Spectroscopic and structural properties of Zinc-Phthalocyanine prepared by pulsed laser deposition

Mohammed T. Hussein and Mohammed Jawad H. Kadhim
College of Science, University of Baghdad

Author E-mail: mohammedtake@gmail.com

Abstract. Zinc Phthalocyanine (ZnPc) was prepared by pulsed laser deposition using Q-Switching Nd:YAG laser with wavelength 1064nm, frequency 6Hz and energy 240mJ at room temperature under vacuum condition with 10^-3torr. Ultra violet-Visible spectra were used to evaluated the optical properties included the absorption coefficient, extinction coefficient, refractive index and energy gap of the ZnPc films and the results were discussed. The energy gap of ZnPc film with different thickness are varied from (1.7 to 1.5 eV) at Q- band and from (3 to 2.7 eV) at B- band for increasing thickness from (150 to 500 nm). The optical transition was found to be direct and allowed transition. X-ray diffraction (XRD) was used to analyze the ZnPc organic thin films with different thickness that the preferential orientation around (111) at 7 degree. FTIR spectra for ZnPc and metal free phthalocyanine (H2Pc) is used to find the molecular vibration. It can be observed that a strong peak around 3500 Cm^-1 which refers to N-H bond for metal free phthalocyanine where absents for ZnPc and appear a new strong line around 730 Cm^-1 which refers to Zn metal.

1. Introduction

Zinc Phthalocyanine (ZnPc), due to the spectroscopic and photovoltaic properties have been extensively studied and can be applied in several field: physics, chemistry, medicine, and other science. Most phthalocyanine have absorption in the visible region, larger absorption coefficient [1-3], high photochemical stability[4] and on these reasons they are potential candidates for used in solar - to - electric photovoltaic energy conversion. Organic photovoltaic semiconductors, such as zinc phthalocyanine (ZnPc) using as a Donor active media (p-type) is application for gas sensing [5-9] and photovoltaic devices [10-14]. Currently, there are many researchers which aimed to the development of efficient low cost photovoltaic energy conversion guided by the guest for organic semiconductor materials in the form of multilayer devices. Zinc phthalocyanine (ZnPc), as well- known organic photovoltaic semiconductor with a large absorption coefficient [4-15] high thermal and photochemical stabilities [4]. Pulsed laser deposition (PLD) as an option of an easy laser based technique to make ZnPc films. M. Novotay et al. showed that ZnPc films depositied by pulsed laser deposition using KrF laser wavelength 248nm and frequency 5Hz on substrates in vacuum [16].

The aims of this investigation is to study the spectroscopic and structural properties of organic semiconductor Zinc Phthalocyanine (ZnPc) thin films prepared by pulsed laser deposition (PLD) technique using Q-Switching Nd:YAG laser.

2. Experimental

ZnPc thin films were growth by (PLD) technique using Q–Switching Nd:YAG laser wavelength 1064nm, frequency 6Hz and energy 240mJ under vacuum condition with 10^-3torr on glass substrate at room temperature. The slides(substrates) were cleaned by using detergent with water.
to remove any dust that might be attached to the surface and rubbing gently for 15 minutes. Slides were placed in a clean beaker containing distilled water. The processing has been replaced by replacing the distilled water with pure alcohol solution and the slides were wiped with soft paper. The glass substrate was located 3cm from the ZnPc target. The ZnPc target billet diameter of 10 mm and thickness 2mm at weight of target is 0.25 gram with press of 6tons. The optical properties of ZnPc films with different thickness deposited at room temperature were studied in the wavelength range (250 – 800 nm) by using UV-Vis. shimadzu 1800 spectrophotometer. The output data of wavelength, transmittance and absorbance are used in a computer program to deduced the optical energy band gap and fundamental optical absorption edge and all optical constants. Fourier Transformed Infrared Spectrum for ZnPc powder was recorded by shimadzu double beam FTIR spectrometer for ZnPc powder mixed with KBr. The structure of the ZnPc films have been examined by x-ray diffraction using x-ray diffract meter system shimadzu XRD 6000 which records the intensity as a function of Bragg angle. The scanning angle (2θ) was varied in the range of (5 -50) degree with speed 5 (deg./min). Films thicknesses were measured by Interferometer fringes method.

3. Results and Discussion

3.1 FTIR spectroscopy

The FTIR spectrum for ZnPc powder was measured at room temperature and compared with metal free phthalocyanine $H_2PC$ spectrum as shown in Fig (1). FTIR for ZnPc powder shows the bond bending represented by the range (400-2000) cm$^{-1}$ while the bond stretching represented by the range (2000-4000) cm$^{-1}$. It can be observed that a strong peak around 3500 cm$^{-1}$ which refers to N-H bond for metal free phthalocyanine where absents for ZnPc and appear a new strong line around 730 cm$^{-1}$ which refers to Zn metal.

3.2 The absorbance spectra

The absorbance spectra for ZnPc thin films with different thicknesses at (150nm)and (500nm) related with number of laser shot at room temperature as shown in fig(2). The figure shows that both of two spectra have two band, one in UV region which is called B-band at range about (300-350nm) and the other in visible region which is called Q-band at range (600-650nm). It shows the absorbance increase strongly with thin films thickness increase, and the minor changes occur in flat area in range (400-500nm). The absorbance for B and Q band increase strongly with thin films thickness according to Beer-Lambert law. Also spectra show that the maximum absorption peak shifts towards the longer wavelength with increase of thin films thicknesses. The increasing thickness causes increasing in crystal defects and localized level.

