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RESEARCH ARTICLE

Effect of the UV-Irradiation on the Linear Optical Properties of Ni-Phthalocyanine Thin Film

Saif Hasan Hameed[1], Addnan H. Al-Aarajiy[2*]

Department of Physics, College of Science, University of Babylon, Hilla, Iraq

***Corresponding Author:** Addnan H. Al-Aarajiy*

Abstract

A thin film of Nickel-phthalocyanine has been deposited with a thickness of 250 nm on glass, prepared by thermal evaporation using the Edward E306A coating at room temperature Rt. The high vacuum pressure during evaporation was about 10^{-5} m bar. The distance between the boat and the substrate was fixed at 20 cm. at the evaporation method, where the study of spectral behavior and optical properties of thin films of Nickel phthalocyanine (NiPc) by irradiation with ultraviolet (UV) at different times 0,10,20,40 and 80 min respectively, where we noticed that an increase of irradiation time leads to an increase absorbance and decrease the energy band gap. The absorption spectra recorded in the range of 190-1100 nm wavelengths showed the existence of two absorption bands, Soret or B-band and Q-band. The UV-Vis spectra showed that thin films deposited on same substrate types have directly energy-gap. The energy gap values of the prepared thin films were calculated from Tauc equation.

Keywords: *Thin film, Metal, Nickel phthalocyanine, Energy gap, Thermal evaporation.*

Introduction

Phthalocyanines (Pcs), which were discovered unexpectedly in 1907 as a by-product in an industrial preparation of ortho disubstituted benzene derivatives, are derivatives of porphyrin characterized with high symmetry [1].Nickel Phthalocyanine is an organic semiconductor widely used as an optoelectronics devices as thin films. Thin-film technologies are being developed as a means to substantially reduce the cost of electronic systems. Thin film modules are expected to be cheaper to manufacture owing to their reduced material costs, handling costs, energy costs, and capital costs [2].

Phthalocyanines have intense color and excellent chemical and thermal stability. The versatility, architectural flexibility, non-toxicity and ease of processing make them eligible candidates for use in a wide range of technological applications such as digital cameras, mobile phones and personal computers [3]. Highly efficient reactive oxygen species generation and ease of chemical modification, phthalocyanines have emerged as a promising class of second-generation photosensitizers for photodynamic therapy [4].

Nickel Phthalocyanine is an organic semiconductor that contains alternate single and double bonds. The aim of the present work Because of the energy gap is the controller of the thermal, electrical, and optical properties we try to effect on it by uv-irradiation.

Experimental Part

The NiPc powder used in this study was obtained from Sigma Aldrich Company USA in the form of microcrystalline materials, and was used as the source material for thermal evaporation. The substrates were placed at a distance of 20 cm from the source thin films of NiPc, of same thicknesses. were deposited by vacuum evaporation technique on thoroughly cleaned glass substrate at room temperatures under l pressure (10^{-5} mbar) using Edwards 306 system.

The thickness of the films was measured by using Michelson interferometer technique, UV-Visible recorder Spectrophotometer UV-160, is used to measure the absorbance and transmittance spectrum in the range (190-

1100) nm region for NiPc thin films. The absorption coefficient (α) was calculated from absorbance spectrum and the optical constants which are represented by refractive index (n), extinction coefficient (k) and the two part of dielectrict constant (εr and εi) have been studied. Fig.1 shows molecular structure of the NiPc (Nickel Phthalocyanine) used as an active material

