International Journal of Physics and Applications.
ISSN 0974-3103 Volume 2, Number 3 (2010), pp. 149--156

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Optical Properties of Moclinic and Triclinic Lead Phthalocyanine Thin Films

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Abstract

The optical properties of thin films of Lead Phthalocyanine (PbPc) films on polyborosilicate glass substrates prepared by vacuum deposition, the thickness of the film is 150 nm, 300 nm and 450 nm at 303 K. Thickness of 450 nm is annealed at 323 K and 373 K. The results obtained from X-ray diffraction measurement indicate the monoclinic structure with a (001),(320),(111) and (420) orientation and triclinic structure with (400) orientation. The film consist of triclinic (200), (300) and (400) phases for 323 K annealed sample and (100) reflection of triclinic phase for 373 K annealed sample. The optical studies of PbPc films at 30° C have been determined both absorption and reflectivity data for wavelength in the UV and visible regions. It shows evidence for the existence of two absorption bands, which we have identical as exciton absorption at low energy below 2.4 eV. The variation of transmittance with wavelength of PbPc films for different thicknesses. It reveals that transmittance vary independently with film thickness. The transmittance spectra of PbPc films for thickness 450 nm at different annealed temperatures. It is observed that transmittance decreases with increase in temperatures.

Keywords: Phthalocyanine, X ray diffraction, monoclinic, triclinic and transmittance.

Introduction

In the research on Phthalocyanines, some attention has been given to Lead Phthalocyanine (PbPc) because of its characteristic structural and electrical properties. Lead Phthalocyanine are attractive material for device applications in various field such as Opto electronics, gas sensors, OLEDs, FETs, etc. [1-3]. A variety of studies have been made on its potential application as a gas sensor, particularly for NO_2 [4-6].

In the view of its general electrical properties of the material and also the effect of impurities, particularly adsorbed and absorbed oxygen [7-9]. It is known that the electrical and gas sensing properties of lead phthalocyanines are critically dependent upon a range of material parameters, including the film morphology, which in turn is determined by preparation parameters such as deposition rate, substrate temperature and post-deposition annealing [10-12]. The electrical behaviour of PbPc has improved and the problems associated with low mobility values [10,11]. Maruyama reported that the validity of the application of band models are, in common with many organic semiconductors [13], still in need of clarification. PbPc films the effect of oxygen on conduction mechanisms on both monoclinic and triclinic layers and the use of diagnostic techniques such as Fourier transform IR absorption spectroscopy to characterize the film morphology and oxygen content.[9,11,12].

Considerable amount of work has been carried out on the various physical and chemical properties of metal phthalocyanines. It is necessary to study the optical properties of PbPc thin films in order to obtain useful information such as optical band gap, transition, optical constants and the development of device technologies. In this paper, we report on characterizing the optical properties of both monoclinic and triclinic layers, relevance to sensor development and the band model analysis of the PbPc materials.

Experimental Details

The powder of lead phthalocyanine (80% dye, sigma Aldrich company, Bangalore, India) was kept in a molybdenum boat of 100 amps and heated with high current controlled by a transformer. The transformer is capable of supplying 150amps at 20volts is used to provide the accessory current for heating the molybdenum source which was used for the evaporation process. Deposition of PbPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr was achieved by slowly varying the current. The rate of evaporation was properly controlled and maintained constant during all the evaporations. The deposition rate and film thickness were controlled to be 0.05nm/sec and 150nm, 300nm and 450nm respectively, by monitoring the frequency of a quarter crystal oscillator.

Double beam spectrophotometers are generally of recording type. The instrument composes automatically sample beam energy with reference beam energy. The ratio of two would be transmittance of the sample. This procedure is followed over a sequence of wavelength. A graph is plotted with transmittance (absorbance) as ordinate and wavelength as abscissa given in the transmittance spectrum of the sample under analysis.

