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Effect of chemical analyte interactions on electrical and optical properties of iron phthalocyanine thin films

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Thin films of Iron phthalocyanine have been deposited onto glass substrates by thermal evaporation technique at room temperature. The observed X-ray pattern suggests the presence of α crystalline phase of iron phthalocyanine in the as-deposited thin films. The electrical measurements (dc conductivity and photoconductivity) have been taken at different temperatures in the range 305-389 K. These films have been studied as chemical sensors such as methanol and ammonia. Electrical measurements indicate that these thin films have moderate sensitivity towards methanol and ammonia vapors.

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1. Introduction

Metalphthalocyanines (MPcs) are stable organic semiconductors having excellent electrical and optical properties and are of great technological and fundamental interest, both because of their own properties and because of their similarity to other classes of compounds. Most of the phthalocyanines are p-type semiconductors due to an absorbed oxygen which acts as an acceptor level in band gap [1]. The oxygen impurities, which are unavoidably introduced in the preparation of organic semiconductors [2] appear to play the dual role of both acceptors and traps levels [3]. However, these impurities, as well as voids and defects which give rise to extrinsic conductivity [4] can be removed by heat treatment. They are stable towards chemical and heat. The conductivity of these materials depends on the gaseous environment, and thus gas sensors based phthalocyanines have recently attracted considerable interest [5]. Adsorption of gases on the surface of Pc thin films induces change in the electrical conductivity of Pc films [6]. The eximious stability characteristics of Pc compounds have led to their extensive applications in laser beam printers and photocopiers [7], in non-linear optics [8], as liquid crystals [9], as Chemical sensors [10], in optical data storage [11]. Very recently these compounds have been successfully tested for the detection of volatile organic compounds also by optical techniques [12]. Phthalocyanine films can exist in several crystalline polymorphs. Most common polymorphs are metastable α and stable β phases. The main differences between different polymorphs are the tilt angle of the molecules within the columns (stacks of molecules with molecular planes parallel to each other) and the mutual arrangement of the columns [13]. Transformations from α phase to β phase using successive sublimation [14,15] or annealing or deposition at higher temperatures [16,17] have been reported. The absorption spectra of different polymorphs of some phthalocyanine compounds show significant differences among each other [16].

2. Experimental

In the present study, the FePc powder (sublimed grade, dye content 99 %) from Aldrich, is used without further purification. Methanol and ammonia from Qualigens Fine Chemicals, India, are used without further purification. Thin films of this material are prepared in a conventional vacuum coating system on well degassed Corning 7059 glass substrates. The substrates are cleaned chemically. Finally, the vapour cleaning with acetone and methanol is done. The substrates are heated at 120^0C to remove any moisture or methanol present. Thermal evaporation of the material is carried out from the Mo boat. Pre-deposited thick indium electrodes on well-degassed Corning 7059 glass substrates are used for the electrical contacts. A planar geometry of the film (length ~ 1.78 cm, electrode gap ~ 8×10^{-2} cm) is used for electrical measurements. The thickness of the film is found 3000 A° with a Surface Profiler Decktak 3030 ST. The films are kept in the deposition chamber in the dark for 24 h before mounting them in the metallic sample holder to attain thermodynamic equilibrium [17]. The photoconductivity of the FePc films are studied by mounting them in a specially designed metallic sample holder where heat filtered white light (200 W tungsten lamp) can be shone through a transparent quartz window. A vacuum of about 10^{-3} mbar is maintained throughout these measurements. Light intensity is measured by a digital Luxmeter (Testron, model TES-1332). The photocurrent (I_{ph}) is obtained after subtracting the dark current (I_d) from the current measured in the presence of light. The accuracy in Iph measurements is typically 1 pA which is measured by a picometer (DPM-111). The films are annealed in the range 305–389K for 2h in a vacuum of about 10^{-3} mbar for different samples and the dark and photoconductivity measurements are carried out. To study the optical properties of FePc thin film, the transmission spectrum has been recorded using a double beam Hitachi-330 UV/VIS/NIR spectrophotometer having resolution of 0.07 nm in the transmission range 400-900 nm. The crystalline and amorphous nature of the thin film is characterized by using X-ray diffraction technique (Model: Philips, Goniometer: PW3050/60, geometry configuration: θ-θ, detector: Cu K_α).

