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Optical Properties of Cobalt Phthalocyanine Thin Films

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ABSTRACT

Cobalt Phthalocyanine (CoPc) thin films with different annealing temperatures (298,358,408,458)K have been prepared by thermal evaporation technique on glass substrate at RT under vacuum of 10-5 mbar Using Edwards 306 system with rate of deposition equal to 15 nm/minute. The optical measurement includes UV-Visible Spectra, which showed that increase in annealing temperatures, leads to increase absorbance of films, the CoPc thin films have direct energy gap (Eg) for all samples, Also the optical constants such as absorption coefficient, refractive index, extinction coefficient and dielectric constant have been calculated and it was found that they are slightly dependent of annealing temperatures.

KEYWORDS Cobalt Phthalocyanine, Thermal evaporation, Thin film ,Energy gap.

Introduction

Organic semiconductors are a very important class of materials having wide range of properties,The semi-conducting properties of molecular materials can be explained form the covalent bonding between carbon atoms[1]. σ_bonds made from the sp2 hybridization of 3 valence atomic orbitals of the carbon atom:2s,2px and 2py.For such a hybridization state, the fourth orbital 2pz lies perpendicular to the σ_bond plane. It is the lateral overlap of these out of plane 2pz atomic orbitals, which gives the π_bonds [2], Absorption spectra display the existence of strong absorption bands in the range of 400 and 800 nm caused by the π- π* transitions of the conjugated macrocycle of 18 π_-electrons.The optical properties of these materials are dependent on the crystal phases and its structure[3]. Phthalocyanines are found in different phases i.e. α-, β- and γ-phases. The most common crystal phases occurred in are α and β that have two crystallite structures, The phase separation could be responsible for the de gradation of the optical properties [3] The α- phase is metastable and obtained as a thin film deposited on a cold substrate in vacuum[4]. The β -phase can be obtained in single crystal form or as a thin film formed by deposition of phthalocyanine on heated substrates [4]. The β-form is the thermodynamically stable one. α -form is metastable and can be converted to β-form by temperature treatments with structures tetragonal and orthorhombic respectively [5].

Experimental

Powdered Cobalt Phthalocynine used in this study was obtained from Aldrich chemical company and was used as the source material for thermal evaporation. Before starting the deposition, the glass substrate was cleaned in an ultrasonic bath for 10 min using acetone, followed by rinsing in distilled water. The substrate was dried in open air in a cleaned room. A molybdenum boat was used as a heating source. Thin films of CoPc of thickness 150 nm, were deposited by thermal evaporation technique on thoroughly cleaned glass substrate at different annealing temperatures (298, 358, 408, 458) K using Edwards 306 system. During deposition, the pressure in the vacuum chamber was kept constant at about 10−5 mbar and the deposition rates of all the films were at about 15 nm/min, Also the substrate are placed at a distance of 15cm from the molybdenum boat. Thickness of the film is measured by Fizeau fringes technique. Visible ultra-violet and near infrared absorption Spectra(200-1100)nm of CoPc thin films are recorded using a uv-vis 2601 spectrophotometer.

Result and Discussion

The FT-IR spectrum for CoPc Powder was measured at room temperature as shown in Fig.(1). FT-IR for CoPc powder shows the bond bending represented by the range (400-2000) cm^{-1} while the bond stretching represented by the range (2000-4000) cm^{-1}.bond vibration at (754) cm^{-1} have been assigned for (cobalt – Nitrogen). The peak (920)cm^{-1} is for bending bond of benzene(914-1089)cm^{-1} ,Peak 1320 in The band at (1334-1320)cm^{-1} is for stretching bond of C-N. peak 1440 is for stretching bond of Benzene (1469-1595) ,peak 1525 is for bending bond of C=C,C=N.