The crystal structure of the PbPc films were examined by θ-2θ X-ray diffraction using a Cu Kα source. Absorption spectra of the PbPc films were measured at room using double beam spectrometer. Reflectivity was measured with an integrity sphere attached to the spectrometer, to measure the hemispherically reflected component of the sample of both specular and diffuse reflection components. An MgO pressed powder sample was used as a standard for the reflectivity measurements.

Results and Discussion

XRD analysis of PbPc Thin Films

The X-ray diffraction patterns of thermally evaporated PbPc thin films of thickness 450 nm prepared at room temperature is shown in Fig. 1. The patterns shows peaks at 2θ values 6.85^{o}, 14.16^{o} and 24.55^{o} that were assigned to monoclinic (001), (320) and (111) lines respectively and a peak at 2θ value 30.26^{o} coinciding with the triclinic (400) line is seen. The peak values are in good agreement with the previous literature works [14, 15]. Thus evaporated PbPc films at room temperature are monoclinic at lower thickness or a mixture of monoclinic and triclinic forms at higher thickness [15, 16] . These evaporated films are polycrystalline in nature. PbPc molecules in the monoclinic modification are composed of well-defined structure which clusters themselves, consist of orderly arranged molecular stacks. Within the stacks there exist two substructures which have opposite orientations of the shuttlecock Pc structure. Such a structure explains the weak diffraction peaks of monoclinic crystals [10, 14, 15, 17]. In this phase, the molecules stack linearly to form a molecular column parallel to the c axis [15, 16].

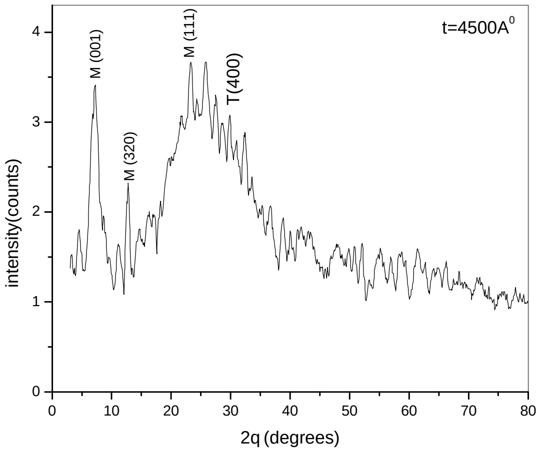

Figure 1: XRD Patterns of PbPc Films for thicknesses 450 nm.

XRD analysis of PbPc Thin Films -Effect of temperature

The XRD patterns of PbPc films for thickness 450 nm at high temperatures is shown in Fig. 2. The peaks obtained at room temperature were assigned to the monoclinic phase with some triclinic grains.The XRD graphs at 373 K shows peaks at 2θ values 7.43^{o}, 14.9^{o}, 22.4^{o} and 30.3^{o} assigned to the triclinic (100), (200), (300) and (400) lines respectively. The results are consistent with the previous literature works [14, 15]. From the XRD patterns at high temperature it is concluded that as temperature increases the number of peaks for triclinic phase increases. In the triclinic structure, the molecular stack along the a-axis orienting their convex and concave sides alternatively. Annealing at 373 K changes the structure to triclinic with (100) as the direction of preferential orientation. So when annealing is carried out in air at 373 K, triclinic phase becomes predominant [16]. The annealed films are also polycrystalline in nature.

PbPc in the monoclinic modification is composed of clusters themselves consist of orderly arranged molecular stacks. Within the stacks there exist two substructures which have opposite orientations. One structure contains “shuttle cocks” with Pb ions below the phthalocyanine and other substructure the “shuttle cocks” are upside down [18]. This type of structure is the most likely explanation for the week diffraction peaks obtained from the monoclinic from the monoclinic samples.

