Estimation of the Dispersion and Absorption Parameters of Thermally Evaporated Magnesium Phthalocyanine Thin Films

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Abstract. Magnesium phthalocyanine MgPc thin films are prepared at room temperature by thermal evaporation technique. The spectral absorption parameters are determined by applying the molecular orbital theory but the other optical parameters are deduced using band-model consideration. The optical constants n and k are evaluated using spectrophotometric measurements of transmittance and reflectance at nearly normal incidence of light in the wavelength range 190-2500 nm. The absorption spectrum recorded in the UV-VIS region shows two absorption bands of phthalocyanine molecule, namely the Soret band (B) and the Q-band. The Q-band shows its characteristic splitting (Davydov splitting), and ΔQ is 0.17 eV. The absence of a distinct peak near 4.27 eV in MgPc could be due to the absence of d-electrons of the Mg atoms. The analysis of the spectral behaviour of the absorption coefficient in the absorption region near fundamental edge reveal indirect transitions. The fundamental and the onset energy gaps could also be estimated as 2.73 ± 0.01 eV and 1.40 ± 0.15 eV, respectively, for the as deposited films. From analysis of dispersion curves, the dielectric constants and other dispersion parameters are also obtained. All previous parameters are obtained for as deposited and annealed films at 350°C for two hours. Discussion of the obtained results and comparison with the previously published data are also given.

Keywords: Organic thin film; optical absorption; optical constants.

1. Introduction

The properties of metal phthalocyanines such as their thermal and chemical stability, ability to form well-ordered thin films and wide absorption band within the optical region, make them very attractive for applications in optical logic display devices[1], electrotophotography, solar cells[2,3], sensitizes and colour filters[4] and optical recording[5]. They can easily be sublimed to get pure thin films without decomposition. Due to their strong absorption in the ultraviolet and visible region, phthalocyanine and its metal complexes are considered as electrophotographic materials[6], optical recording media[7] and nonlinear optical materials[8].

Variety of attempts have been made by researchers to investigate the physical and chemical properties of MgPc. The effect of metal atom on the absorption spectra of phthalocyanine films has been investigated[9]. Electrical and optical characterization of MgPc films predicted that the spectrum of MgPc can be used as a selective absorption coating in the visible region at room temperature[10]. On the other hand, Rajesh and Menon[11] presented the results of the refractive index and dielectric constants from the absorption and extinction coefficient of MgPc thin films over the wavelength range 300-900 nm. The electrical conductivity, thermal activation energy, optical band gap and their dependence on post deposition air annealing for MgPc were investigated[12]. The absorption, transmission and reflection spectra of phthalocyanine and its complexes (Mn, Mg, Fe, Co, Zn and PbPc) have been investigated in the wavelength range from 300 to 1000 nm[13].

In the present work, thin films of MgPc have been fabricated by thermal evaporation onto quartz substrates under vacuum of 10^{-4} Pa. Optical constants and oscillating parameters were determined in a spectral range of 190-2500 nm. Moreover the visible and near ultraviolet absorption spectra have been measured. The fundamental and the onset energy gaps are estimated and discussed.

2. Experimental Details

MgPc powder (99.97%) in this study is obtained from Kodak, UK. MgPc thin films of different thicknesses were prepared by conventional thermal evaporation technique using a high vacuum coating unit

(Edwards type E306A).The films were deposited onto optically flat quartz substrates at room temperature from a quartz crucible source heated by a tungsten coil in a vacuum of 10^{-4} Pa. Deposition (rate 2.5 nms^{-1}) and thickness were controlled using a quartz crystal thickness monitor (Edwards, Model FTM6) and subsequently calibrated by Tolansky method[14].

Transmittance T(λ) and reflectance R(λ) of the films were measured at normal incidence in a spectral range of 190-2500 nm using a double-beam spectrophotometer (JASCO model V-570 UV- VIS- NIR).

