International Journal of Thin Films Science and Technology
An International Journal

Study on the UV-Visble of Ni-Phthalocyanine thin film Optical Properties

M.T. Hussein[1], E. M. Nasir [2], A. H. Al-Aarajiy[3]
University of Baghdad – College of Science – Department of Physics ,Baghdad- Iraq
E-mail: (1) MohammedTaki97@yahoo.com , (2) emnasir_7@yahoo.com (3)adnan_babil@yahoo.com

Received: April 2011; Accepted: August 2012

Abstract : Thin films of Nickel Phthalocyanine (NiPc) are prepared of a base pressure of 10^{-5} m bar using Edwards 306 system of thermal evaporation technique .The films are deposited on to glass substrate at various thickness (50, 265 , 350) nm. The optical properties and spectral behavior of NiPc films as a function of thickness were studied at room temperature using UV - Visible – NIR absorption spectra. Increase in thickness, leads to increase absorbance of films and shifts peak position of all bands towards low energy side of spectra. Direct allowed transitions near the sort absorption edges were observed. Present studies reveal that the optical energy gap of NiPc thin film is around (3.3-3.25) eV for direct energy band gap respect to B bands, and around (1.68-1.63) eV for direct energy band gap respect to Q bands. The UV-Visible bands of Ni-Phthalocyanine are broadened and overlap in the solution in dioxane compare with thin film. The energy gap is slightly dependent on the thin film thickness. The optical constant of absorption coefficient α, refractive index, n, and extinction coefficient, k, were calculated and it was found that they are slightly dependent of film thickness.

Keywords: thin film, metal, organic, semiconductor, nickel phthalocyanine, Energy gap

---

1-Introduction:

Organic semiconductors owe their semiconducting properties to the presence of conjugated double bonds in their molecular structure. Carbon atoms forming conjugated double bonds are sp2 hybridized and give rise to both σ-and π-bonds, whose energy levels are split into occupied bonding orbitals with a lower energy, and unoccupied anti-bonding orbitals of higher energy[1]. Organic dyes have attracted attention as novel materials in high-density optical data recording (ODR) media due to their chemical stability, low heat conduction, and diversity of optical properties. Phthalocyanine is an organic semiconductor widely used for sensor applications and transistor fabrication, which has excellent stability against heat, light, moisture and oxygen [2]. Also Phthalocyanine are porphyry derivatives and cover a broad range of different molecules with similar structure. Since their first synthesis at the beginning of last century, phthalocyanines have established themselves as materials of high interest for the industry. Their interest relied initially on their intense coloring properties, motivating an extensive use as pigments. However, after the discovery of their semiconducting properties in 1948, the interest of the phthalocyanines has spread to a much wider range of industrial applications [3].

In recent years, the fabrication and study of electric, electronic and photonic devices employing organic semiconductors have attracted much attention [1- 5]. This is mainly due to their advantages of low cost, simplicity of device fabrication, and interesting electrical and optical properties Nickel Phthalocyanine (NiPc) is insoluble in water so it seems reasonable to investigate NiPc as a humidity sensor. NiPc is thermally stable and its thin film can be deposited by thermal evaporation without dissociation [1-4].

Nickel Phthalocyanine is an organic semiconductor that contains alternate single and double bonds. The aim of the present work is to study the influence of variation of film thickness on spectral behavior in the UV-Vis- NIR range, and on the optical constants of thermally evaporated NiPc thin films.

2-Experimental:

Fig.1 shows molecular structure of the NiPc (Nickel Phthalocyanine) used as an active material. The NiPc powder used in this study was obtained from Aldrich chemical company and was used as the source material for thermal evaporation. A molybdenum boat was used for heating the sample. The substrates were placed at a distance of 15 cm from the source thin films of NiPc, of thicknesses 50, 265, 350 nm, were deposited by vacuum evaporation technique on thoroughly cleaned glass substrate at room temperatures under lower pressure (10^{-6} Torr) using Edwards 306 system. The thickness of the films was measured using Michelson interferometer technique. Spectrophotometer, type Shimadzu and UV-Visible recorder Spectrophotometer UV-160, is used to measure the transmittance and absorbance spectrum in the range (300-1100) nm region for NiPc thin films. Fluorescence spectra were measured using Shimadzu spectroflouro photometer.

The absorption coefficient (α) was calculated from absorptance spectrum and the optical constants which are represented by refractive index (n), extinction coefficient (k) and the two part of dielectric constant (ε_r and ε_i) have been studied.