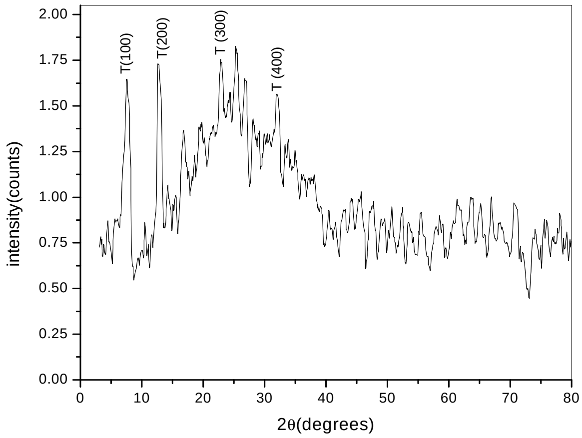

Figure 2: XRD Patterns of PbPc Films for thickness 450 nm at 373 K temperature.

Transmittance - Effect of thickness

Fig. 3 shows the variation of transmittance with wavelength of PbPc films for different thicknesses. It reveals that transmittance vary independently with film thickness. Organic molecules of Phthalocyanine and their derivatives exhibit anomalous optical characteristics because of their unique aromatic molecular ring structure. It is well known that they posses two kinds of energy bands. One of them is called the Q band which is equivalent to the α band in porphyrins and other one is called B band which is equivalent to the γ or soret band in porphyrins. The origins of the Q band and B band are an a_{1u} to e_g ($n\rightarrow \pi^*$) and an a_{2u} to e_g ($\pi \rightarrow \pi^*$) transition respectively [19]. The transmittance graph shows that B (soret) band is less than 400 nm and Q band is in between 570-750 nm. The wavelength region above 800 nm seems to be transparent for transmission spectroscopy. It is observed on close examination that the B or soret band is due to a_{2u} to e_g ($\pi \rightarrow \pi^*$) and Q-band a_{1u} to e_g ($n\rightarrow \pi^*$) transitions [20].

The variation of absorbance and extinction coefficient with wavelength of PbPc films for different thicknesses is shown in Fig. 4 and 5. Similar trend is observed for both spectrum. It is observed from the above figures that absorbance and extinction coefficient vary independently with film thickness. It is observed from the absorbance peak that in the near UV, B or the soret band appear below 400 nm where $\pi \rightarrow \pi^*$ transition takes place. The Q-band $n \rightarrow \pi^*$ transition appeared in the visible at about 600-735 nm. This band has a doublet for all samples associated with exciton formation [21]. and a new band appeared at about 440 nm [22].

Fig. 6 shows the photon energy dependence of α^2 of PbPc films for 450 nm thickness. Extrapolation of this plot to $\alpha^2 = 0$ determines the optical band gap energy. The transparent band shows that the absorption decreases slowly with increasing photon energy for triclinic and decreasing more sharply with photon energy for the monoclinic films. The absorption has been confirmed for many phthalocyanine complexes and is related to the formation of single excitation [77, 23, 24]. The monoclinic structure shows a doublet at 1.86eV and 1.74eV and triclinic shows a high intensity band at 1.61. The plot shows two absorption bands, identified as Q band or exciton absorption at low energies (below 2.4 eV) and fundamental absorption at higher energies (greater than 2.4 eV). A direct allowed band gap is found to exist at this energy 2.4 eV. It is observed from the graph that the lowest band gap is about 1.2 eV. This band gap energy is estimated as the onset of absorption spectrum. These values are confirmed from the previous literature works [14, 22, 25]. The band gap energies for different thicknesses, it is seen that band gap decreases with the increase in film thickness. It may be due to the increase in grain size and a decrease of strain or due to the action of atmospheric oxygen or the presence of impurity electronic levels on the surface of the films which produces an acceptor level in the forbidden band [26, 27].

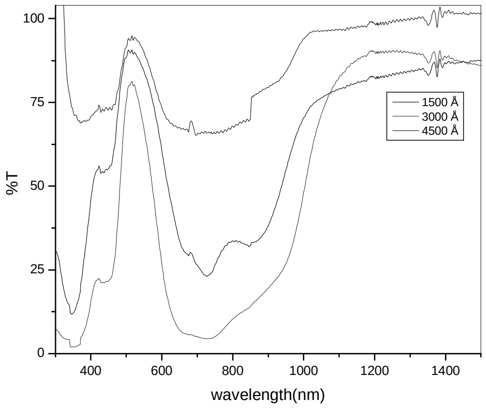

Figure 3: Variation of transmittance with wavelength of PbPc films for different thicknesses.