3. Method of Calculation

The absolute values of the measured transmittance (T) and reflectance (R) after correction of the absorbance and reflectance of the substrate are given by[15]

$$T = \left(\frac{I_{ft}}{I_q} \right) \left(1 - R_q \right) \tag{1}$$

where I_{ft} and I_q are the intensities of light passing through the film-quartz system and that through the reference quartz, respectively and R_q is the reflectance of quartz substrate. R is given by

$$R = \left(\frac{I_{fr}}{I_m} \right) R_m \left(1 + \left[1 - R_q \right]^2 \right) - T^2 R_q \tag{2}$$

where I_m is the intensity of light reflected from the reference mirror, I_{fr} is the intensity of light reflected from the sample reaching the detector and R_m the mirror reflectance.

To calculate the refractive index, n, and the absorption index, k, of films a computer program comprising a modified search technique[15] based on minimizing $(\Delta R)^2$ and $(\Delta T)^2$ simultaneously was used, where

$$(\Delta R)^2 = \left| R_{(n,k)} - R_{\exp} \right|^2 \tag{3}$$

$$(\Delta T)^2 = \left| T_{(n,k)} - T_{\exp} \right|^2 \tag{4}$$

where T_{exp} and R_{exp} are the corrected values of T and R respectively, and $R_{(n,k)}$ and $T_{(n,k)}$ are the calculated values of T and R, using the Murmann's equations.

4. Results and Discussion

The spectral distribution of $T(\lambda)$ and $R(\lambda)$ measured at nearly normal incidence in the wavelength range 190-2500 nm for as deposited MgPc films in the thickness range 530-580 nm are shown in Fig.1a where Fig. 1b shows T (λ) and R (λ) for a selected thickness of 550 nm for as deposited and after annealing at 350ºC for two hours. It is noted that the sharpness of the transmissivity bands is greater in annealed films than as deposited ones. The presence of such bands recommends these films as good band pass or as good band stop optical filter material depending on wave length. It is noted that at longer wavelengths ($\lambda > 900$ nm) all films become transparent and no light is scattered or absorbed (*i.e.* R + T = l). The inequality (R + T < 1) at shorter wavelengths ($\lambda < 900$ nm), known as absorbing region, is due to the existence of absorption. After the determination of the film thickness, the bi-variance search technique has been employed[15] to determine the real and imaginary parts of the complex refractive index from the absolute values of transmittance and reflectance of films, using Murmann's formulae. Taking into account, the experimental error in measuring film thickness to be ± 2% and in T and R to be ± 1%, the error in the calculated values of n and k was estimated as 3% and 2.5%, respectively.
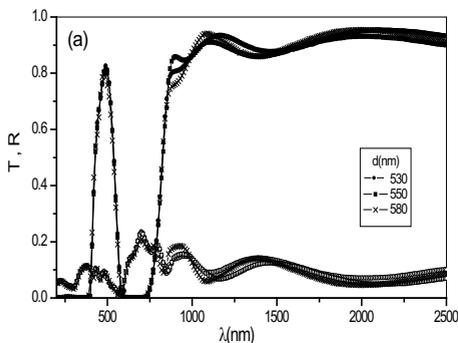

Fig. 1a. **The spectral distribution of T(λ) and R(λ) for as deposited films in the thickness range 530-580 nm.**
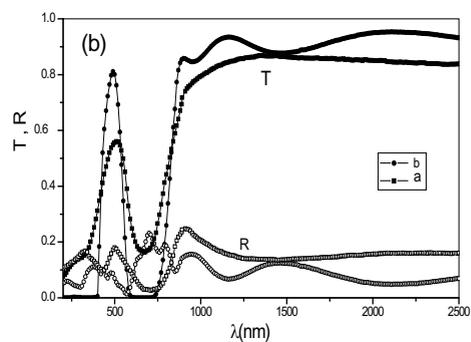
Fig. 1b. **The spectral distribution of T(λ) and R(λ) for (a) as deposited and, (b) annealed thin films of 550 nm.**

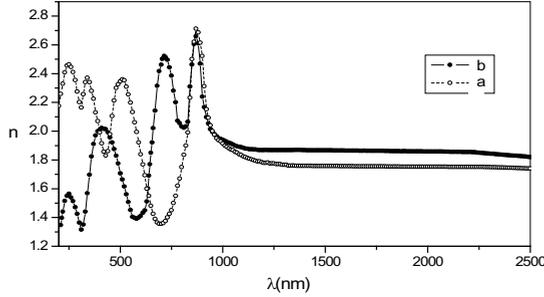Figure 2 shows the dispersion spectrum for the as deposited and annealed MgPc films in the wavelength range 190-2500 nm.

