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Determination and Analysis the Influence of X-ray Irradiation on Optical Constant of Magnesium Phthalocyanin

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Abstract: The morphologies of the magnesium phthalocyanine (MgPc) thin films were investigated by scanning electron microscopy (SEM). The absorption spectra recorded in the UV–Vis region for the as deposited and irradiated films showed two well-defined absorption bands of phthalocyanine molecules, namely the Q-band and Soret band (B). The Optical properties of thermally evaporated manganese phthalocyanine thin films have been characterized using spectrophotometric measurements of transmittance and reflectance at the normal incidence of light in the wavelengths range over 200–2500 nm. The refractive index n and the absorption index k were calculated. The analysis of the optical gap E_{opt}, the transport gap and the dispersion parameters for as-deposited and irradiated films. X-ray irradiation was estimated and showed an indirect allowed transition energy gap E_g^{ind} of 2.735eV and 2.81 eV for the as-deposited and the irradiated MgPc thin films. According to the single oscillator model, some related parameters such as oscillation energy (E_0), the dispersion energy (E_d), the optical dielectric constant (ε_∞), the lattice dielectric constant (ε_L) and the ratio of free carrier concentration to its effective mass (N/m^*) were estimated.

Key words: optical absorption; MgPc thin film; *X*-ray irradiation.

INTRODUCTION

Phthalocyanines are macrocyclic compounds not found in nature that are able to coordinate hydrogen and metal cations in their centres, by coordinate bonds with the four isoindole nitrogen atoms. Most of the metals have been found capable of coordinating with the phthalocyanine macrocycle. Metallophthalocyanine complexes (MPc) are particularly attractive as potential catalysts for organic reactions because of their inexpensive and simple preparation technique on a large scale and their chemical and thermal stability (Iliev.V.I. *et al*., 1995 and Galezowski.W. *et al*., 2008). The study of these compounds is very essential to understand the behaviour of their electronic physical properties under various conditions: such as changes in temperature, pressure, frequency, ambient gases, etc. (Atta.A.A. 2009).The electronic properties of metal Phthalocyanine compounds (MPc's) have received increasing attention because of their importance as prototype semiconductors and their uses in technological applications such as generating various types of switching devices (El-Nahass .M.M. *et al*. 2008 and Henari.F.Z. 2001). Magnesium phthalocyanine (MgPc) is well known as an industrially utilised blue pigment (Herbst.W. *et al*. 1993). MgPc has recently attracted attention as a material useful for laser printers (Loutfy.R.O. *et al*. 1985) as well as for optical disks based on GaAsAl laser diode (Daidoh.T. *et al*. 1988). Interest in magnesium phthalocyanine and its complexes exhibiting (4+1)-coordination of the central Mg atom (Kinzhybalo.V. *et al*. 2007) and arises from their similarities to chlorophyll (Clayton.R.K. 1975). The purpose of this study is to prepare MgPc thin films using thermal evaporation technique and to investigate their structure besides the influence of X-ray irradiation on their optical properties.

Experimental Procedure:

Magnesium phthalocyanine powder (99.97%) in this study is obtained from Kodak, UK. Thin films of MgPc were prepared by conventional thermal evaporation technique using high vacuum coating system (Edward E306 A, England). The schematic diagram of the molecular structure of MgPc is shown in Fig. 1. Thin films were evaporated from quartz crucible source charged by MgPc and heated by a tungsten coil in a vacuum of 10^{-4} Pa during deposition. Thin films with thickness 580nm were deposited onto pre-cleaned quartz substrates maintained at room temperature and the deposition rate was controlled by using a quartz crystal thickness monitor (Edwards, FTM6) and checked by tolansky method. The film exposed to high-energy X-ray (6MeV); the dose irradiation was 25 kGy by using a linear accelerator (Philip's electronics UK version SL15). The structural characteristic of the surface morphology of thin films was checked using the scanning electron microscope (SEM) (Philips XL30). Transmittance (T) and reflectance (R) of the as-deposited and irradiated films were measured at normal incidence in the spectral rang from 200 to 2500 nm by using a double-beam spectrophotometer (JASCO model V-570 UV– vis-NIR) attached with constant angle specular reflection attachment (5^o).

