggregation can be improvised in 2D manner. Mainly substituted Pc compounds were usually employed as sample materials, because of their good solubility in organic solvents such as chloroform and benzene. However some unsubstituted Pcs are soluble in appropriate mixtures of strong organic acids and organic solvents. Present work deals with the multilayer thin film of unsubstituted Zinc Phthalocyanine (ZnPc) prepared from a solution of ZnPc in a mixed solvent of N-Methyl Pyrrolidone (NMP) and Chloroform (CHCl_3).

The molecular architecture and crystallinity of LB deposited thin film was determined in terms of growth at the nanometer scale, using X-ray diffraction and UV-Vis absorption spectroscopy. The surface morphology of the films was examined by Atomic force microscopy and Scanning electron microscopy. The electrical photo conductivity measurements of the films were also carried out.

Experimental Details

Preparation of Thin Films.

The Langmuir-Blodgett (LB) films were formed using a Langmuir trough (Apex Instruments Co.) with a calibrated Wilhemy plate balance. The LB trough was filled with Milli-Q water having pH (~6.0), left idle for about 16 hours and then water surface was cleaned repeatedly till surface pressure $\pi \sim 0$ mN/m. The ZnPc (Sigma-Aldrich) was used as received. The molecular structure of ZnPc is shown in Fig.1. The spreading solution was prepared by dissolving the ZnPc at a concentration of 1mg/ml into a mixture of N-Methyl Pyrrolidone (NMP) and Chloroform (CHCl_3 , Merck, Analytical Reagent) [1:10 (v/v)] solvent. Then using a microliter syringe 200 μL of solution was

spread and left undisturbed for 20 min for evaporation of solvent. Then surface pressure – molecular area (π -A) isotherm was recorded by compressing the spread monolayer over water surface at a rate of 5 mm/min till the surface pressure attains $\pi \sim 35$ mN/m. The spreading monolayer film was then transferred onto solid substrates using the vertical dipping method at a surface pressure $\pi \sim 35$ mN/m where a compact Langmuir film was formed. Here, the LB film deposition was done at 27 °C and at a 4 mm/min dipping speed for subsequent up-down strokes of substrate through the air-water interface. Drying time for first up stroke was kept 20 min and then for each subsequent upstroke i.e. above subphase was kept 10 min and similarly for downstroke i.e. below subphase was 5 min. Hence we deposited a multilayer film of 40 layers ZnPc using the above procedure. The Quartz slides are used as solid substrate for UV-Vis measurements. Glass slides are used as solid substrate for AFM, SEM, XRD and XPS measurements and ITO substrate was used for I-V measurements both in dark and under light.

Characterization Techniques

The optical absorption was recorded by PerkinElmer (Model Lambda 950) UV-Vis-NIR spectrophotometer. The structural study of the films were carried out by X-ray diffraction measurements using Bruker D8 Advance X-ray diffractometer which uses Cu-K_α radiation ($\lambda=1.543 \text{ \AA}$) and a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector). For chemical analysis of the LB film, XPS measurement was performed with Omnicorn Multiprobe spectrometer fitted with an EA 125 hemispherical analyser and a monochromatized Al K_α (1486.6 eV) source. All data are collected at pass energy 40 eV with analyser angular acceptance $\pm 1^\circ$. Atomic force microscopy (Digital Instruments Nanoscope-IV, with Si_3N_4 100 μm cantilever, 0.56 N/m force constant) study was done to observe the morphological and structural details in contact mode. FESEM (model: Supra 55, Germany, operating voltage 1 kV and 2 kV) was used to record scanning electron micrograph images of ZnPc LB thin films. I-V dc measurements are carried out using Keithley 2400 equipment for ZnPc LB film deposited onto ITO coated glass substrate to determine its conductivity at each phase. To investigate the photoconductivity of the LB films, they are illuminated with a halogen lamp of 100 mW/cm^2 .

Results and discussion

π -A Isotherm of ZnPc.

The Langmuir-Blodgett (LB) films were formed using a Langmuir trough (Apex Instruments Co.) with a calibrated The Surface Pressure- Molecular Area (π -A) isotherm of ZnPc monolayer spread over the water surface at 25 °C is shown in Fig.1(a). It was found that the compound form stable floating film at the air/water interface. The isotherm shows onset of the surface pressure, when the ZnPc molecules attain an area of 93 \AA^2 /molecule in the monolayer. On compression, the surface