3. Results and discussion

3.1 XRD OF FePc

Fig. 1 shows the XRD pattern of as-deposited FePc film on a glass substrate at room temperature. We observe a broad diffraction band between 17 to 32^0 suggesting, thereby, that most of the composition of thin film is amorphous. However, a peak at an angle of 6.8994 corresponding to d value = 12.812 Å is also observed. It arises due to (2 0 0) plane of α crystallites belonging to the monoclinic symmetry [18]. Observed XRD pattern, therefore, suggests that in the as-deposited thin film FePc is present with α-crystallites unit cell. The spacing of lattice planes of the crystallites and b axes are arranged parallel to the surface of the FePc layer. It is clear from SEM spectra (Fig. 2) of FePc thin film that there are few crystals and rest of the material is amorphous which is in good agreement with XRD as shown in 1.

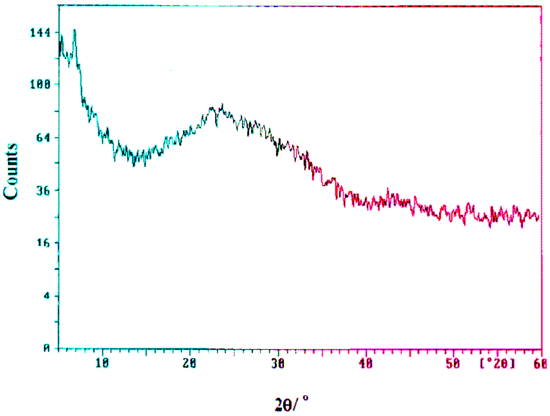

Fig. 1. XRD pattern of FePc thin film.

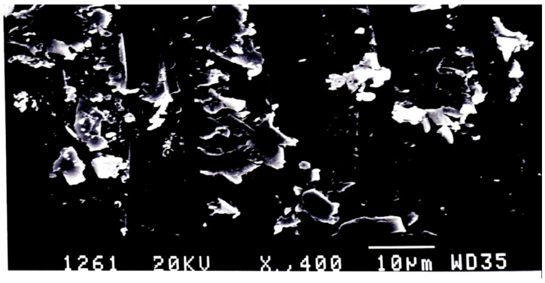

Fig. 2. SEM Photograph of FePc thin film

3.2 Electrical measurements

Electrical conductivity studies on FePc thin films are used to determine thermal activation energy and to study the effect of substrate temperature on the activation energy. In inorganic semiconductors, the semiconducting properties are brought about by thermal excitation, lattice defects, impurities and nonstoichiometry. Fig. 3 and Fig. 4 shows the temperature dependence of dark conductivity (σ_d) and photoconductivity (σ_{ph}) for thin film of FePc. The temperature dependence on conductivity is expressed as

$$\sigma_d = \sigma_0 \exp (- \Delta E / k T)$$

where ΔE is the activation energy for dc conduction and k is the Boltzmann's constant.

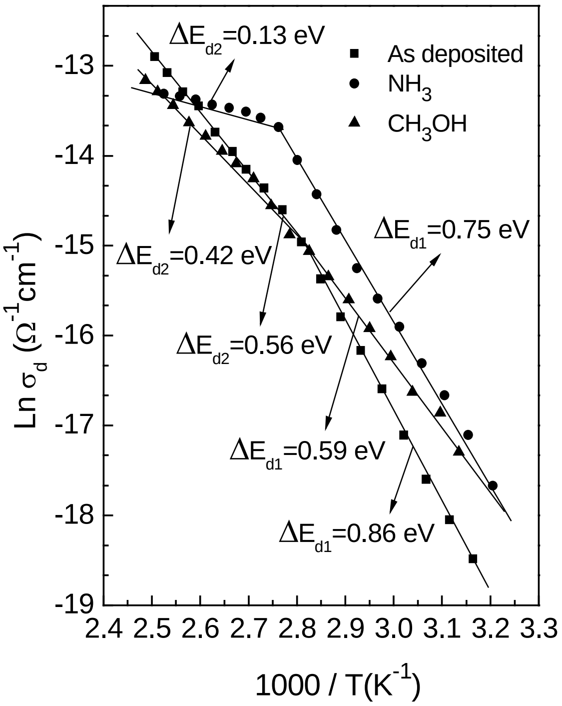

Fig. 3. Temperature dependence of dark conductivity (σ_d) for thin film of FePc unexposed and exposed with vapors of ammonia and methanol.