3.3 The absorption coefficient

The absorption coefficient $\alpha$ is calculated using the equation [17]:

$$\alpha = \frac{2.303A}{t} \hspace{1cm} (1)$$

Where A is the absorbance and t is the thickness. The absorbance(A) represent the logarithm of the reciprocal of the transmittance (T) according to Beer-Lambert:

$$A=\text{Log}(1/T) \hspace{1cm} (2)$$

The energy (E) of the incident photon can be calculated from the equation:
\[ E(eV) = h\nu = \frac{1240}{\lambda} \]  

Where \( h \) is the plank constant and \( \nu \) is the frequency of light incident. The dependence of the absorption coefficient on the wavelength for different thickness of the deposited ZnPc is shown in Fig(3). One can see from these figures that the absorption coefficient of the ZnPc thin films is described by a strong absorption in the B band at the shorter wavelength region between (300-350nm) and with sharp edge on the long wavelength side from (350-400nm) also a strong absorption for the Q band at wavelength region between (620-675nm) and with sharp edge on the long wavelength side from (725-800nm). In the B and Q bands the absorption coefficient exhibits high values of \( \alpha \) (\( \alpha=2.5x10^4cm^{-1} \) for 500nm and \( \alpha=3.5x10^4cm^{-1} \) for 150nm) for wavelength 300nm. Which means that there is a large probability of the allowed direct transition. The absorption coefficient decreases with thickness increasing for ZnPc thin films because of localized level number increasing inside energy gap with ZnPc thickness increasing.

### 3.4 Optical energy band gap

The optical energy band gap values (\( E_g \)) for ZnPc thin films have been determined by using Tauc formula[18] :

\[ \alpha h\nu = B(h\nu - E_g)^{1/2} \]  

Where \( B \) is a constant inversely proportional to a morphousity , \( h\nu \) is the photon energy (eV) , \( E_g \) is the optical energy gap (eV) , \( r \) is constant and many take values 1/2 , 3/2 , 2 and 3 depending on the material and the type of the optical transition . In Fig(4) the value of the optical energy gap decreases slightly with increase in thickness , this behavior is due to the growth of grain size and increasing of the defect states near the bands.

### 3.5 X-ray diffraction analysis

The diffraction pattern of prepared thin films of ZnPc at room temperature for thickness 150 nm in Fig(5) shows that the intensity about 230 (cps) at 2theta 7.1 (degree) . Also with 500 nm thickness in Fig(6) shows that the intensity about 700 (cps) at same 2theta with preferential orientation (111) , the increasing for intensity meaning that the material toward more crystal.

### 4. CONCLUSIONS

Zinc phthalocyanine (ZnPc) thin films were successfully prepared by PLD using Q-Switching laser Nd:YAG . The greatest absorbency is indicated that there are two band of absorption of spectra one in UV and other in visible region. ZnPc thin films have direct band gap and it decreasing with increasing thicknesses. The thin films thicknesses were polycrystalline. When the thicknesses increased the degree of crystallinity also increased.

### REFERENCES

[1] D.Spikes, Photochem. Photobiol. 43, 691(1986).
[2] Rosenthal, Photochem. Photobiol. 53, 859(1991).
[3] Robel, A. Boguta, and R. M. Ion, Int. J. Photoenergy 2, 87(2000).
[4] C. C. Leznoff and A. B.P. Lever, Phthalocyanines : Properties and Applications (VCH, New York, 1996).
[5] J. W. Wright, Prog. Sens. Sci. 1,31(1989).
[6] B. Bott and J. A. Jones. 1986. Sens. Actuators. 9. 19.
[7] A. K. Abass, A. Krier, and R. A. Collins. 1993. J. Phys. D26, 1120.
[8] C. Hamann, G. Kampfrath, and M. Muller. 1990. Sens. Actuators B 1, 142.
[9] A. K. Abass, R. A. Collins, and A. Krier. 1993. J. Phys. Chem. Solids 54, 373.
[10] F. R. Fanand and L. R. Faukner. 1978. J. Chem. Phys. 69, 3341.
[11] J. Whitlock and P. Punayotatos. 1991. Thin Solid Films. 205, 69.
[12] J. B. Whitlock, P. Punayotatos, G. D. Sharma, D. D. Cox, and G. R. Bird. 1993. Opt. Eng. (Bellingham) .32, 1921.
[13] J. Wagner, T. Fritz, and H. Bottcher. 1993. Phys. Solid A .136 .423.
[14] G. D. Sharma. 1995. Synth. Met. 74, 227.
[15] D. Wrobel, A. Boguta, and R. M. Ion. Int. 1983. J. Photoenergy .2. 229.
[16] M. Novotny, J. Bulir, A. Bensalah-Ledoux, S. Guy, P. Fitl, M. Vmata, J. Lancok, and B. Moine. 2014. Optical properties of zincphthalocyanine thin films prepared by pulsed laser deposition. Appl. Phys. A117(1), 377.
[17] Z. Bao, A.J. Lovinger and A. Dodabalapur. 1996. Appl. Phys. Lett. 69, 3066.
[18] L. Kazmarski and A. H. Clark. 1980. Polycrystalline and Amorphouse Thin Films and Device. Edited by Lawrence Academic Press. New York.

Fig(1): FTIR spectra for ZnPc and H$_2$PC.
Fig (2) The absorbance spectra for ZnPc with different thicknesses.

Fig (3) Absorption coefficient as a function of wavelength for ZnPc thin films with different thicknesses.
Fig(4): $(\alpha h \nu)^2$ versus photon energy for ZnPc thin films with different thicknesses.
Fig(5) X-ray diffraction of the ZnPc thin film with 150nm.

Fig(6) X-ray diffraction of the ZnPc thin film with 500nm.