pressure increases gradually to 10 mN/m, and after this point it increases rapidly which shows that the formation of the solid monolayer. An inflection point is observed at 19 mN/m. This may be an indication of reorientation or certain kind of phase change of ZnPc molecules. From the surface pressure-area isotherm, the limiting area per molecule of ZnPc was estimated to be $41.0 \text{ \AA}^2/\text{molecule}$ [20]. This value is useful for estimating the configuration of ZnPc molecules at the air-water interface. ZnPc molecules have a planar geometry with square type structure (Fig.1(b)). Its side length is 9.7 \AA and diagonal length is 13.7 \AA [21]. If the molecules of ZnPc are densely stacked in a face-to-face orientation and edge-on to the water surface, the average area per molecule would be approximately 33.0 \AA^2 ($9.7 \text{ \AA} \times 3.4 \text{ \AA}$), assuming that the “thickness” of the ZnPc is 3.4 \AA [22]. However, if the molecules of ZnPc are laid down flat on the water surface, the average area per molecule would be approximately 94.4 \AA^2 ($9.7 \text{ \AA} \times 9.7 \text{ \AA}$). The limiting area per molecule calculated from the isotherm of ZnPc molecule is 41.0 \AA^2 , which is inbetween the area per molecule in edge-on and flat lying configuration. Therefore, it is reasonable to consider that as an average the ZnPc molecules are in tilted arrangement over the water surface in the monolayer. The average tilt angle was found to be 64.3° w.r.t. water surface. We can consider that the ZnPc molecules get deposited over the glass substrate in the same particular arrangement as in the monolayer over the water surface because of weak interacting property of glass substrate. The schematic model of structural arrangement of ZnPc molecules over the glass substrate is shown in Fig.1(b).

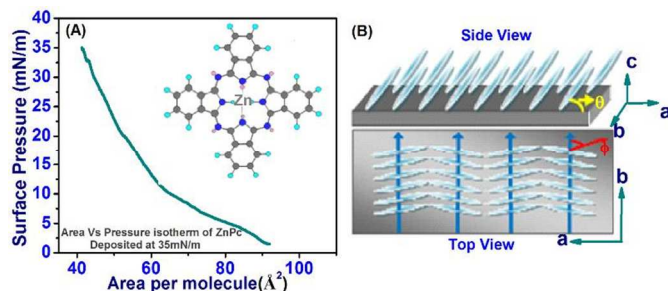


Fig. 1. (A) The surface pressure-molecular area (π -A) isotherm of the spreading monolayer of the ZnPc over the Milli-Q water surface at 25°C , (B) Molecular arrangement of ZnPc molecules over the glass substrate with an average tilt angle (θ) of 64.3° w.r.t substrate surface. Φ is the tilt angle of the molecules within the columns corresponding to α and β phase having $\Phi = 26.5$ and 46.8 respectively.

UV-Vis Spectroscopy Study

The UV-Vis absorption spectra has been used as a tool to investigate the possible aggregation of the ZnPc molecules in the asdeposited film deposited at surface pressure 35 mN/m and also when the film annealed at different temperature. To have better understanding of the aggregation of the ZnPc molecules in the LB film over the substrate, we have studied the absorption spectra of ZnPc in solvent having [1:10] NMP and CHCl_3 as shown in Fig.2(a). Fig. 2(b) represents the absorption

spectra of as-deposited 40 L ZnPc LB film. The absorption spectrum for ZnPc in solvent of NMP and CHCl_3 and asdeposited thin film consist of Q, B, N and C bands which are typical feature of metallophthalocyanine. The B band (or Soret band) having peak at 360 nm and a shoulder at 293 nm points to the coexistence of both monomers and dimers (or higher no of aggregates)[3]. The B band (or Soret) in the UV- Vis region is assigned to the electronic transition from $\pi-\pi^*$ (b_{2u} to e_g) orbitals. The C band is due to $d-\pi^*$ transition, which implies a broader d-band. There is also a small peak N band at 294 nm, which has been attributed to the charge transfer (CT) from the sP_z mixing orbital to the electron system of the macrocyclic ring of the phthalocyanine [23].

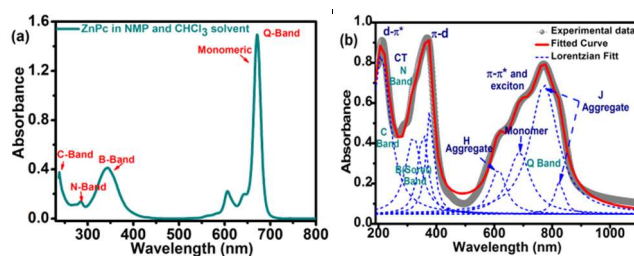


Fig. 2. UV-Vis absorption spectrum (a) of the ZnPc in mixture solvent of NMP and CHCl_3 [1:10 v/v] (b) of the asdeposited ZnPc LB thin film with Lorentzian fitting showing different aggregation presents.