From Fig. 3, It is clear that there are get two straight lines indicating that conduction is an activated process having two activation energies in the temperature range 316 -399 K. There are two linear regions for the plots in Figure 2 and the corresponding activation energies ΔE_{d1} and ΔE_{d2} above and below 350 K is obtained. The thermal activation energy ΔE_{d1} is associated with an intrinsic generation process, i.e. the resonant energy involved in a short lived excited state. ΔE_{d2} is associated with an impurity conduction, i.e. a short lived charge transfer between the impurity and the complex. i.e. ΔE_{d1} = 0.86 eV and ΔE_{d2} = 0.56 eV, above and below 350 K respectively. The Nakada et al [19] indicates that change in slope and hence activation energy is interpreted as a change from extrinsic to intrinsic conduction. Sussman [20] has reported that the distribution of trapping sites is altered by annealing, giving two activation energies. The role of adsorbed oxygen is to create carriers and to act as impurity in the extrinsic conduction region. In the case of Pc, oxygen is bound much more tenaciously. The binding energies in the two regions are unequal. Heat treatments in air or vacuum do not remove oxygen completely. It has been reported that the removal of oxygen causes a redistribution of traps and hence a drop in thermal activation energy [21]. Shihub and Gould [22] have shown that annealing decreases the density of defects and thereby changes the electrical conductivity of copper phthalocyanine thin film.

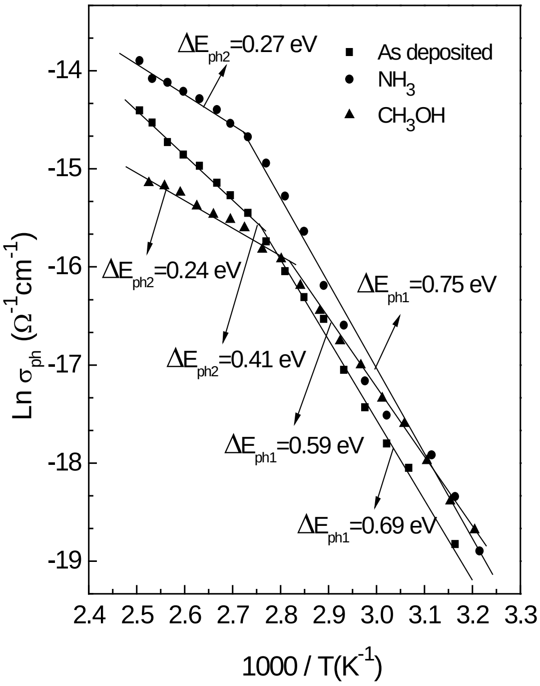

Fig. 4. Temperature dependence of photo conductivity (σ_{ph}) for thin film of FePc unexposed and exposed with vapors of ammonia and methanol.

It is also clear from the Fig. 3 that two different linear regions having two different activation energies still exist when film is exposed to ammonia or methanol. In case of ammonia, the value of ΔE_{d1} and ΔE_{d2} are obtained 0.75 eV and 0.13 eV respectively and in case of methanol, these values are obtained as 0.59 eV and 0.42 eV respectively. The value of σ_d decreases from (1.79 ± 0.02) x 10^{-8} $\Omega^{-1}cm^{-1}$ to $(1.20\pm0.02) \times 10^{-8}$ $\Omega^{-1}cm^{-1}$ after the ammonia exposure and from $(1.79\pm0.02) \times 10^{-8}$ $\Omega^{-1}cm^{-1}$ to $(1.54\pm0.02) \times 10^{-8}$ $\Omega^{-1}cm^{-1}$ after the methanol exposure at 303K. At low temperatures, there will not be any thermal defects and hence the value of activation energy is higher in case of FePc thin films. At high temperatures, there will be additional levels in the band gap due to the creation of color centers (defect centers) and hence activation energy is lower in case of these thin films. When FePc thin films are exposed with ammonia and methanol, there is electron transfer from adsorbed species to the p-type phthalocyanines (FePc thin film) thereby decreasing the density of hole carriers and thus decreasing the conductivity. The electron donating ability of ammonia is much stronger than methanol so it can form many stable complexes with metal ions.