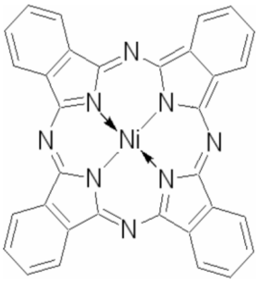

Fig. 1 Molecular structure of NiPc [3]

Optical measurement constitutes the most important means of determining the band structure of semiconductors, and the optical constants of thin films provide us with information concerning microscopic characteristics of the material and its determination is very important for using it in any one of such devices. Optical transmittance (**T**) and absorptance (**A**) spectra were performed over the wavelength (λ) within the range of (300-1100) nm. These data were used to calculate the absorption coefficient (α), band gap energy (Eg) and the optical constants (extinction coefficient, refractive index, and real and imaginary parts of dielectric constant)

The relation between the intensity of incident light (Io) and the transmitted intensity (I_T) is represented by an exponential form [5]:

$$I_T = I_o \exp(-\alpha t) \tag{1}$$

where α being the absorption coefficient and t is the film thickness. According to this equation, the optical absorption coefficient of thin films were evaluated from the transmittance data using the relation

$$\alpha=\ln[1/T]/t \tag{2}$$

where $\mathbf{T}=I_T/I_o$ is defined as the transmittance [5].

As a result of absorption coefficient data, the nature of transition (direct or indirect) is determined according to Tauc relation [6] given by:

$$\alpha E=B(E-Eg)^r \tag{3}$$

where B is a constant, r is a constant whose value depends on the type of transition, where s is equal to 1/2 and 3/2 for allowed and forbidden direct transition respectively, and r is equal to 2 and 3 for allowed and forbidden indirect transition respectively. The term E in Eq.(3) represent the photon energy which can be calculated from the relation

$$E\,(\text{eV}) = h\upsilon = 1.24/\lambda(\mu\text{m}) \tag{4}$$

where h is Plank constant, υ is the incident photon frequency, and λ is the photon wavelength. $(\alpha E)^{1/r}$ of thin films is plotted against E to decide whether this material has allowed or forbidden direct or indirect band gap transition. Since the variation of $(\alpha E)^2$ with E, at which the absorption coefficient $\alpha \geq 10^4 \text{cm}^{-1}$, for thin films is a straight line indicating that the involved transition is allowed direct one. Extrapolation of the linear portion of the plot to the energy axis ($\alpha E=0$) yielded the direct optical band gap energy value of deposited thin film.

Transmittance and absorptance spectra were used to deduce the optical constants including the refractive index (n), extinction coefficient (k_e) and the real (ε_r) and imaginary (ε_i) parts of dielectric constant. The reflectance (**R**) was evaluated from the relation [7]:

$$\mathbf{A}+\mathbf{T}+\mathbf{R}=1 \tag{5}$$

The index of refraction was estimated from the reflectance data using the equation:

$$n = \left(\frac{4R}{(R-1)^2} - k_e^2 \right)^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \tag{6}$$

where k_e is the extinction coefficient which is determined from the formula [8]

$$k_e = \alpha\lambda/4\pi \tag{7}$$

The real and imaginary parts of the dielectric constant of the films were calculated from the relations [9]:

$$\varepsilon_i = n^2 - k_e^2 \tag{8}$$

$$\varepsilon_r = 2nk_e \tag{9}$$

3-Results and Discussion:

The absorbency spectra in the UV–VIS. region of spectra for NiPc thin films of different thickness 50, 265, 350 nm shows that absorbance of films increases with increasing film thickness and the band gap shifted slightly to smaller energy and this is agreement with[10]as shown in Fig.2(a) and Table.1

There are two absorption bands take notations Q, B (Soret), and this is agreement with many researchers [2,4].The higher energy band occurring at occurring at around 650 nm is generally Known as the Q band , and often exhibits vibrational structure in thin film The Q-band exists in the visible region of spectra while others B exist in the UV region of spectra. Increasing of thickness shifts the peak position of all bands towards low energy side of spectra, results in resolving the peak of Soret band into two peaks at energies of 3.3 and 3.27eV for the thickness 50 and 265 nm. It is also noted that the bands B appear with intensities that are comparatively smaller than of Q-band. In the Q-band region, it is noticed from Fig.2(a) that the doublets are the only features in absorbency spectra NiPc films