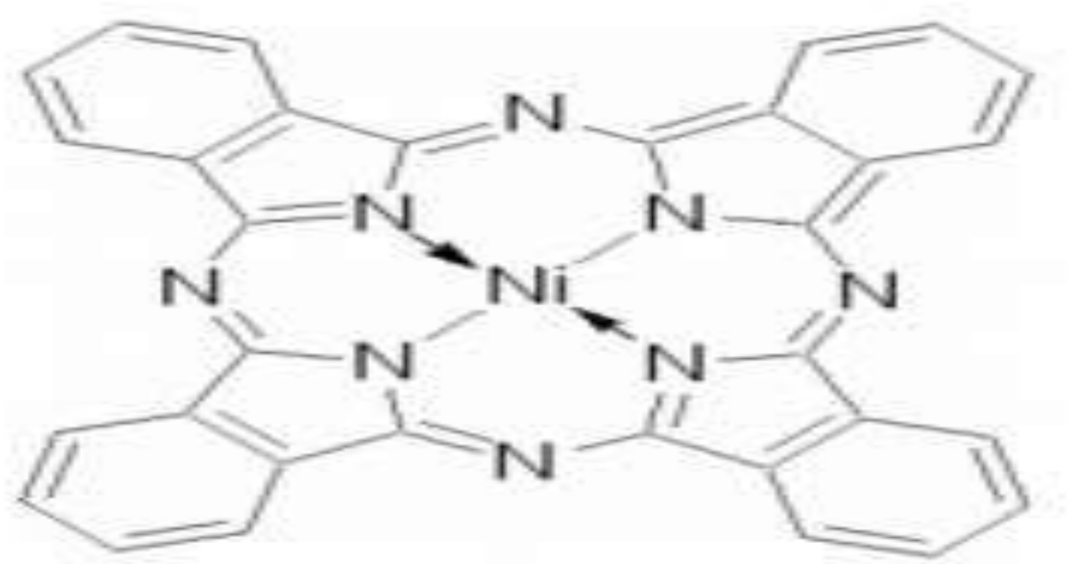

Fig. 1: Molecular structure of NiPc [5]

Optical transmittance (T) and absorptance (A) spectra were performed over the wavelength (λ) within the range of (190-1100) 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 Absorption can be defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_o) [6]

$$A = \frac{I_A}{I_o} \quad \text{.........................(1)}$$

Transmittance is given by the ratio of the intensity of the transmitting rays (I_T) through the film to the intensity of the incident rays (I_o) on it as follows [6]

$$T = \frac{I_T}{I_o} \text{......................... (2)}$$

We can also find a transmittance as a function of wavelength through the exponential relationship for both absorbance and transmittance which [6]

$$A = \log\left(\frac{1}{T}\right) \text{............... (3)}$$

The optical absorption coefficient of thin films were evaluated from the transmittance data using the relation

$$\alpha = \ln[1/T]/t \text{ .... (4)}$$

The nature of transition (direct or indirect) is determined according to Tauc relation [7] given by:

$$\alpha E = B(E - E_g)^r \text{.....................................(5)}$$

Where r is a constant whose value depends on the type of transition, when r is equal to 1/2 and 3/2 for direct and forbidden direct transition respectively, and r is equal to 2 and 3 for allowed and forbidden indirect transition respectively. Photon energy in eq (5) which can be calculated from the relation

$$E\ (eV) = h\upsilon = 1.24 / \lambda\ (\mu m) \text{ .... (6)}$$

Where υ is the incident photon frequency, h is Plank constant, and λ is the photon wavelength.

The index of refraction was valued from the reflectance data by the equation:

$$n = \left(\frac{4R}{(R-1)^2} - k^2 \right)^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \quad \ldots\ldots\ldots\ldots\ldots(7)$$

Where k is the extinction coefficient which is determined from the formulation [8]

$$k_e = \alpha\lambda/4\pi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

The real and imaginary parts of the dielectric constant of the films determined from the formulation [9]

$$\varepsilon_i = n^2 - k_e^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

$$\varepsilon_r = 2nk_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

Results and Discussion

The absorbance spectrum have been obtained using spectrophotometer device as shown in Figure (2) for different irradiation times 0,10,20,40 and 80 minutes respectively.