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The optical constants at each wavelength are calculated from the absolute values of T and R (El-Nahass. M.M. *et al.* 2008). The absorption coefficient, α, can be calculated from the following equation

The refractive index, n can be calculated as follows:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{1}$$

The absorption index

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{T} + \sqrt{\frac{(1-R)^2}{4T^2} + R^2}\right] \tag{2}$$

$$k = \frac{4\pi\alpha}{\lambda} \tag{3}$$

Taking into account that the experimental errors for film thickness measurements are ±1%, for T and R calculations are ±1%, for refractive index n is ±2.5% and for absorption index k is ±2.3%.

RESULTS AND DISCUSSION

Structural Characterization:

The surface topography of MgPc films was studied by using SEM technique. Fig. 2a shows the SEM image of the as-deposited MgPc film on glass at room temperature. The grains with different sizes. Fig. 2b shows the surface morphology of the irradiated film; where the particles are observed to be formed vibrios-shaped with nanoparticle with the average size 50-100 nm.

Optical Characterization:

The spectral behaviour of transmittance, T(λ), and reflectance, R(λ), in the wavelength range 200-2500 nm for as-deposited and irradiated films of thickness 580 nm illustrated in Fig. 3. The spectra divided into two regions: (I) the inequality R+T<1 at shorter wavelengths 900 nm implies the absorption existence and (II at longer wavelength, λ>900 nm, the film becomes transparent and no light was scattered or absorbed, T+R~1, (non-absorbing region). A slight pronounced variation in transmittance, it is observed that the X-ray irradiation shifts the transmission edge towards lower wavelengths indicating an increase in the optical energy gap value. It is also observed that the intensity of transmittance peaks within the absorption region decreases by irradiation.

Fig.4. shows the mean values of absorption coefficient, α for the as-deposited and irradiated MgPc films. A close examination of the absorption band in the visible region, known as 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 (El-Nahass *et al.* 2003). The low energy peak of the Q-band has been variously explained as a second π-π* transition. It can also be noticed that the splitting characteristic (Davydov splitting), ΔQ, equals 0.15 eV. 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.Peaks observed at high photon energy the weak absorption peak at 4.27 eV is called N-band, which has been attributed to the charge transfer (CT) from the sp_z mixing orbital to the electron system of the macro cyclic ring of the phthalocyanine (El-Nahass *et al.* 2004).The C-band is another region of absorption at 5.63 eV due to π-π* transition. The effect of irradiated on the absorption spectra is also shown in Fig. 4. As observed, the irradiated process causes a decrease in the intensity of the absorption bands. Energy of orbital transition of MgPc thin films are listed on table 1.

At the fundamental absorption edge the energy dependences of the interband absorption coefficient are given by the following expressions *(El-Nahass.M.M. et al. 2010).*

$$(\alpha h\nu)^r = C\left(h\nu - E_g \pm E_{ph}\right) \tag{4}$$

where r =1/2 and 3/2 for direct allowed and forbidden transitions, respectively; r=2 and 3 for indirect allowed and forbidden transitions, respectively; E_{ph} is the absorbed or the emitted phonon energy and C is a parameter depending on transition probability.

The $(\alpha h\ \nu)^{1/2}$ vs (h ν) plot for the as-deposited and the irradiated films is shown in Fig. 5(a,b). The values for the corresponding energies are obtained and listed in Table 2. It should be noted that the first energy value is the optical E_g^{opt} gap corresponds to the onset of optical absorption, but the last energy value is the fundamental energy gap (Zhokhavets.U. *et al.* 2003). From the table the optical gap and on the fundamental gap increasing by affected of irradiation. This characteristic behaviour of indirect allowed transitions in solid materials is similar to NiPc (El-Nahass.M.M. *et al.* 2004).

Fig. 6 shows the reflection spectrum for the as deposited and irradiated MgPc films in the photon energy range 6.2-0.496 eV. There is anomalous dispersion (h $\nu \le$ 1.378eV), as well as normal dispersion in the wavelength range (h $\nu \ge$1.378eV). Four peaks at 5.39, 2.76, 1.67 and 1.42 eV can be seen. There are strong variations in the intensity of this peak as a result of irradiation with slight changes in their position. In the normal dispersion region the dispersion of refractive index has been analyzed using the single oscillator model which is expressed in the form (El-Nahass *et al.* 2004).