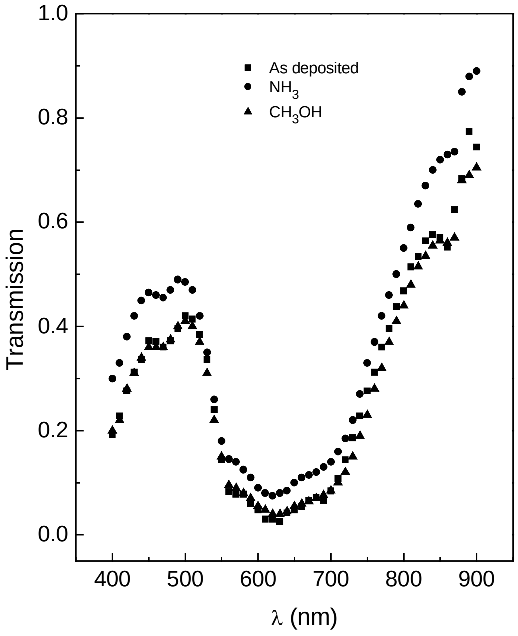

Fig. 5. Transmission spectra of FePc thin film unexposed and exposed with vapors of ammonia and methanol.

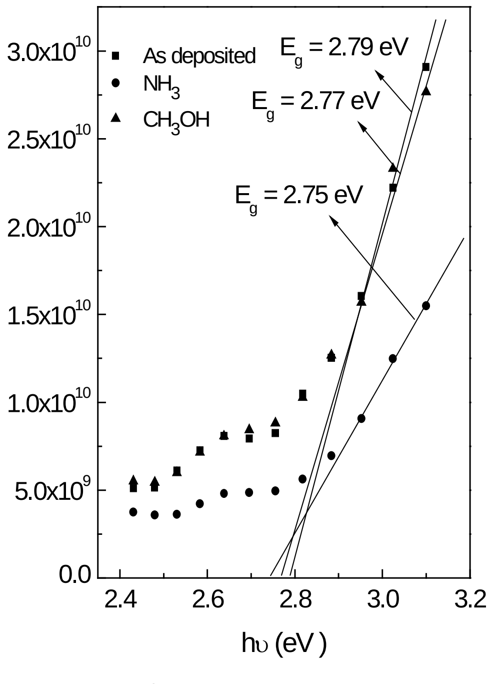

Fig. 6. Plot of $(\alpha h\nu)^2$ vs $h\nu$ for FePc thin film unexposed and exposed with vapors of ammonia and methanol.

Fig. 4 shows the temperature dependence of photoconductivity for the thin films of FePc both unexposed and exposed with vapors of methanol and ammonia. Figure shows that for unexposed FePc thin film, there are two different linear regions having two activation energies: ΔE_{ph1} = 0.69 eV and ΔE_{ph2} = 0.41 eV, above and below 345 K. It is also clear from the figure that there are two different linear regions having two different activation energies in exposed cases with ammonia and methanol. In case of ammonia, the value of ΔE_{ph1} = 0.75eV and ΔE_{ph2} = 0.27 eV and in case of methanol, the value of ΔE_{ph1} = 0.59 eV and ΔE_{ph2} = 0.24 eV. The value of σ_{ph} decreases from $(7.18\pm0.02) \times 10^{-9}\ \Omega^{-1}cm^{-1}$ to $(4.58\pm0.02) \times 10^{-9}\ \Omega^{-1}cm^{-1}$ after the ammonia exposure and from $(7.18\pm0.02) \times 10^{-9}\ \Omega^{-1}cm^{-1}$ to $(4.98\pm0.02) \times 10^{-9}\ \Omega^{-1}cm^{-1}$ after the methanol exposure at 303 K. In case of FePc thin film, after shining the light, the electron traps compensate with the addition of electron donors such as ammonia and methanol. These extra electrons and holes are immediately trapped by electron traps and acceptors and thus decreasing the photo conductivity of FePc thin film.

3.3 Optical measurements

The optical transmission spectra is one of the most productive tools for understanding and developing the band structure and energy gap of both crystalline and amorphous systems. A thin film is deposited on the glass substrate and has thickness (d) which is determined by Surface Profiler Decktak 3030 ST. The absorption coefficient (α) is calculated using the relation $\alpha = -\ln T/d$ where T is percentage transmission. Figure 5 shows transmission spectra for thin film of FePc unexposed and exposed with vapors of ammonia and methanol.