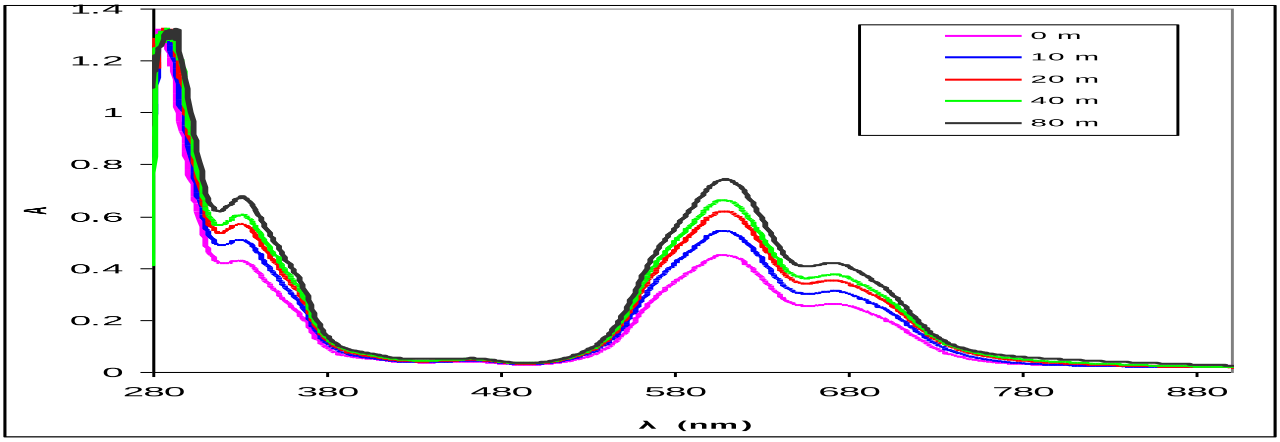

Fig.2 (a) Absorbance spectra of NiPc

Absorbance spectra for NiPc thin films were recorded in the region 190-1100 nm. We notice from the figure that there are two peaks in the area of UV at wavelengths (286) and (311) as well as we notice that there are two peaks in the region of the visible spectrum at wavelengths (596) and (660) these peaks give me altitude and location Spectra shows that with increased ultraviolet irradiation rate of thin films, the maximum absorption is shifted towards long wavelength, Increased exposure to ultraviolet radiation increases crystalline defects and localized levels, Consequently, creating additional levels in the material reduces the energy gap.

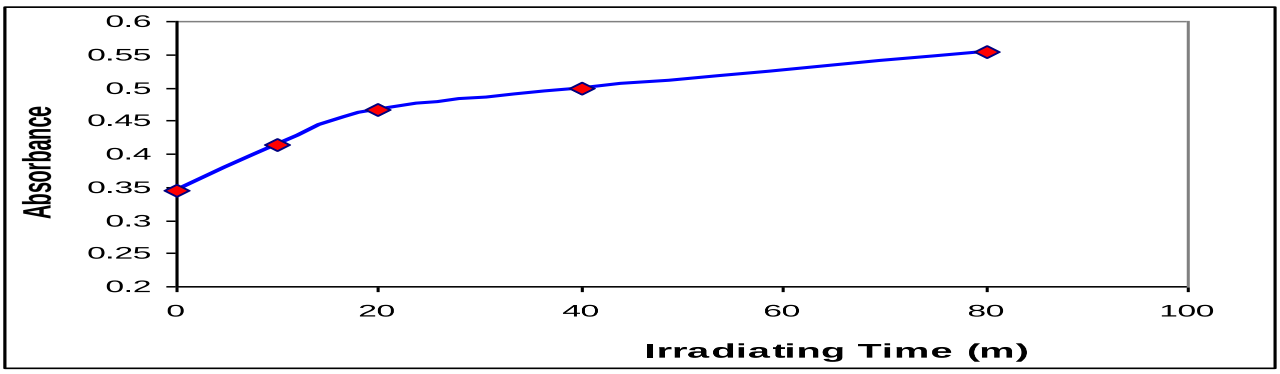

Fig.2 (b) Effective of Absorbance spectra on NiPc thin film to radiation by different exposure rate of energy of UV Irradiation

Fig. 2(b) shows the relationship between absorption and irradiation time will be two areas increase in the first and semi-stability in the second and we expect there is stability after 80 minutes. The absorbance spectra of the thin films of Nipc, which have a different exposure time for ultraviolet radiation, clearly show that the increased UV exposure leads to increased absorption. The Transmittance spectrums have been obtained as shown in Figure (3).