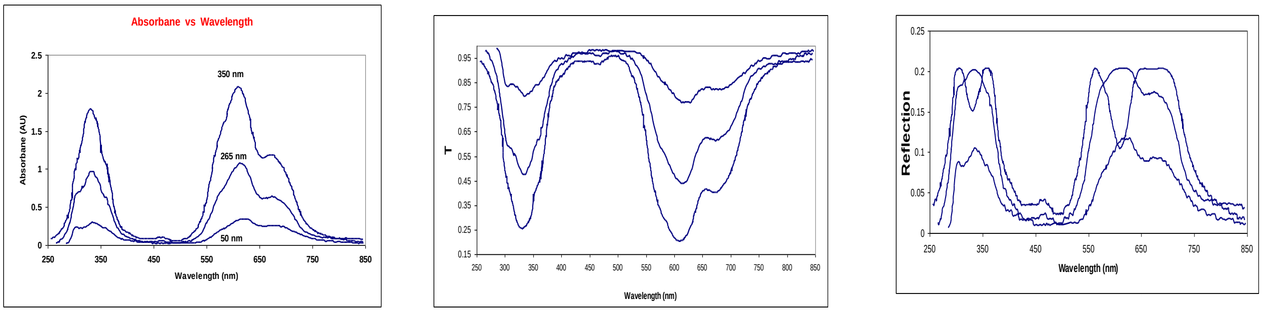

Fig. 2 Nickel Phthalocyanine spectra (a) Absorbance (b) Transmittance(c) Reflectance for thin films thicknesses (1)50 nm (2)265nm(3)350 nm

Table.1 The values of A,T and R and energy gap at 0. 5 μm

thick (nm)	**A**	**T**	**R**	Eg(eV) Q_{band}	Eg(eV) B_{band}
50	0.112	0.771	0.115	1.68	3.3
265	0.357	0.438	0.203	1.65	3.27
350	0.682	0.207	0.109	1.63	3.25

The spectra originate from the orbitals within the aromatic 18Π electron system and from overlapping orbitals of the central metal. The direct electronic transitions from Π to Π orbitals in the 300–450 nm range results in an intense band called the Soret band, which gives the absorption edge. The conduction is due to the charge transfer from SP_z mixing orbit to the Π electron system of the macrocyclic ring of phthalocyanine. The fundamental absorption edge is analyzed within the framework of the one electron theory.[4]

The tensile stress produced due to the constraint imposed by the substrate temperature affects the electronic structure and thereby results in new absorption spectra. The central metal atom of the phthalocyanines influences the optical absorption spectrum. In metalophthalocyanines, the central metal atom is in a position of nearest approach to nitrogen atoms in parallel molecules and this increases the orbital overlap between parallel pairs of molecules. Hence, any crystal phase change would affect the energy gap between conduction and valence bands [2]. Also from Fig.2(b,c), which represents the spectra of transmittance and reflection, one can notice that, At wavelength <800nm,the values of T, and reflectivity, R decreases with increasing film thickness. There are four transmission bands whose sharpness is greater with increasing of film thickness. The presence of such bands recommends these films as good band pass or as good band stop optical filter material depending on wavelength. At wavelength >800nm, T _ R and their total sum is equal to unity, the films are transparent.

The higher energy peak of Q-band has been assigned to first p–p* transition on the phthalocyanine macrocycle, The lower energy peak has been explained as an exciton peak [9,10]. The splitting of Soret band is Davydov splitting. The structural information that can be gathered from analysis of shape of Q and B-bands is that molecules of NiPc are in tilted arrangement. NiPc have partially occupied d-bands due to existence of Ni atoms as a central atom in their molecular structures.

Fig.(2) show that there is a sharpness in the fundamental absorption edge in the wavelength range 380–450nm. This sharpness is higher in 350nm of thickness films than in as law thickness. Fig. 3(a and b) represents the difference of absorptance spectra for NiPc films at the solution and thin films ,these bands are broadened and overlap so that Phthalocyanines absorb light throughout the entire visible region of electromagnetic spectrum.

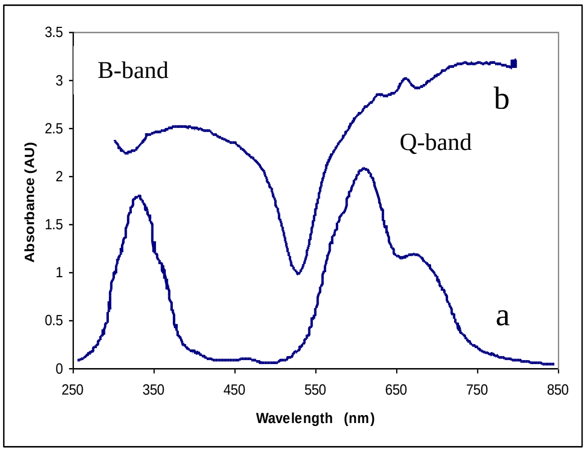

Fig.3 B and Q bands in absorbance spectra for NiPc (a) Thin film (350 nm) (b) Solution (10^{-4}M)