The overall decrease of transmission in figure 5 is caused by predominantly physical changes which occurred within the thin film layer due to exposure to the vapors of ammonia and methanol. Lowering the transmission means increasing absorption of light, and this may follow either due to chemical changes of the film itself or to its thickening (eventually both). The latter case seems more reasonable, since chemical changes are not supposed to produce such rapid increase in absorption. Thus when FePc thin films are exposed with ammonia and methanol may have changed their morphology, just due to adsorption of these species, which probably could have penetrated the film, at least at the film-gas interface. In consequence, the film's structure may "swell", thus increasing its volume and hence also its thickness. It is actually evident that similar alteration of the film may have occurred and this would result in transmission decrease. Moreover, this conclusion is supported by the fact that the transmittance in both cases decreases proportionally within the entire spectral range.

To obtain information about direct or indirect inter-band transitions, the fundamental absorption edge data could be analyzed within the frame work of one electron theory of Bardeen et al. [23]. This theory has been used to analyze the absorption edge data of molecular solids such as phthalocyanine derivatives [24]. The absorption ($\alpha > 10^4$ cm^{-1}) is related to direct band transitions [25]. The variation in absorption coefficient with photon energy for direct band-to-band transitions is of the form

$$\alpha = \alpha_0 (h\nu - E_g)^n \qquad (1)$$

Where E_g is the optical energy gap and α_o is constant. The value of n is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption, n = 1/2 for allowed direct transition, n = 3/2 for forbidden direct transition and n = 2 for allowed indirect transition, n = 3 for forbidden indirect transition [26]. The factor α_o depends on the transition probability and can be assumed to be constant with in the optical frequency range. The dependence of $(\alpha)^{1/n}$ on the photon energy (hυ) for onset fundamental energy gap are plotted from the transmission spectra of thin film of FePc according to Tauc's procedure [27]. These values of the energy gap result in the intense band called the Soret band and can be interpreted as a maximum in refractive index because the absorption index at that photon energy is quite small [28]. This energy gap can be attributed to the intense absorption in the red region for CuPc, PtPc, and PbPc [28]. Any crystal phase change would affect the gap between the conduction band and valence band in phthalocyanines, because the orbital overlap between parallel pairs of molecules will be affected [29].

For FePc thin films, the best fit was obtained for n= 1/2 which exhibits existence of allowed direct transition which aggress with the reported values [30]. The direct allowed band gap was determined by plotting $(\alpha h\upsilon)^2$ as function of photon energy hυ as shown in Figure 6 for FePc thin film unexposed and exposed with vapors of ammonia and methanol. It is clear from the figure that the value of E_g decreases from 2.79 eV to 2.75 eV and 2.77 eV respectively after exposure with vapors of ammonia and methanol. We have observed very small changes in the optical gap of these phthalocyanine thin films before and after exposures with ammonia and methanol. However, the decrease in the values of E_g can be explained as follows: The HOMO-LUMO gap of FePc is decreased when axial ligand such as ammonia and methanol is attached, since ammonia and methanol have sigma-donar capacity but weak π bonders. Therefore, when the ligand is attached to FePc, the HOMO of FePcs is increased, but the LUMO is increased in less extent and so the HOMO-LUMO gap of FePc is decreased. Ammonia is stronger electron- donating ligand than methanol. Large ligand-field strength will cause a higher HOMO and so give rise to smaller the HOMO-LUMO gap.

4. Conclusions

XRD pattern shows presence of α crystalline phase in the as-deposited FePc thin film. When FePc thin film is exposed with ammonia and methanol, there is electron transfer from adsorbed species to the FePc thin film, thereby, reducing the density of hole carriers and thus decreasing the dark conductivity. After shining the light, the electron traps in FePc thin film compensate with the addition of electron donors such as ammonia and methanol. These extra electrons and holes are immediately trapped by electron traps and acceptors and thus decreasing the photo conductivity. The decrease in the value of energy gap (E_g) of FePc thin film after exposure with vapors of ammonia and methanol is due to decrease in the HOMO-LUMO gap of FePc when axial ligand such as ammonia and methanol is attached. Ammonia has stronger electron- donating ligand than methanol and hence large ligand-field strength will cause a higher HOMO and so give rise to smaller the HOMO-LUMO gap.

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