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

Where E_o is the single oscillator energy, which simulates all the electronic excitations involved and E_d is the dispersion energy which measures the extent transition. 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.7. The value of E_o and E_d, and the high frequency dielectric constant ($\varepsilon_\infty = n^2$) are determined and listed in Table 3. Other parameters can be deduced from the Drude theory relation as in *(El-Nahass.M.M. et al. 2003).*

$$n^2 = \varepsilon_L - \frac{e^2}{\pi c^2}\frac{N}{m^*}\lambda^2 \qquad (6)$$

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. 8. The lattice dielectric constant, ε_L and the values of the carrier concentration, N/m* are given in Table 3 for the as deposited and irradiated MgPc films. The disagreement between the values of ε_∞ and ε_L may be attributed to the free carrier contribution (El-Nahass *et al.* 2004).

Conclusions:

MgPc films were prepared by thermal evaporation technique. SEM image of the as-deposited MgPc show that the grin with different sizes. SEM image of the irradiated film have been found to be formed vibrios-shaped with nanoparticle with the average size 50-100 nm. The optical properties of MgPc thin film before and after irradiated have been studied in the spectral range 200–2500 nm. The absorption coefficient show two absorption bands of the phthalocyanine (Pc) molecule, the Soret band (B) and the Q-band. The Q-band shows its characteristic splitting (Davydov splitting). These absorption spectra have generally been interpreted in terms of π-π^* excitation. The type of electronic transition responsible for optical properties was indirect allowed transition the fundamental and the onset indirect energy gaps could be observed at 2.735 and 1.41 eV and increasing by effected of X-ray irradiation. The dispersion parameters of the films are affected by irradiation.

Table 1: Energy Of Orbital Transition Of Mgpc thin films.

MgPc	Visible(Q) (eV)		ΔQ(eV)	Soret (B) (eV)			N-Band (eV)	C-Band (eV)
As- deposited	1.8	1.95	0.15	3.26	3.54	3.83	4.27	5.63
Irradiate	1.8	1.9	0.11	3.31	3.49	3.76	4.27	5.63

Table 2: Values of energy gaps of MgPc thin films.

MgPc	Fundamental gap	Optical gap	
	E_g eV	E_g eV	E_{ph} eV
As- deposited	2.735	1.41	0.04
Irradiate	2.81	1.48	0.041

Table 3: Dispersion parameters of the as deposited and irradiated MgPc films.

MgPc	ε_∞	ε_L	N/m*(10^{45} kg^{-1} m^{-3})	E_o eV	E_d eV
As- deposited	3.42	3.52	50	5.2	12.53
Irradiate	3.66	3.77	62	4.8	13.38

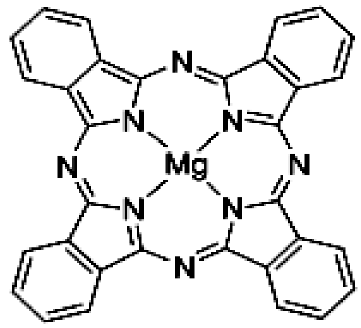
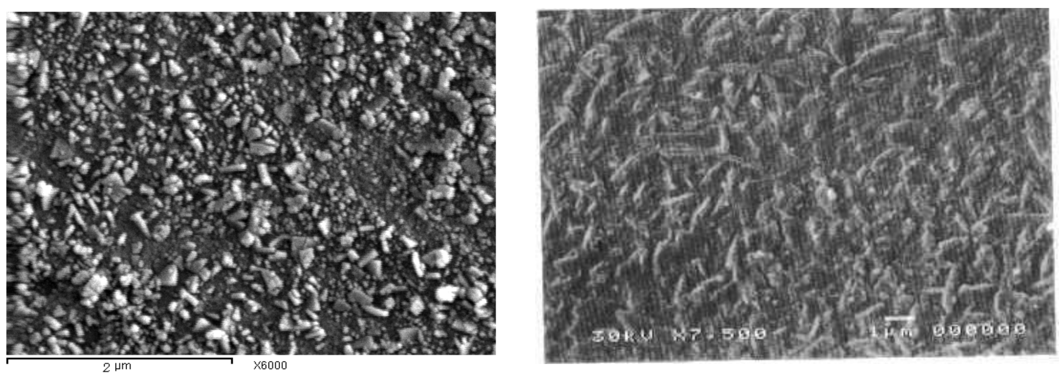


Fig. 1. Molecular structure of MgPc.