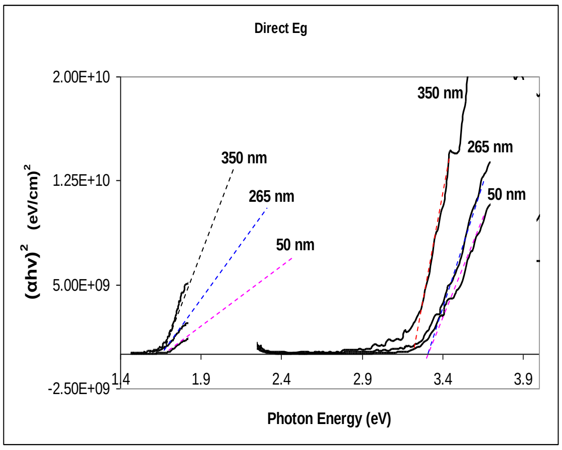

Fig.4 Direct energy band gaps for UV-Visible spectra

The energy gap is determined by plotting Tauc equation, and taking the extrapolation of the linear portion where ($\alpha \geq 10^4$ cm^{-1}) of the $(\alpha h\nu)^2$ as a function of hν curve to α=0, then, To determine the type of optical transition near the absorption edge of the Q and Soret bands), we have examined $(\alpha h\nu)^2$ versus hν and found that the relation yielded a linear dependence, which describes allowed direct transitions are occurring in such films. Fig. 4 shows Direct energy band gaps for UV-Visible spectra of NiPc films for thickness 50, 265, 350 nm respectively. The direct energy gap value was found to be as shown in the Table(1), which nearly in agreement with the other literatures[1-5,10-11].

The optical constants of these films have been calculated as shown in Table(2). One can see that it depend on thickness, and its values are agreement with other literatures[9-11].

Table.2 The optical constant at 0.5 μm

thick (nm)	**α x10^4 $(cm)^{-1}$**	**k**	**n**	**ε_1**	**ε_2**
50	5.195	0.254	1.989	3.893	1.012
265	3.109	0.152	2.633	6.912	0.803
350	4.492	0.219	1.957	3.782	0.861

The spectral distributions of absorption coefficient, α, for NiPc thin films depend on the absorbance spectra. The absorption coefficient curve confirmed the splitting of Soret band and the existence of 3.3eV peak in spectra of NiPc films. The calculations of n , k ,(ε_r) and (ε_i) were performed for films with different film thickness ranging from 50–3500nm.The results of calculations showed that n and k are slightly dependent of films thickness for NiPc.

The florescence spectra of Ni-phthalocyanine at different thicknesses 50, 265, and 350 nm respectively are shown in Fig.5. The values of peak positions for Q-band and B-band are nearly equals to this value which deduce from the absorbance spectra, Also The florescence spectra curve confirmed the splitting of Soret band.

4-Conclusions:

From the present work, we can conclude that the NiPc films of thickness 50, 265, 350 nm on glass substrate have been prepared successfully by vacuum evaporation technique. From the absorbance spectra for NiPc films, we observed that the maximum absorption peaks shift towards the higher wavelength with the increase of thickness. The type of electronic transition responsible for optical absorption is direct allowed transition. And the value of absorption and reflection increases with the increases of thickness whereas the transmission is decreased. The optical energy gap for NiPc films decreases with the increase of film thickness. The absorption coefficient, extinction coefficient, refractive index and the (real, imaginary) part of dielectric constant depend on thickness. The florescence spectra curve confirmed the splitting of Soret band. The values of peak positions for Q-band and B-band are nearly equals to this value which deduce from the absorbance spectra.