According to molecular exciton theory, the selection rule predicts that the absorption band of the molecular aggregates will show red and blue shift when the angle α which is defined as the angle between the plane of the monomer and the line connecting the centers of the molecular plane, is in the range $0^\circ < \alpha < 54.7^\circ$ for J-aggregate and $54.7^\circ < \alpha < 90^\circ$ for H-aggregate respectively.

In order to have proper knowledge of the molecular packing structure in solution and asdeposited LB thin film, the Q band which exists in the visible region of the spectrum has been studied thoroughly. The absorption spectra of ZnPc in a mixture solvent of NMP and CHCl_3 show a single Q-band absorption corresponds to monomeric absorption with absorption maxima at 672 nm. The ZnPc molecules as known tend to form various aggregates even at very low surface pressure in the monolayer over the LB trough which is mainly owing to their extended flat aromatic macrocyclic core, which favors the $\pi-\pi$ stacking [24]. This results in occurrence of new absorption peaks towards lower and higher wavelength side i.e. at 613 nm, 772 nm and 822 nm in the absorbance spectrum of the LB thin film w.r.t. the monomeric absorption peak as observed in the solvent. The new peaks are obtained by fitting the Q band with four different lorentzian curves by non linear peak fitting method as shown in Fig. 2 (b). This particular blue and red shift indicates the formation of aggregates in the LB thin film. Four bands having peak position at 613 nm, 686 nm, 782 nm and 822 nm corresponds to the coexistence of three types of aggregations over the solid substrate i.e. H, J and monomeric aggregates. It results in different excitation due to electronic interaction

between the constituent molecules and also the intermolecular transfer interaction of the excited holes and electrons. The absorption peak at 613 nm corresponds to the H-type aggregate (blue shift) and absorption peak at 782 nm & 822 nm corresponds to the J-type aggregates, while the peak at 686 nm can be tentatively attributed to monomer band or the some other medium transition aggregates [24]. From the Fig. 2(b) it can be observed that the percentage of ZnPc molecules in J aggregates is much higher than the H aggregates. Therefore it can be concluded that the asdeposited LB thin film having higher percentage of edge to edge stacking of ZnPc molecules in comparison to edge on i.e. face to face stacking of the ZnPc molecules over the substrate surface.

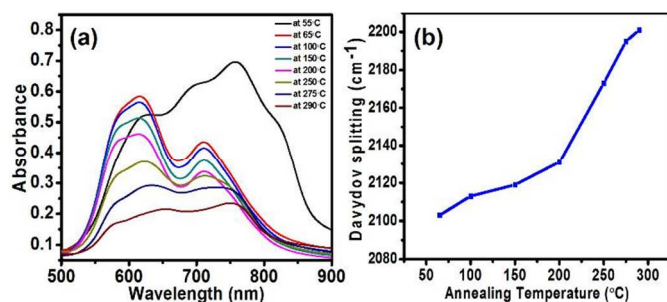


Fig. 3(a). Absorption spectrum of Q-Band and (b) Davydov splitting of the two Q-Band of the ZnPc LB thin film at different annealing temperature.

Effect of annealing. The Q absorption band of the ZnPc LB thin film remains same as that of asdeposited state upto annealing temperature 55 °C and when annealed above 65 °C shows a sharp change as shown in Fig. 3(a), which indicate the possible change in the aggregation or orientation of the ZnPc molecules over the substrate surface. This is generally attributed to vibronic coupling i.e. Davydov coupling in the excited state. The Davydov coupling broadens and splits each of the electronic transitions observed according to the number of translationally inequivalent molecules in the unit cell [25]. Now, Q absorption band is distinctly split into two absorption peaks, one at 633 nm which is related to dimers and higher order aggregates which corresponds to H aggregates only. Similarly the other at higher wavelength 699 nm is related to monomers from the literature [26]. However no peak corresponds to J aggregates has been observed, this confirms that the ZnPc LB thin film annealed above 65 °C have almost all ZnPc molecules in nearly edge on i.e. face to face stacking over the substrate surface. The higher energy peak at 633 nm is connected with the electronic transition from $\pi-\pi^*$ (a_{1u} to $2e_g$) orbitals of the phthalocyanine macrocycle [27], while the low energy peak at 699 nm is attributed to excitonic transition [28]. Here we do not observe any Davydov coupling for the Soret band (B band) which has been observed by M. M. Nahass [29].