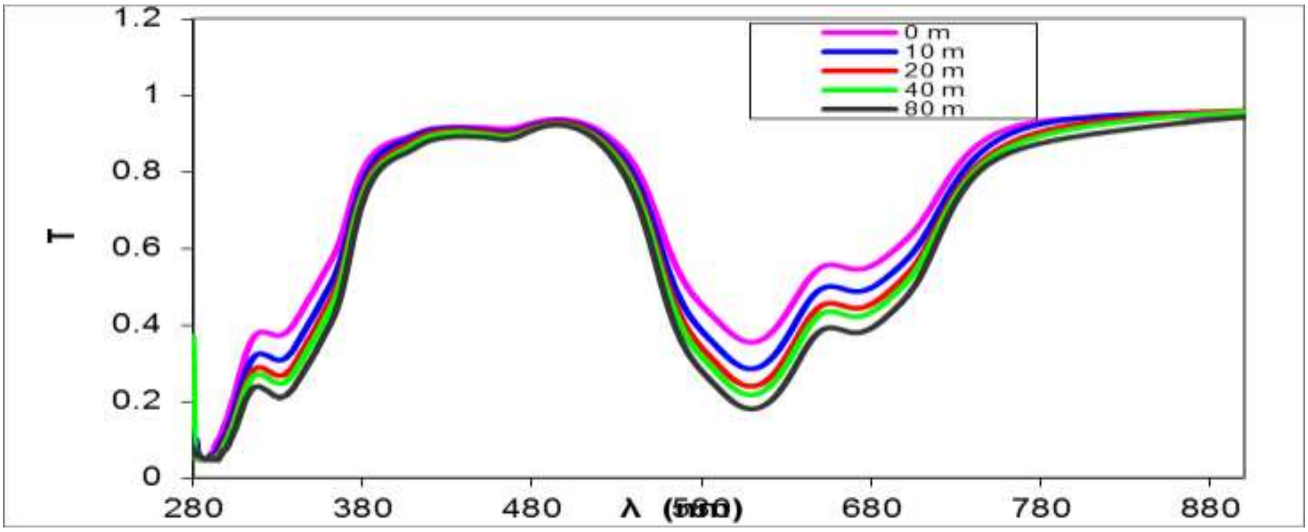

Fig.3 (a) Transmittances spectra of NiPc

The transmittance spectra for NiPc thin films, having UV exposure rate for high energy of UV- ray are shown in Figure 3 (a) The figure shows that the maximum transmittance value is at the range (400-500) nm, While before this range is absorbance. The transmittance decreases clearly with thin film exposure rate increasing for both B and Q, Where we note that the increase of irradiation led to increased absorbance and therefore cause a decrease in the value of transmittance.