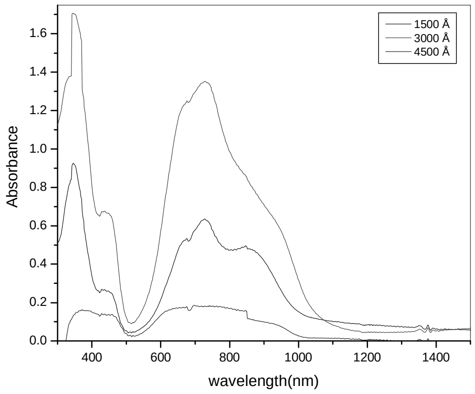

Figure 4: Variation of absorbance with wavelength of PbPc films for different thicknesses.

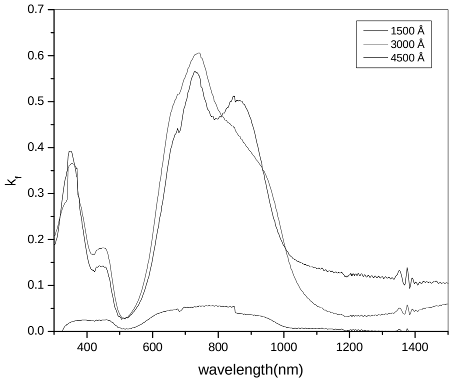

Figure 5: Variation of extinction coefficient (k_f) with wavelength of PbPc films for different thicknesses.

Transmittance - Effect of temperature

Fig. 7 shows the transmittance spectra of PbPc films for thickness 450 nm at different annealed temperatures. It is observed that transmittance decreases with increase in temperatures. The variation of absorbance and extinction coefficient (k_f) with wavelength of PbPc films at different annealed temperatures are shown in Fig. 8 and 9. The spectrum reveals that both the absorbance and k_f increases with increase in annealed temperatures.

Fig. 10 shows the photon energy dependence of α^2 of PbPc thin films for thickness 450 nm annealed at 373 K temperature. Extrapolation of this plot to $\alpha^2 = 0$ determines the optical band gap energy. From the plots, it is concluded that this material exhibits only the direct allowed transition [14, 22, 25] and is observed that band gap increases with increase in annealed temperatures. It can be due to the decrease of localized states in band gap or due to the reduction in the number of unsaturated defects [28-

30]. Generally phthalocyanines absorb light on either side of the blue- green region and can be used as photoconductors and colour filters [20]. The optical analysis of lead phthalocyanine also confirms the above result.

Conclusion

Films of Lead Phthalocyanine of thicknesses 150nm, 300nm and 450nm are prepared by vacuum deposition method. From the XRD patterns of PbPc films, it is clear that as thickness increases, triclinic grains (T) are seen along with monoclinic (M) forms of PbPc. Thus evaporated PbPc films at room temperature are monoclinic at lower thickness or a mixture of monoclinic and triclinic forms at higher temperature. These evaporated films are polycrystalline in nature. PbPc molecules in the monoclinic modification are composed of well-defined structure which clusters themselves, consist of orderly arranged molecular stacks. Within the stacks there exist two substructures which have opposite orientations of the shuttlecock Pc structure. From the XRD patterns at different temperature it is concluded that as temperature increases the number of peaks for triclinic phase increases. Optical studies of PbPc films shows the existence of two absorption bands at low energies less than 2.4 eV and high energies greater then 2.4 eV. It is observed from the graph that the lowest band gap is about 1.2 eV. The spectrums reveals that both the absorbance and extinction coefficient increases with increase in annealed temperatures. The band gap decreases with the increase in film thickness.

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