The absorption spectra of the ZnPc LB films at different post annealing temperature have been shown in Fig. 3(a). The Davydov splitting is found to increase with increase in post

annealing temperature as seen in the Fig. 3(b). In the XRD study it is shown that the d_{hkl} value decreases with increase in annealing temperature, therefore it can be concluded that the decrease in d_{hkl} value, results in increase in interaction between the adjacent molecules in the ZnPc film which result in increase in Davydov splitting. However the aggregation behavior of the ZnPc molecules in the LB thin film over the substrate surface does not show any major change on annealing and it remains to be in H and monomer aggregate form over the substrate surface. Only a slight shift of the peak of H and monomer aggregates has been observed towards the higher wavelength side and it may be related to phase change of the ZnPc LB film. It is observed from Fig. 3(a) that the peak intensity of the lower energy component start increasing w.r.t to the higher energy component in the Q-Band only after 200 °C which can be taken as the transition temperature for phase transformation of the ZnPc thin film from α -phase to β -phase. Phase transformation to β -phase gets completed at about 290 °C. As earlier studied ZnPc thin film sample deposited either by thermal vapour unit and vacuum deposition unit was observed to remain in the α -phase till the lower energy absorbance peak having less intensity in comparison to the higher energy absorbance peak and it reverses for β -phase obtained by annealing the ZnPc thin film at higher temperature [30, 31]. Therefore, it can be concluded that the ZnPc LB film is in α -phase from 65 °C upto 200 °C and then in higher temperature above 290 °C it remain in β -phase. The intensity of the whole absorption spectrum decreases with increase in annealing temperature, which may be due to degradation or desorption of the ZnPc chromophore with increase in annealing temperature.

X-Ray Diffraction study

The XRD study was carried out to observe the crystal structure of 40 L ZnPc LB thin film deposited on glass substrate with variation of annealing temperature. Fig. 4(a) shows the XRD pattern of powder sample of ZnPc and 40 L ZnPc LB thin film annealed at different temperature. The XRD trace of the powder ZnPc is identified to be β -form [32]. Comparing the XRD pattern of the LB asdeposited ZnPc thin film (Fig.4(b)) with the ZnPc powder, it can be confirmed that a crystalline phase transformation has occurred in the ZnPc LB thin film while deposition over the glass substrate. The asdeposited ZnPc LB thin film shows a small intense peak at $2\theta = 6.78^\circ$ from which it can be confirmed that the film having little crystallinity, and the deposited ZnPc layers are all ordered in either monoclinic or triclinic crystalline phase [33]. The crystallite size (D), strain (ϵ) and presence of dislocations (δ) strongly influence the structural properties of the ZnPc thin films. The crystallite size calculated by using the Scherer formula [33] from the full-width half maxima (FWHM) (β)

$$D = 0.94\lambda / (\beta \cos \theta)$$

Where λ is the wavelength of the incident X-ray, θ is the diffraction angle.

The strain (ϵ) was calculated from the formula $\epsilon = (\beta \cos \theta) / 4$

The dislocation density (δ) which is defined as the length of dislocation per unit volume of the crystal was evaluated from the formula [34, 35],

$$\delta = 1/D^2$$

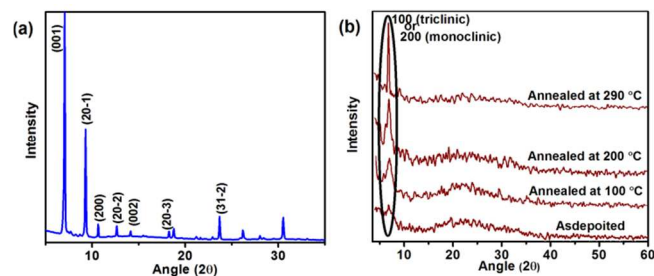


Fig. 4. XRD patterns (Cu- K_{α} radiation) of the (a) ZnPc powder sample showing positions of the allowed Bragg reflections of β -ZnPc with corresponding miller indices, (b) 40 L ZnPc LB thin film deposited on glass substrate at different annealing temperature.