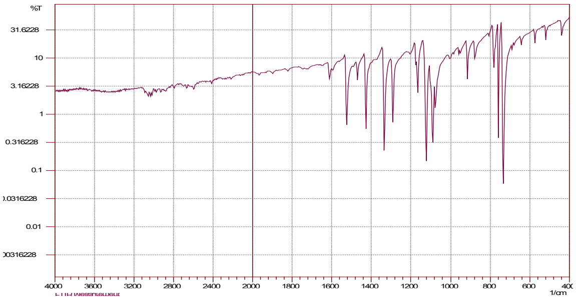

Fig. (1) FT-IR spectra for CoPc

the spectrum shows the absent of stretching band N-H which is appears in H_2Pc spectrum in 3700 cm^{-1}as shown in Fig.(2).

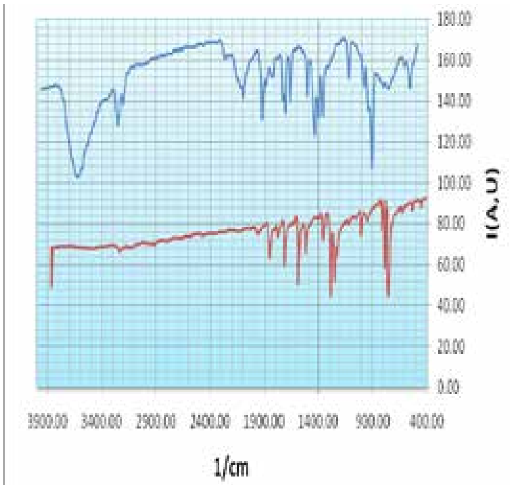

Fig.(2) FT-IR spectra for H2Pc and CoPc Powders .

The absorbance spectra for CoPc in case of thin film at different annealing temperature as shown in Fig.(3). The figure shows that both of two spectra have two band ,one in UV region which is called B-band(or soret) at the range about (300-370)nm ,and the other in visible region which is called Q-band at the range about (550-750)nm ,and can see a flat area in range (380-530) nm for CoPc thin film spectrum , Q-band consist of two close peaks. It shows simply the absorbance increases strongly with annealing temperatures increase (298,358,408)K, this behavior because of a good crystal arrangement at increase of annealing temperatures. The absorbance decrease at 458K, This result is due to change in phase from (α to β) [6] [7].

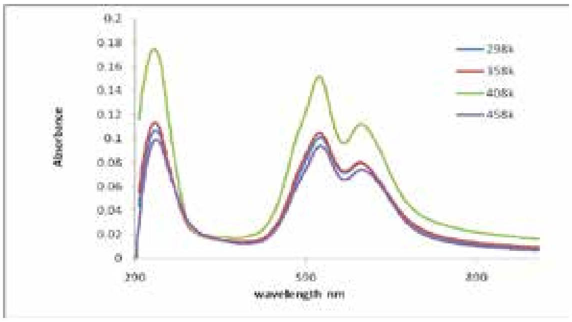

Fig. (3) :Absorbance as a function of wavelength for copc thin films at different annealing temperatures

The variations in absorbance with annealing temperature for B band are greater than the variations in Q band. The effect of annealing temperature on absorbance of peaks of Q,B bands are shown in Fig.(4), we can see increasing in absorbance for B,Q band with increasing annealing temperatures but absorbance decrease for B,Q band after 400K which may be due to the phase transition from α to β.

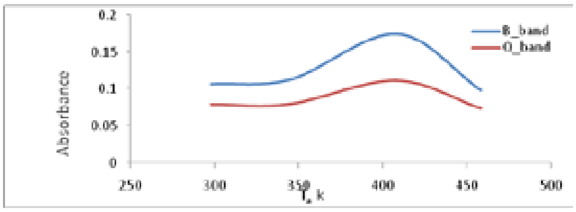

Fig. (4): Effect of annealing temperatures of copc thin films on absorbance of B and Q band

The absorption coefficient a is related to the photon energy hƱ by Tauc equation $\alpha h\mho = B(h\mho - Eg)^r$. Where Eg is the optical band gap.