Fig. 2. The dispersion curve of refractive index n(λ) for (a) as deposited, and (b) annealed MgPc thin films.

An anomalous dispersion (λ ≤ 900 nm) as well as normal dispersion (λ ≥ 900 nm) is observed. In the normal dispersion region (λ ≥ 900 nm) the dispersion of refractive index has been analyzed using the single oscillator model expressed in the form[16]

$$\frac{1}{n^2 - 1} = \frac{E_o}{E_d} - \frac{1}{E_o E_d}(h\nu)^2 \qquad (5)$$

Where E_o is the single oscillator energy, which simulates all the electronic excitations involved, and E_d is the dispersion energy. In practice, the dispersion parameters E_o and E_d can be obtained by a simple plot of $(n^2 - 1)^{-1}$ against $(h\nu)^2$ as shown in Fig. 3. It is observed that the plots are approximately linear above 0.6 eV. The value of E_o, E_d and the high frequency dielectric constant ($\varepsilon_\infty = n^2$) were determined and listed in Table 1.
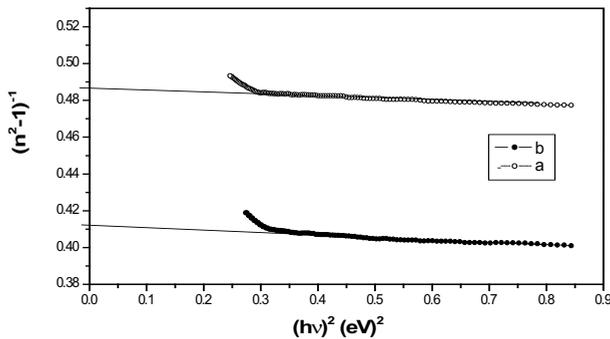

Fig. 3. The relation between $(n^2-1)^{-1}$ against $(h\nu)^2$ for (a) as deposited, (b) annealed films.

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Table 1. Dispersion parameters of the as deposited and annealed MgPc films .

MgPc	ε_∞	ε_L	N/m* (10^{45})	E_o eV	E_d eV	M_{-1}	M_{-3}
As deposited	3.42	3.52	50	5.1	12.28	2.40	0.092
After annealing	0.3	3.11	90	5.67	11.59	2.1	0.063

On the other hand, r[th] moments (M_{-1} and M_{-3}) of the imaginary part of the dielectric constant are given by[17]:

$$M_r = \frac{2}{\pi} \int_E^\infty E \varepsilon_2(E) dE \qquad (6)$$

$$M_{-1} = \frac{E_d}{E_o}. \qquad (7)$$

$$M_{-3} = \frac{E_d}{E_o^3} \qquad (8)$$

Other parameters[17] can also be deduced using the determined (n) values from

$$n^2 = \varepsilon_L - \frac{e^2}{\pi c^2} \frac{N}{m^*} \lambda^2 \qquad (9)$$

where ε_L is the lattice dielectric constant and (N/m*) is the ratio of the carrier concentration to the electron effective mass. The dependence of n^2 on λ^2 is linear at longer wavelength as shown in Fig. 4. The lattice dielectric constant ε_L and the values of N/m* are obtained in Table 1 for the as deposited and annealed MgPc films. The disagreement between the values of ε_∞ and ε_L may be due to the free carrier contribution[18].
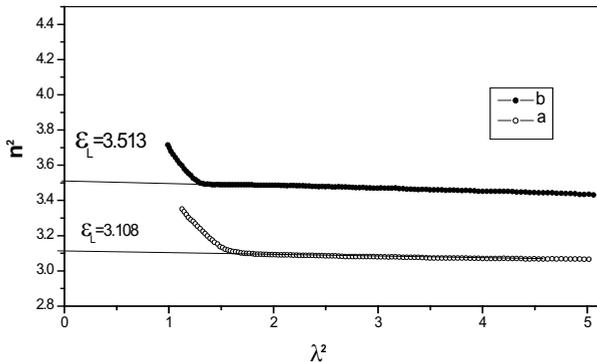

Fig. 4. The relation between n^2 against λ^2 for (a) as deposited, and (b) annealed films.