Effect of annealing. The ZnPc LB thin film shows only one major Bragg reflection as shown in Fig. 4(b). It is observed that the 2θ position of the Bragg peak increases from 6.78° to 7.04° on annealing the ZnPc LB thin film from asdeposited state to the temperature 290°C , which indicates the compression of the ZnPc lattice probably due to thermal relaxation. From the UV-Vis spectroscopy study we could not confirm the phase of the asdeposited ZnPc thin film, which shows three types of aggregations and corresponds to both face on and edge on stacking of ZnPc molecules. The ZnPc LB film annealed at 100°C is assigned as α -ZnPc phase from UV-Vis study and the Bragg reflection peak is indexed as 100 for monoclinic or 200 for triclinic crystalline phases [32,36], having ordered arrangement of edge on i.e. standing up ZnPc molecules giving a crystallinity to the LB film [7,37-38]. The increase in the intensity and decrease in FWHM of the Bragg peak on annealing indicates that the scattering volume of the ZnPc thin film increases. This confirms that the crystallinity of the ZnPc LB thin film increases on annealing. Strain (ϵ) and dislocation density (δ) for ZnPc LB thin film both decreases with increase in annealing temperature. The ZnPc crystallite size (D) in the LB thin film was observed to increase steadily with increase in annealing temperature upto 200°C (Fig. 5(a)), which indicate normal growth of the ZnPc nanoparticle under one phase i.e. α -phase as confirmed from UV-Vis spectroscopy study. But for the ZnPc LB thin film annealed at 290°C , show a large increase in crystallite size indicating abnormal growth of ZnPc nanoparticle with change in its probable phase i.e. to β -phase as confirmed from the UV-Vis spectroscopy study. The orientation of the flat ZnPc molecules remains more or less perpendicular to the substrate surface for both identified phases as shown in Fig. 1. and it stacks parallel to the substrate surface [39,40].

The d-spacing i.e. the interplanar spacing between the stacking ZnPc molecules over the substrate surface was observed to decrease from 13.0 \AA to 12.0 \AA (Fig. 5(a)) on

increase in annealing temperature from room temperature to 290°C . This is due to increase in particle size of ZnPc over the substrate on annealing which results in the increase of Van der Waal forces between the ZnPc molecules. The decrease in d-spacing can be considered as one of the reason for change of phase of ZnPc LB film on annealing.

The microscopic strain calculated for the ZnPc thin film was found to be decreasing with increase in annealing temperature as shown in Fig. 5(b). The observed decrease in strain in the ZnPc thin film is mainly because of increase in thermal relaxation, decrease in influence of the interface on the ZnPc layers and decreasing of surface tension of the ZnPc layer.

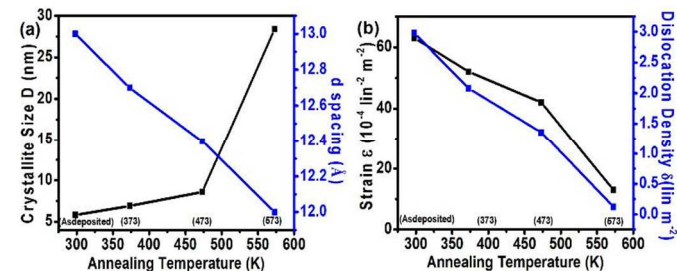


Fig.5. The variation of the (a) Crystallite size D (nm) and d-spacing, (b) Strain ϵ and Dislocation Density δ of ZnPc thin film on annealing.

X-ray Photoelectron Spectroscopy

For excitation, non-monochromatized Al K_{α} radiation is used. For every compound the binding energy scale was determined with reference to the carbon C1s peak centered at 284.2 eV . It is to be noticed that the asdeposited ZnPc thin film sample have the C1s peak containing the respective signal from the carbon atoms. The XPS survey spectra were taken with Al K_{α} of the ZnPc asdeposited thin film sample. The main peaks present are Zn2p, N1s, C1s.

The survey spectrum is a too coarse analysis for an accurate study of all the elements, thus for every single element new settings are needed. The peak positions data of the elements, presented in the table below, are taken from the literature database [41].

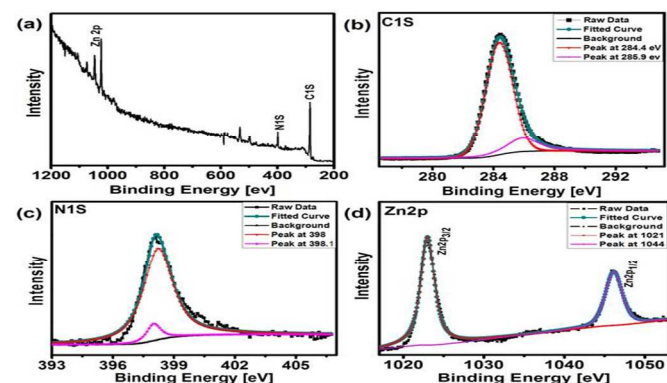


Fig.6 (a) XPS survey spectrum, (b) C1s core level spectrum, (c) N1s core level spectrum and (d) Zn2p core level spectrum of the asdeposited ZnPc 40 L LB thin film.

Table 1. Peaks position of some spectral line of Zn, C & N.

Element	Spectral Line	Binding Energy (eV)
Carbon	C1s	282-288 eV
Nitrogen	N1s	395-402 eV
Zinc	Zn2p	1018-1050 eV

The C1s and N1s core level spectrum of the asdeposited ZnPc 40 L LB thin film are plotted in Fig. 6(b) and Fig. 6(c). A Shirley type background has been subtracted from these spectra.