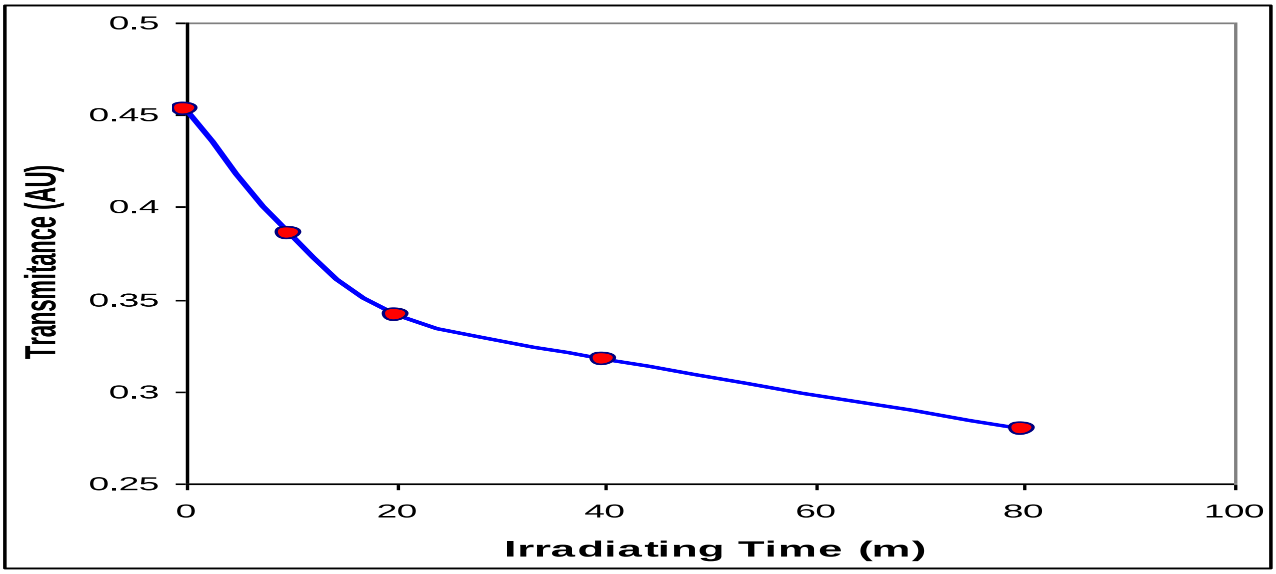

Fig 3 (b) effective of Transmittance on NiPc films with different exposure rate of UV- ray Irradiation

Fig.3 (b) shows The relationship between transmittance and irradiation time will be two areas reduce in the first and semi-stability in the second and we expect there is stability after 80 minutes. The transmittance spectra of the thin films of NiPc, which have a different exposure time for ultraviolet radiation, clearly show that the increased exposure leads to reduce transmittance.The effect of deferent of exposure rate s for UV-irradiation energy on transmittance had been studied; one can see the transmittance decreases normally with UV exposure rate increasing. The reflectance spectrums have been obtained as shown in Figure 4 (a).