The absolute values of transmittance and reflectance are used to determine the complex refractive index ($n^* = n - ik$) and the complex dielectric constant ($\varepsilon = \varepsilon_1 - \varepsilon_2$) (where the real dielectric constant $\varepsilon_1 = n^2 - k^2$ and the imaginary dielectric constant $\varepsilon_2 = 2nk$). The real part generally relates to dispersion, while the imaginary part provides a measure to the dissipative rate of the wave in the medium[11]. Figures 5a and 5b represent the variation of ε_1 and ε_2 with the photon energy for the as deposited and annealed MgPc thin films respectively.
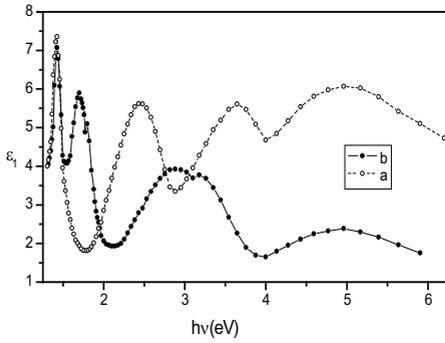

Fig. 5a. **The real dielectric constant ε_1 against hν for a) as deposited, and b) annealed MgPc film.**
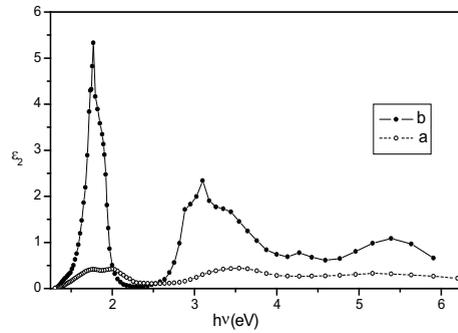
Fig. 5b. **The imaginary dielectric constant ε_2 against hν for both a) as deposited, and b) annealed MgPc.**

It is also possible to calculate the volume and surface energy loss functions related to the real and imaginary parts of the dielectric constant (VELF and SELF) as shown in the following relations[17]

$$VELF = \frac{\varepsilon_2^2}{(\varepsilon_1^2 - \varepsilon_2^2)} \tag{10}$$

$$SELF = \frac{\varepsilon_2^2}{((\varepsilon_1 + 1)^2 + \varepsilon_2^2)} \tag{11}$$