The C1s peak has an asymmetric line shape with a longer tail on the high binding energy side. The unsubstituted phthalocyanines compounds have two types of contributions which give rise to the C1s peak. The peak at 284.4 eV shows contribution of the aromatic carbons (which is the main contribution for unsubstituted phthalocyanines), and the peak at 285.9 eV corresponds to that of the pyrrolic carbon atoms (found at 1.5 eV higher binding energy than the aromatic carbons in benzene). For each molecule, the N1s peak contains the contributions of meso-bridging and pyrrole nitrogens. As seen in Fig. 6(c), the N1s peak is found at 398.1eV for P0-Zn and P1-Zn and 398 for P2-Zn.

The Zn2p core level spectra as shown in Fig.6(d) have two spin-orbit split components, Zn2p_{1/2} and Zn2p_{3/2}. For 40 L ZnPc LB thin films, the Zn2p_{3/2} and Zn2p_{1/2} binding energies are determined to be 1021.6 eV and 1044.7 eV, respectively.

Surface Morphology Study

FESEM Study. The FESEM image is used to observe grain size, shape of the grown nanostructures and surface texture of the ZnPc thin film. The average diameter of the nanoparticles over the surface of the asdeposited thin film has been observed to be within 12-20 nm and for ZnPc thin film annealed at 65 °C has been observed to be within 15-25 nm as shown in Fig. 7(a) and Fig. 7(b) respectively. The asdeposited ZnPc thin film has been observed to have spherical shaped nanoparticles. The ZnPc nanoparticles start merging with each other showing normal growth to form bigger spherical nanoparticles till 200 °C as described in our earlier study. FESEM image of ZnPc thin film annealed at 290 °C (Fig. 7(c)) shows the formation of elongated nanorod like structure over the substrate surface, which is related to the secondary grain growth process of the ZnPc nanoparticles at higher annealing temperature. The nanorod size was observed to be 1 to 2 μm in length and 34 to 260 nm in diameter. This change of shape of the ZnPc nanoparticle from spherical to nanorod structure is related to phase change of the ZnPc from metastable α-phase to stable β-phase [42]. The elongated nanorods are stacked together in one particular direction in every domain and are separated by grain

boundary region. The π-π interaction between the face to face arranged molecules of the ZnPc is the fundamental reason for the growth of nanorods [43]. The grown nanorods in small domain areas having one particular direction of growth which suggest favorable ordered stacking of ZnPc molecules along that direction through the process of self organization. This favourable orientation stacking is consistent with free energy minimization of the surface, as it is known that the phthalocyanine molecules prefer to stack along b-axis i.e., the plane on plane arrangement of molecules is more stable than the plane by plane arrangement because of its lower energy [44]. A model (Fig. 8) has been presented to show the growth mechanism of the nanoparticles from spherical to elongated nanorod shape during phase transformation from α to β-phase on annealing in LB thin film. The effective stacking of ZnPc molecules along the b-axis increases on annealing has been shown in the model.

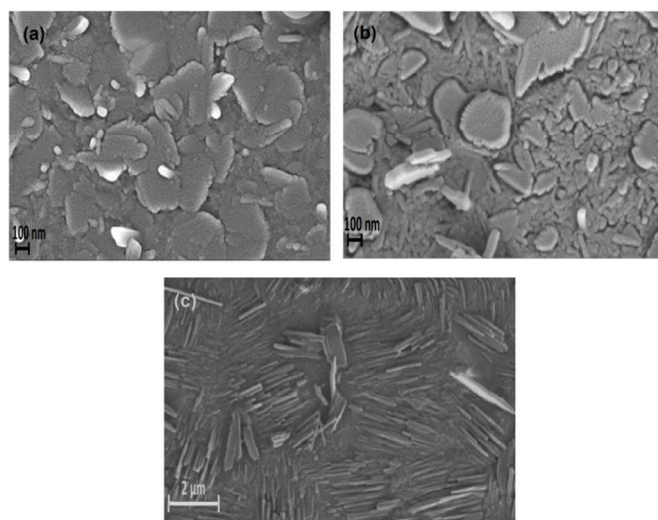


Fig. 7. FESEM image of the 40 L ZnPc LB thin films (a) in asdeposited state and on annealed at (b) 65 °C and (c) at 290 °C.

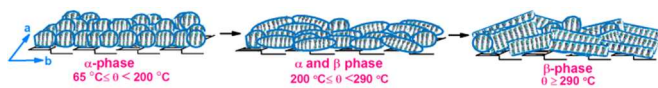


Fig. 8. Model represents the growth mechanism with increase of stacking of ZnPc molecules along b axis in the LB thin film during phase transformation from α to β-phase on annealing.