(a) (b)

Fig. 2: The SEM micrographs for (a) as-deposited (b) irradiated MgPc thin films.

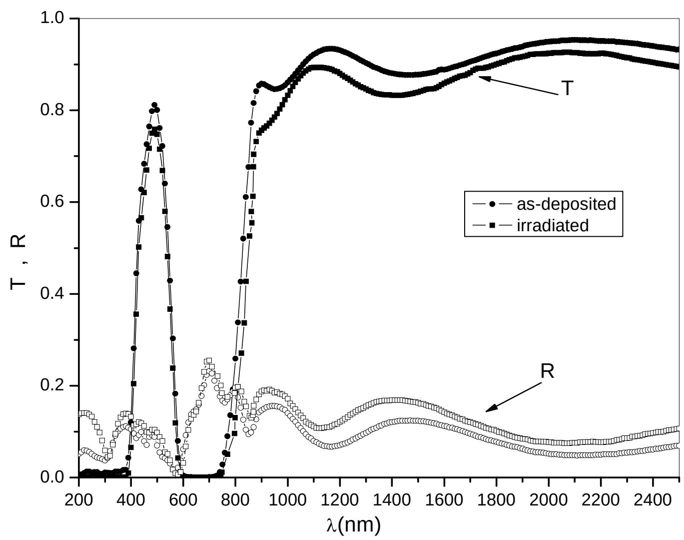


Fig. 3: Spectral behaviour of optical transmittance, T, and reflectance, R, for as-deposited and irradiated MgPc thin films.

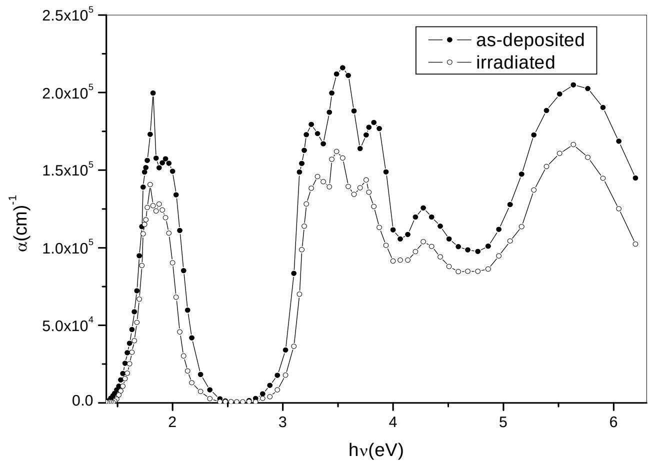
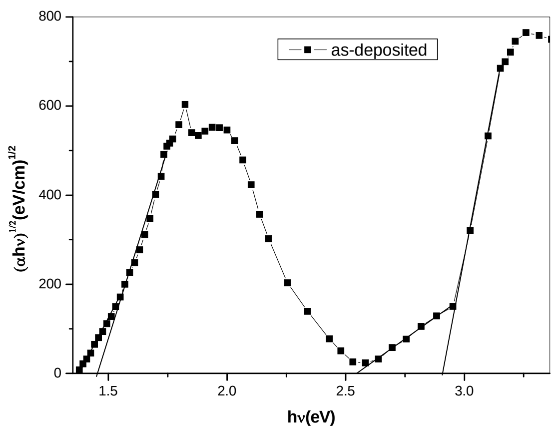
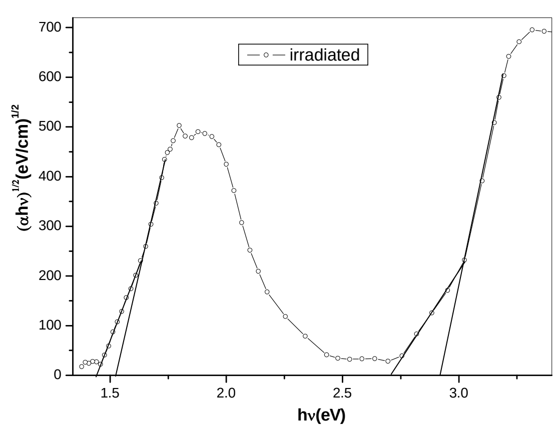