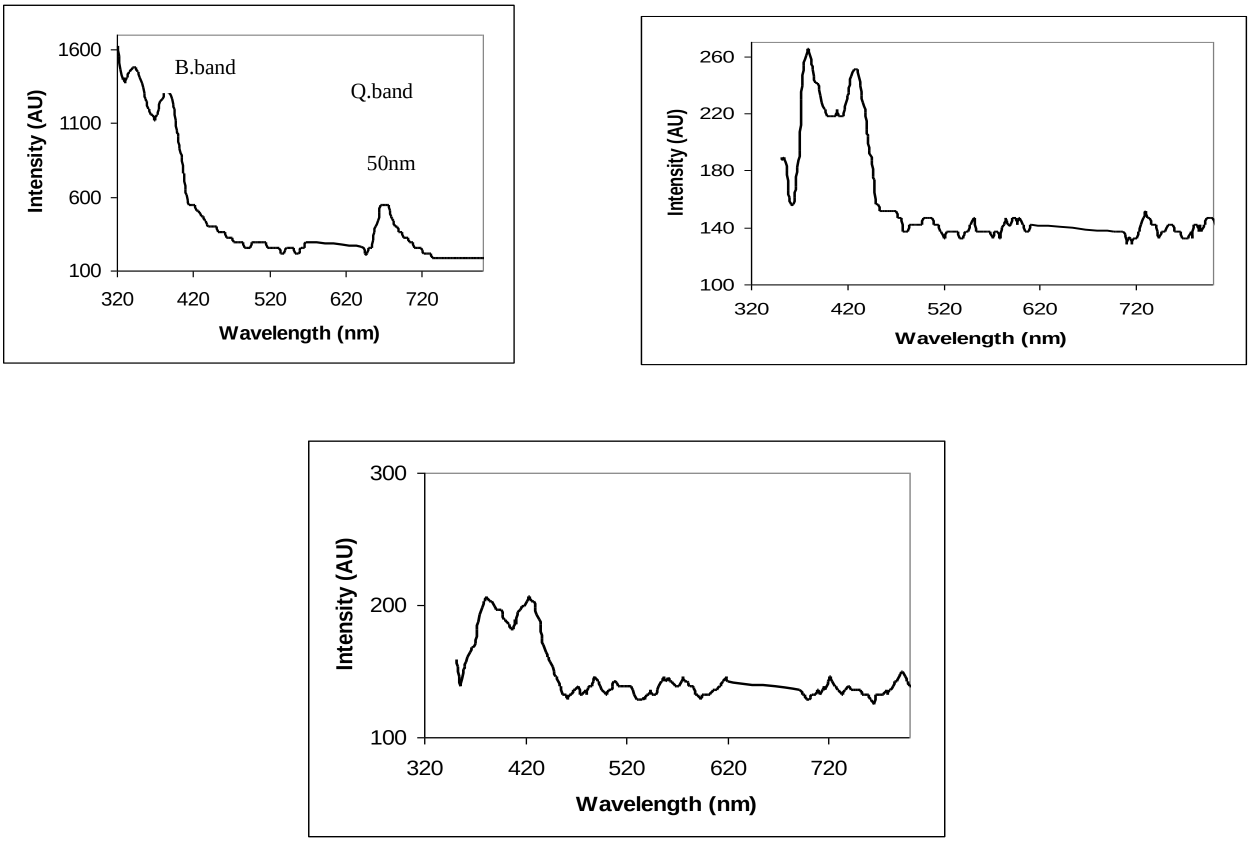

Fig. 5 Fluorescence Nickel Phthalocyanine spectra for thicknesses 50, 265, 350 nm

References:

1) Dimas Gercia de Otevza, 2007, Fluorinated copper-phthalocyanines in model, thesis submitted to university of Madrid systems for organic electronic devices
2) BENNY JOSEPH and C. S. MENON,2007, Studies on the Optical Properties and Surface Morphology of Nickel Phthalocyanine Thin Films, E-Journal of Chemistry, Vol. 4, No.2, pp 255-264.

350nm

3) Mutabar Shah, Muhammad Hassan Sayyad and Khasan S. Karimov,2008, Fabrication and Study of Nickel Phthalocyanine based Surface Type Capacitive Sensors, World Academy of Science, Engineering and Technology 43 2008, 392-394.
4) K.N. Narayanan Unni, C.S. Menon), 2000, Electrical, optical and structural studies on nickel phthalocyanine thin films, Materials Letters 45 _2000. 326–330,
5) Asma. A. Hendi,2011, Determination and Analysis the Influence of X-ray Irradiation on Optical Constant of Magnesium Phthalocyanin, Australian Journal of Basic and Applied Sciences, 5(10): 38-44, 2011
6) R.E. Hummel, "Electronic Properties of Materials", 3rd edition, Springer, New York (2001).
7) J. Tauc, "Amorphous and Liquid Semiconductors", Plenum Press, London and New York (1974).
8) D. Schroder, "Semiconductor Material and Device Characterization", John Wiley & Sons (1990).
9) L. Kazmerski, "Polycrystalline and Amorphous Thin Films and Devices", Academic Press (1980).
10) M.M. El-Nahass a, H.M. Zeyada b, M.S. Aziz b, N.A. El-Ghamaz, 2004, Structural and optical properties of thermally evaporated zinc phthalocyanine thin films, Optical Materials 27 (2004) 491–498.
11) M. M. El-Nahass, F.S. Bahabri* ands.R.Al-Harbi, 2001, Optical Properties of Copper Phthalocyanine (CuPc) Thin Films, Egypt. J. Sol., Vol. (24), No. (1), (2001)