5.1. AFM Study

The ZnPc LB thin film annealed at 65 °C having monomodal grain size distribution as shown in Fig. 9(a). The average grain size of ZnPc nanoparticles is found to be 21 nm. In normal grain growth, the average grain size increases continuously and the grain size distribution remains monomodal. The grain size distribution for the normal grain growth is fitted to lognormal

function to find out the normal grain diameter D , which is given as.

$$f(D)=1/\sqrt{2\pi}\sigma D[\exp[-\ln^2(D/D_c)/(2\sigma^2)]] \quad (7)$$

The grain size distribution of the annealed ZnPc thin film remains monomodal upto 200 °C along with continuous increase in ZnPc grains size as shown in earlier study, which confirms that the ZnPc thin films have a normal growth of grains till this annealing temperature. Similarly, the grain size distribution obtained for the ZnPc thin film annealed at 290 °C is found to be abnormal (Fig. 9(b)) and it is fitted using Gaussian distribution function as given

$$f(x)=1/(\sigma\sqrt{2\pi}) e^{-(x-\mu)^2/(2\sigma^2)} \quad (8)$$

and convoluting the grain size distribution graph we have obtained three peaks corresponding to an average ZnPc grain size of 39 nm, 72 nm and 120 nm. The abnormal grain growth has lead to formation of ZnPc grains having an average size of 72 nm and 120 nm, which grow at a higher rate in comparison to the average ZnPc grain size of 39 nm which is having in normal growth rate. In thin films, the abnormal grain growth is not solely driven by the reduction in grain boundary energies [45]. The differences in surface energy (the energy associated with top and bottom surfaces of the film) supply an additional driving force for the growth of abnormal grains. It comes into play when grain size is comparable to film thickness.

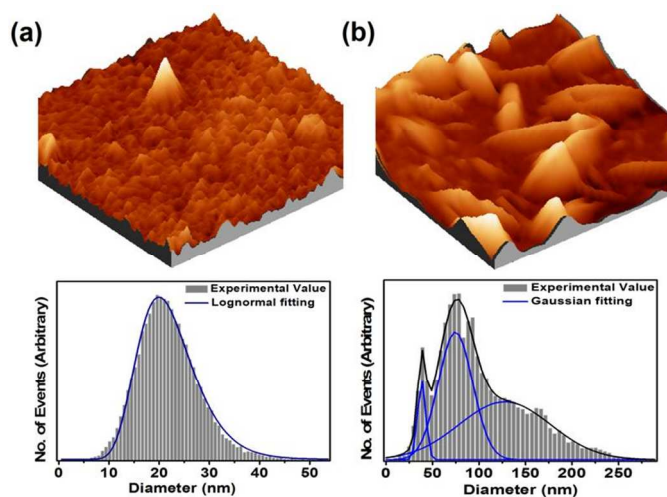


Fig. 9. Atomic Force topographic image with corresponding grain size distribution of ZnPc LB thin film annealed at (a) 65 °C (b) 290 °C.

Surface Electrical Study

In order to have an overview of the growth effect of ZnPc molecules on annealing towards the electrical property of ZnPc LB thin film, we have carried out current vs. voltage measurements of ZnPc LB thin film annealed at 65 °C and at 290 °C deposited over ITO glass substrate in dark and under light illumination of 1 sun = 100 mW/cm² using solar simulator (Newport, at AM 1.5 G) as shown in Fig. 10. The surface cell configuration showing the molecular architecture has been shown in the inset of the Fig. 10. From UV-Vis absorbance study, the ZnPc LB thin film was observed to be in α -phase and