Fig. 4: Spectral behaviour of the mean value of absorption coefficient for as-deposited and irradiated MgPc thin films.



(a)



(b)

Fig. 5: The Plot of $(\alpha h\, \nu)^{1/2}$ versus ($h\,\nu$) for(a) as-deposited and (b) irradiated MgPc thin films.

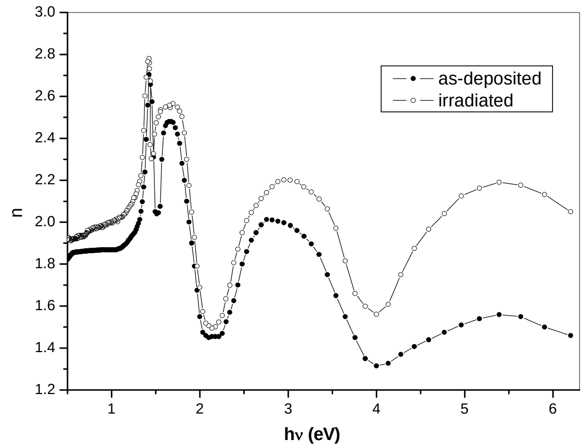


Fig. 6: Spectral behaviour the mean value of the refractive index, n, for as-depodited and irrated MgPc thin films.

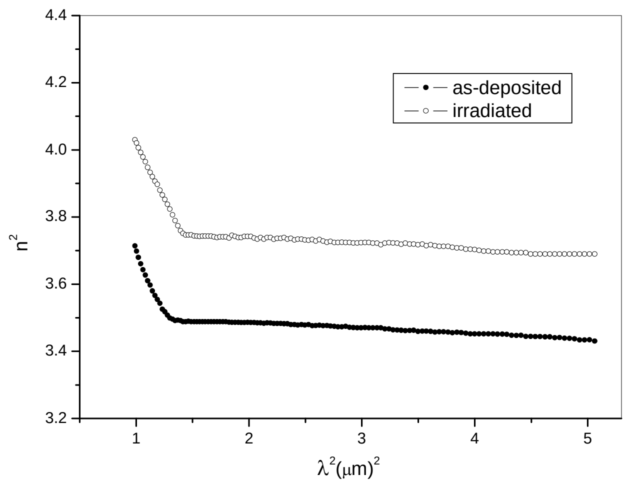


Fig. 7: Plots of $(n^2\text{-}1)^{-1}$ versus $(h\,v)^2$ for as-deposited and irradiated MgPc thin films.

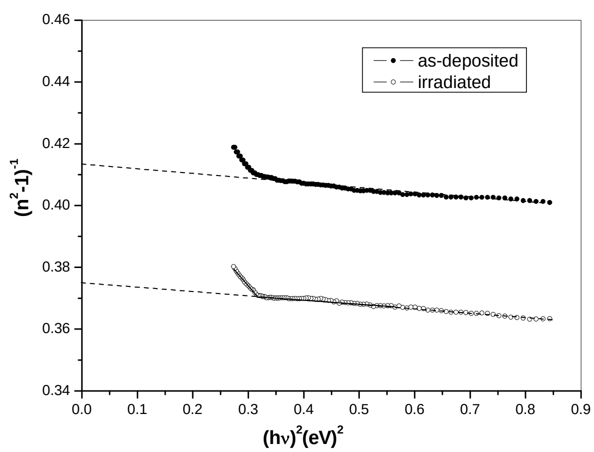


Fig. 8: Plots of n^2 versus λ^2 for as deposited and irradiated MgPc thin films.

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