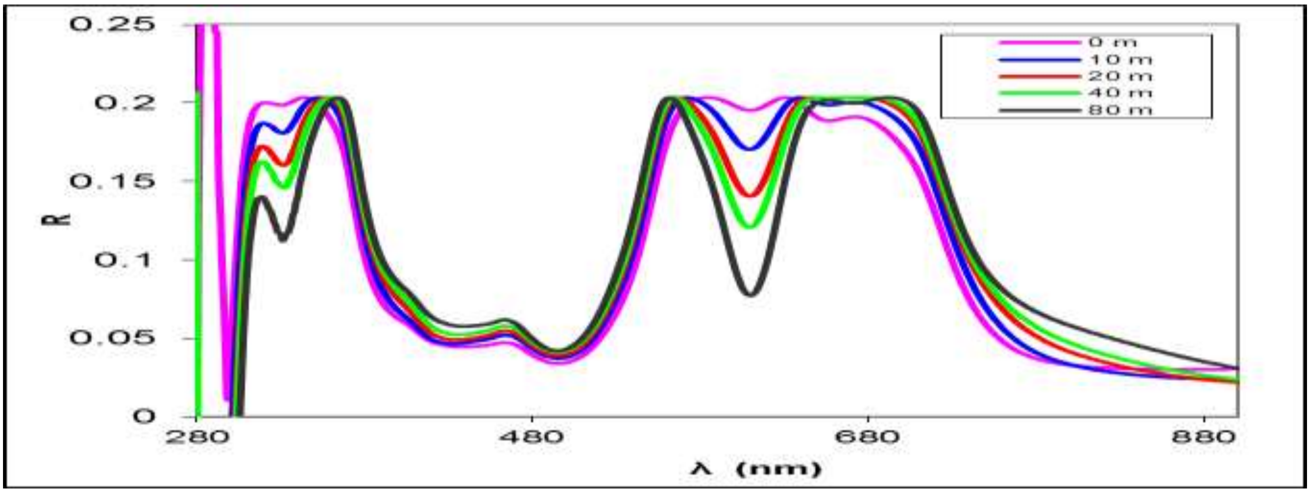

Fig. 4 (a) Reflectance spectra of NiPc

Reflectance spectra for different exposure rate of energy for UV- ray show maximum variation in Q and B bands and minimum variation in wavelength range (400-500) nm. Values of reflectance seem to be semi equal for B and Q bands at the thin film thickness 250 nm. The reflectance spectra for NiPc thin films, having different exposure rate deposited at shown in Figure 4 (a).Where we note that the increase of irradiation led to increased absorbance and therefore cause a decrease in the value of Reflectance.

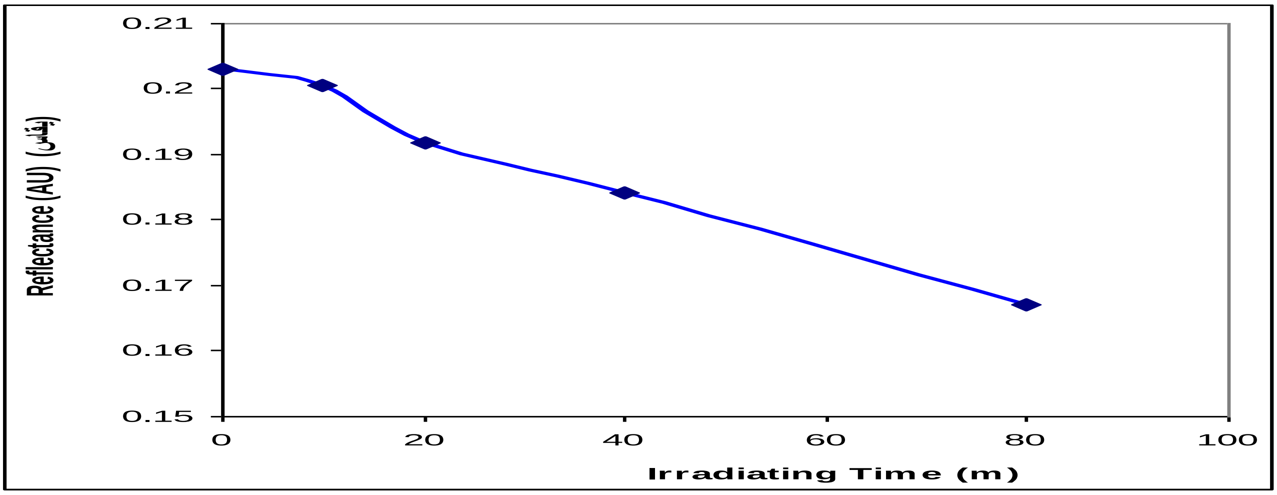

Fig.4 (b) effective reflectance for NiPc films having different exposure rate of UV- ray Irradiation

Fig.4 (b) shows the relationship between reflectance and irradiation time will be two areas reduce in the first and semi-stability in the second and we expect there is stability after 80 minutes. The spectra of the reflectance thin films of NiPc, which have a different exposure time for ultraviolet radiation, clearly show that the increased exposure leads to reduce reflectance.The effect of deferent of exposure rate s for UV-irradiation energy on reflectance had been studied; one can see the reflectance decreases normally with UV exposure rate increasing.