The distribution of the volume and the surface energy loss function of the as deposited and annealed MgPc films as a function of the photon energy are shown in Fig. 6a and Fig. 6b respectively. The spectral distribution of the absorption coefficient $\alpha = 4\pi k / \lambda$ is presented in Fig. 7 for the as deposited and annealed MgPc films.
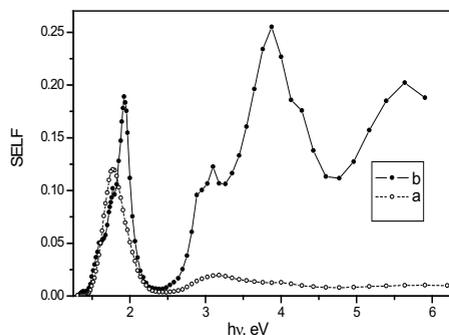
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Fig. 6a. The surface energy loss function (SELF) against hν for a) as deposited, and b) annealed films.
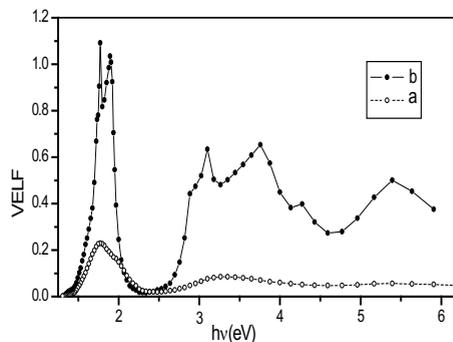
Fig. 6b. The volume energy loss function (VELF) against hν for a) as deposited, and b) annealed films.
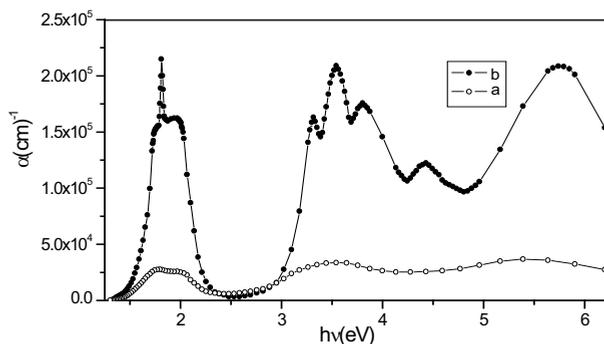

Fig. 7. The spectral behaviour of the absorption coefficient α for (a) as deposited, and (b) annealed MgPc thin films .

The high-energy peak of the Q-band has been assigned to the first π – π* transition through occupied molecular orbital to the lowest unoccupied dielectric constant on the phthalocyanine macrocycle[17]. The low energy peak of the Q-band has been variously explained as a second π − π* transition[17]. The present observation of similar structure of MgPc on the visible and Soret bands is taken as supporting evidence for the explanation of structure in terms of a molecular vibration[19]. The result of the present work of the vibrational quantum is 0.19 eV. In accordance with the previous results of Davydov splitting (ΔQ)[9,17] the absorption spectra for phthalocyanine compounds occur in the high energy region of the Soret band near 4.27 eV. The absence of a distinct peak in the case of MgPc films could be due to the absence of d-electrons of the Mg atoms. Peaks observed at high photon energy near 4.27, 5.54 eV for the as

deposited and 5.1 eV for the annealed MgPc films are characterized for all the investigated phthalocyanines[9,16,17]. Other absorption bands for the as deposited and annealed films are listed in Table 2.

Table 2. Energy of orbital transition of MgPc thin films.

Orbital transition	Visible(Q) (eV)		ΔQ(eV)	Soret (B) (eV)			N-Band (eV)	C-Band (eV)
As deposited	1.77	1.94	0.17	2.9	3.5	3.8	4.27	5.54
After annealing	1.76	1.95	0.26		3.5			5.1

To obtain information about direct or indirect interband transitions, the fundamental absorption edge data could be analyzed within the framework of one electron theory of Bardeen *et al.*[16,17] .This theory can be used to analyze the absorption edge data of molecular solids such as phthalocyanine derivative[13,16]. The dependence of $(\alpha h\nu)^r$ on photon energy $h\nu$ for onset gaps was plotted for different values of r, the best fit was for r = 1/2 . This characteristic behaviour of indirect transitions in non crystalline materials is similar to that for NiPc[16] and CoPc[17] unlike other metal phthalocyanines where the transition is a direct allowed[20,21]. The energy gap is given by