The plot of $(\alpha h\mho)^2$ vs. hƱ for CoPc thin films deposited at different annealing temperatures are shown given in the Fig. (5) For allowed transition where ($\alpha \geq 10^4$ cm^{-1}) $(\alpha h\mho)^2$ is plotted against hƱ to yields a straight line for direct allowed transitions as shown in figure from which the extrapolation of linear portion to $(\alpha h\mho)^2 = 0$ near the absorption edge gives the band gap energy[8].

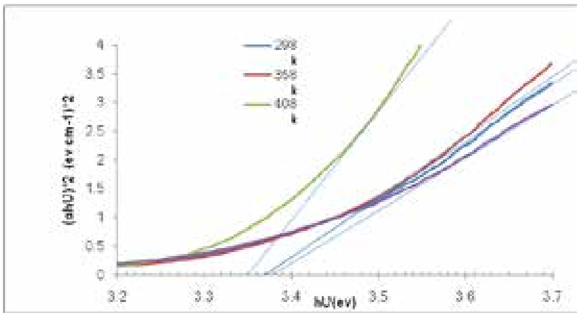

Fig.(5): $(\alpha hv)^2$ versus photon energy hv of incident radiation for copc thin films having different annealing temperaturs

The direct energy gap value and traps levels was found to be as shown in the Table(1), We observed that energy gap decreased with increasing annealing temperature ,energy gap is increase at 458K ,which may be due to the phase transition from α to β.

Ta (K)	E_g (eV)	Trap(1) Energy(ev)	Trap(2) Energy (eV)
298	3.371	1.84	1.66
358	3.37	1.86	1.67
408	3.35	1.91	1.67
458	3.38	1.84	1.66

Table(1): Annealing temperature effect on optical energy band gap and traps for COPC thin film

The comparative variations in optical constants for CoPc thin films at wavelength equal to 580 nm at different annealing temperatures were shown in the Tables(2) ,we can show that optical constant are slightly dependent of annealing temperatures for CoPc.

Table (2): The optical constant for copc thin films at different annealing temperature at 580 nm

T_a(k)	$\alpha*10^{4}$ $(cm)^{-1}$	k	N	ε_r	ε_i
298	1.101	0.050	1.525	2.325	o.155
358	1.173	0.054	1.557	2.423	0.168
408	1.675	0.077	1.766	3.116	0.273
458	1.005	0.046	1.483	2.197	0.137

Conclusion

From the present work, we can conclude that the CoPc films of annealing temperatures (298,358,408,458)K on glass substrate have been prepared successfully by vacuum evaporation technique. From the absorbance spectra for CoPc films, we observed that absorbance increased with increasing annealing temperatures may be due to good arrangement of crystal but absorbance decreased at 458K may be due to phase transition from α to β. The type of electronic transition responsible for optical absorption is direct allowed transition. The optical energy gap for CoPc films decreases with increasing in annealing temperatures. The absorption coefficient, extinction coefficient, refractive index and the (real,imaginary) part of dielectric constant depend on annealing temperatures.

REFERENCES

[1]R. Farchioni and G. Grosso , editors.," Organic Electronic Materials", Springer Verlag, Berlin, (2001). | [2] M. Munzi, C. R. Physique, 3 (2002) 523. | [3] Herrera M, Gonzalez D, Hopkinson M and Navaretti P, J. Semicond. Sci. Technol. 2004, 19, 813. | [4] Allen Twarowski, J. Chem. Phys., 1982, 77, 4698 | [5] Robinson M.T and G.E. Klein, J. Amer. Chem. Soc., 1952, 74, 6294. | [6] Jungyoon E, Sunmi Kim, Eunju Lim, Kiejin Lee, Deokjoon Cha and Barry Friedman,Applied Surface Science, 2003, 205, 274. | [7] Xia H and Nogami M, Opt. Mater., 2000, 15, 93. | [8] Raji P, Sanjeeviraja C and Ramachandran K, Bull. Matter. Sci., 2005, 28, 233. |