Table 1: the values of optical constants when irradiation of thin films by different UV rays

Irradiating Time (m)	Absorption Coefficient α *10^4 (cm^{-1})	Extinction Coefficient (K)	Refractive Index (n)
m	(cm^{-1})		
0	3.16	0.146	1.28
10	3.81	0.176	1.31
20	4.05	0.187	1.32
40	4.59	0.212	1.35
80	5.09	0.235	1.37

Where we observe that by increasing the irradiation, the values of the absorption coefficient, refraction and the coefficient of extinction increase as shown in the table above.

Also the direct energy band gap for UV-Visible spectra of NiPc films is shown in the Figure (5a).

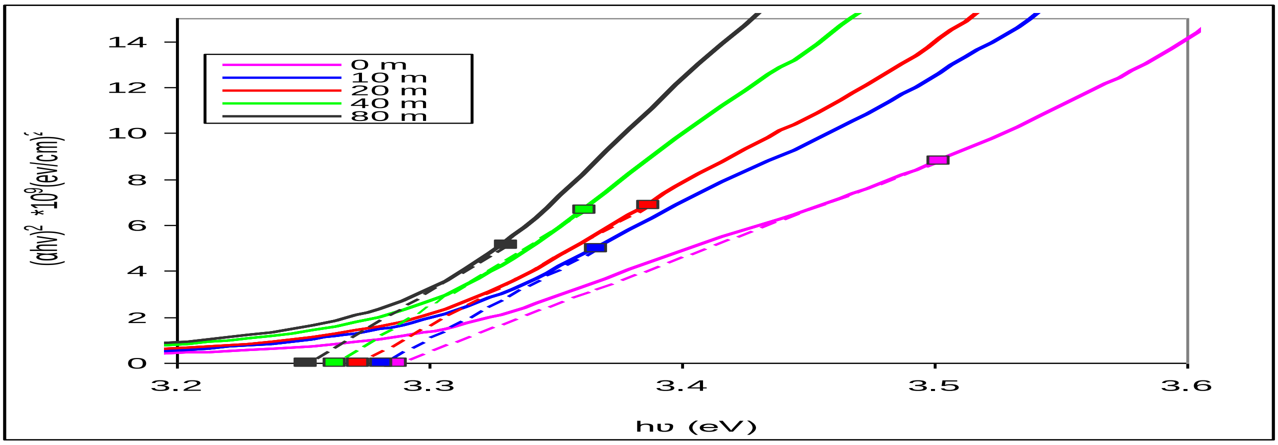

Fig.5 (a) quantity $(\alpha h\upsilon)^2$ versus photon energy

The optical energy gap values (Eg) for NiPc thin films have been determined by using Tauce equation which is used to find the type of the optical transition. The electronic transition when determined as direct transition. The value of the optical energy gap decreases slightly with increase in exposure rate for UV-irradiation, where we note that by increasing the irradiation time leads to an reduce in the optical energy gap Increased of uv exposure increases crystalline defects and localized levels, Consequently, creating additional levels in the material reduces the energy gap.

The relationship between optical energy gap and irradiation time will be two areas reduced in the first and semi-stability in the second and we expect there is stability after 80 minutes. The spectra of the optical energy gap thin films of NiPc, which have a different exposure time for ultraviolet radiation, clearly show that the increased of uv-exposure leads to reduce of optical energy gap. Note from the figure that the energy gap gradually decreases from 3.28 to 3.25 this behavior is due to the growth of grain size and increasing of the defect states near the band.

Conclusions

From the present work, we can conclude that the NiPc films of the same thickness 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 uv irradiation time.

The type of electronic transition responsible for optical absorption is direct allowed transition. And the value of absorption increases with the increases of uv irradiation whereas the transmission and reflectance is decreased. The optical energy gap for NiPc films decreases with the increase of film thickness. The absorption coefficient, extinction coefficient, refractive index depend on uv irradiation time. The values of peak positions for Q-band and B-band are nearly equals to this value which deduce from the absorbance spectra.

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