β -phase when annealed at 65 °C and 290 °C respectively. In spite of the decrease in the quantity of ZnPc chromophore due to desorption from the bulk of the LB film with increase in annealing temperature we have observed that electrical conductivity of the ZnPc LB thin film at 290 °C increases greatly w.r.t. ZnPc thin film at 65 °C in dark and under light illumination. The reason is that we have taken the surface I vs V measurement of the annealed film and it is known that the current flow in the organic devices is mainly confined in the first 50 Å of semiconductor layer [46]. Therefore desorption of ZnPc chromophores at higher temperature will not have any effect on I vs V measurement. We have observed from the AFM and SEM study that the molecular grain growth takes place along the substrate surface on annealing, which result in nanorod formation at 290 °C with comparatively larger ZnPc grain diameter than the ZnPc grains at 65 °C. This confirms that in β -phase the parallel in plane stacking of the planar ZnPc molecules standing perpendicular over the substrate surface gets more ordered and compact throughout. The increase in grain size results in decrease in grain boundary and hence minimizes the obstruction imposed on the transport of the charge carriers because of grain disorderness at the grain boundary. Also the more ordered and compact parallel in-plane stacking of the ZnPc molecules in β -phase helps in efficient transport of charge carriers through the grain and also across the grain boundary [47]. The observed increase in electrical conductivity of the ZnPc LB thin film with phase transformation from α -phase to β -phase can also be justified with the resultant decrease in the interplanar distance of the stacking molecules. From XRD study we observe that the interplanar distance of ZnPc LB thin film decreases on α -phase to β -phase transformation from 13.0 Å to 12.0 Å. The intermolecular π -orbital overlap is strongly dependent on the interplanar distance between the molecules. Therefore reduction in interplanar distance between the stacking molecules leads to increase of intermolecular π -orbital overlap. This result in efficient transport of charge carriers and hence increase in its conductivity. This concludes that β -phase of the ZnPc having better conductivity w.r.t α -phase. Under photoexcitation the amplitude of the device current at any voltage increases for both ZnPc LB thin film annealed at 65 °C and at 290 °C, due to increase in photo generated excitons under illumination which shows good optical absorbance property of ZnPc thin film. This confirms good photovoltaic property of ZnPc thin film. The ZnPc thin film annealed at 290 °C having better enhancement of photocurrent because of increase in charge carrier mobility in β -phase. Tong et al [48] had earlier mentioned that β -phase of CuPc having better photovoltaic performance compared to α -phase due its higher conductivity and as well as higher absorbance at longer wavelength.

Conclusion

We have investigated the aggregation behaviour of the ZnPc molecules in the asdeposited LB thin film and the change in the aggregation behaviour of ZnPc molecules when annealed at different temperature using UV-Vis absorption spectroscopy. The ZnPc has been observed to be in monomeric form in mixture solvent and in asdeposited LB thin film it has been observed to in H, J and monomer aggregate form. The percentage of J aggregate in the asdeposited film is large in comparison to H and monomer aggregate which indicates asdeposited thin film having higher ratio of edge to edge

stacking of ZnPc molecules in comparison to edge on i.e. face to face stacking of the ZnPc molecules over the substrate surface. A sudden change in the aggregation behavior of the molecules has been observed when the ZnPc LB film annealed at 65 °C. It consists of H and monomer aggregates which indicate film is having only face to face stacking of the ZnPc molecules. The ZnPc LB film has been found to have same aggregation behavior till higher annealing temperature.

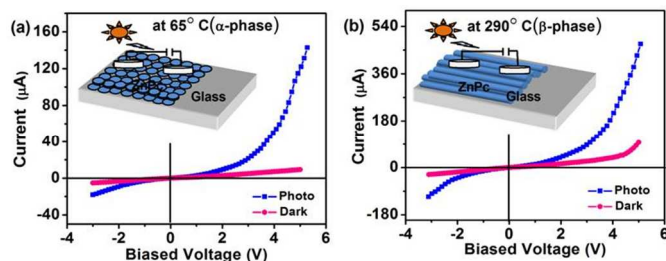


Fig. 10. Measured current vs. voltage characteristics of the annealed ZnPc thin film (a) at 65 °C (α -phase), (b) at 290 °C (β -phase) under dark and photoexcitation whereas the inset shows the schematic diagrams of the surface cell configuration.

The ZnPc thin film remains in α -phase from 65 °C to 200 °C and the α – β phase transformation starts taking place from 200 °C and it get completed at 290 °C as observed from UV-Vis absorption study. From the XRD study we observe a large increase in crystallite size of the ZnPc LB thin film on annealing at 290 °C, which indicate abnormal growth of ZnPc nanoparticle take place and is related to α – β phase transformation of the ZnPc thin film. Similarly FESEM and AFM image confirms the formation of elongated nanorod like structure over the substrate surface when the ZnPc thin film annealed at 290 °C, which is due to the secondary grain growth process of the ZnPc nanoparticles at higher annealing temperature. This change of shape of the ZnPc nanoparticle from spherical to nanorod structure is related to phase change of the ZnPc LB thin film from metastable α -phase to stable β -phase. The π - π interaction between the face to face arranged molecules of the ZnPc is the fundamental reason for the growth of nanorods. The electrical conductivity of the ZnPc LB thin film in β -phase has been found to enhance greatly w.r.t. ZnPc thin film in α -phase under both dark and excitation of photo chromatic light. The ordered and compact parallel in-plane stacking of the ZnPc molecules and also large increase in grain size lead to decrease in grain boundary area in β -phase results in efficient transport of charge carriers through the grain. This study shows that the change of organic molecular arrangement or configuration over the substrate plays an important role in change of optical and electrical property of the material when processed in the form of thin film.

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Notes and references

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