$$(\alpha h \nu)^{1/2} = B (h \nu - E_g^{ind} \pm E_{ph}) \quad (12)$$

where *B* is constant and E_{ph} is the energy of phonons assisted. The indirect allowed band gap was determined by plotting $(\alpha h\nu)^{1/2}$ as a function of photon energy ($h\nu$) for as deposited and annealed MgPc films as shown in Fig. 8.
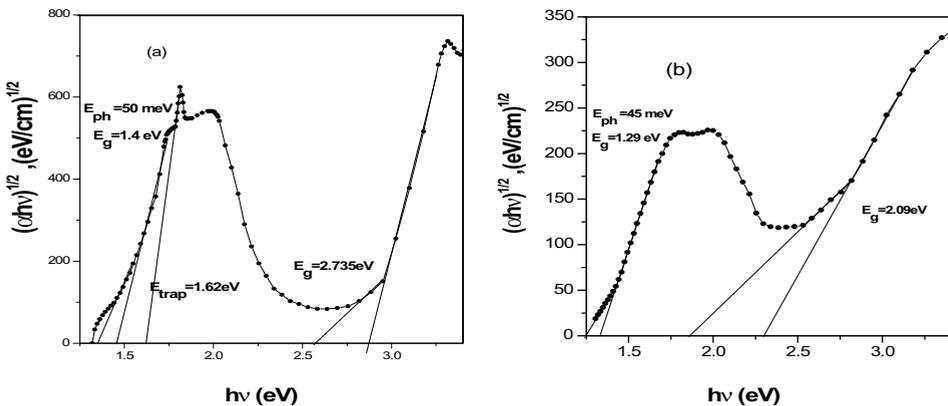

Fig. 8. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ of MgPc (a) as deposited, and (b) annealed films.

The magnitudes of E_g^{ind} and E_{ph} for the as deposited and annealed MgPc films are obtained and listed in Table 3.

Table 3. Values of energy gaps of MgPc thin films according to the band transition and the emitted energy E_e.

MgPc	Fundamental gap	Onset gap	
	E_g^{ind} eV	E_g^{ind} eV	E_e eV
As deposited	2.73 ± 0.1	1.40 ± 0.15	0.05
After annealing	2.26 ± 0.1	1.29 ± 0.15	0.045

5. Conclusions

Optical properties of as deposited and annealed MgPc thin films have been studied in the spectral range 190-2500 nm. The absorption spectral distribution for k of the investigated MgPc films characterized by a distinct peaks in visible region have generally been interpreted in terms of $\pi - \pi^{\star}$ excitation. The absorption spectrum of MgPc differs in several ways, especially in the high energy region of the Soret-band, from other Phthalocyanines. The fundamental energy gap result in the Soret-band can be interpreted as a maximum in refractive index, because the absorption index at that photon energy is quite small. The onset energy gap indicates that the band-to-band absorption has taken place at lower energy.

Acknowledgement

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تعيين معاملات الامتصاص والتشتت لشرائح رقيقة من فيثالوسيانين الماغنيسيوم

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المستخلص. حضرت شرائح رقيقة من مركب فيثالوسيانين الماغنيسيوم العضوي عند درجة حرارة الغرفة العادية وتحت ضغط منخفض، بطريقة التبخير الحراري. حددت عوامل الامتصاص الضوئي الطيفي خلال الانتقالات الإليكترونية، واستخدم نموذج الحزم لتعيين العوامل الضوئية، وذلك بقياس طيف الانعكاسية، وطيف النفاذية للضوء الساقط عموديا على الشرائح المحضرة في المدى من الأطوال الموجية بين ٢٠٠ إلى ٢٥٠٠ نانوميتر. أظهر طيف الامتصاص بعض القمم المعبرة عن امتصاص جزيئات هذا المركب للضوء، والمعروفة بحزمة Q وحزمة B. حزمة Q تتميز بظهور الانفصال المعروف بانفصال ديفدوف، وبتغير مقداره ٠,١٨ إلكترون فولت. عدم ظهور القمة المعتادة عند ٤,٣إلكترون فولت في هذا المركب، يعود إلى غياب إلكترونات المدار d لذرات الماغنيسيوم. بتحليل طيف معامل الامتصاص في منطقة الامتصاص أمكن تعيين فجوة الطاقة ١,٤٥ إلكترون فولت ونوع الانتقال الإليكتروني غيرالمباشر. وبتحليل منحنيات التشتت أمكن إيجاد ثوابت العزل، وعوامل التشتت، وكل هذا كان للشرائح المحضرة مباشرة ولتلك التي تم تلدينها لمدة ساعتين بعد التحضير وعند ٣٥٠ درجة مئوية. تمت مناقشة النتائج ومقارنتها بنتائج محضرة بطرق أخرى منشورة.