Temperature effect on optical properties of nickel (ii) phthalocyanine tetrasulfonic acid tetrasodium salt (NiPcTs) organic thin films

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Abstract

This study describe the effect of temperature on the optical properties of nickel(ii) phthalocyanine tetrasulfonic acid tetrasodium salt (NiPcTs) organic thin films which are prepared by spin coating on indium tin oxide (ITO-glass). The optical absorption spectra of these thin films are measured. Present studies reveal that the optical band gap energies of NiPcTs thin films are dependent on the annealing temperatures. The optical band gap decreases with increase in annealing temperature, then increased when the temperature rising to 473K. To enhance the results of Uv-Vis measurements and get more accurate values of optical energy gaps; the Photoluminescence spectra of as-deposited and annealed NiPcTs thin films was studied. FTIR measurements for NiPcTs thin films also carried out in this work and gave good information about the NiPcTs bonds and its locations as a compared with H_2Pc as a reference.

Key words
Organic semiconductors, Phthalocyanines, Optical properties.

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تأثير درجة الحرارة على الخصائص البصرية لأغشية المركب العضوي (NiPcTs) الرقيقة

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الخلاصة

تصف هذه الدراسة تأثير درجة الحرارة على أغشية المركب العضوي (NiPcTs) المحضرة بطريقة الطلاء البرمي على قواعد زجاجية مطلية بطبقة من (ITO). تم قياس اطياف الامتصاصية لهذه الأغشية الرقيقة. توصلت الدراسة الحالية الى أن فجوة الطاقة البصرية لأغشية (NiPcTs) الرقيقة تعتمد على درجة حرارة التلدين. ان فجوة الطاقة البصرية تتناقص مع زيادة درجة حرارة التلدين ومن ثم تزداد عندما ترتفع درجة الحرارة الى 473K. لتعزيز نتائج قياسات UV-Vis والحصول على قيم أدق لفجوة الطاقة فان أطياف الاستضاءة لأغشية NiPcTs المرسبة في درجة حرارة الغرفة وكذلك الأغشية الملدنة تمت دراستها. ان قياسات FTIR لأغشية NiPcTs الرقيقة ايضا أجريت في هذا العمل وأعطت معلومات جيدة حول أواصر المركب NiPcTs وكذلك مواقعها بالمقارنة مع المركب H_2Pc كمرجع.

Introduction

Metal phthalocyanines (MPc) are molecular organic semiconductors [1] and have attracted extensive attention in numerous applications, such as organic solar cells [2], sensors [3, 4], field effect transistors [5], and optical data storage [6, 7]. This wide range of applications of phthalocyanine compounds are due to their unique optical and electronic properties [8] as well as their chemical and thermal stability [9]. Another reason that makes them so interested in many applications is the low cost and simple device preparation via solution processing [10], like roll-to-roll processing [11], ink-jet printing [12], or spin casting [13].

Simplicity of the film deposition technique, cost effectiveness, and less material consumption can be obtained from the wet processing method to deposition of organic thin films [8].For large scale device applications mainly in the form of micro electro machined devices (MEMs) or electronic nose as well as cost effective disposable sensors, it is necessary to manufacture the devices by simpler technique such as solution spinning, printing, micro-drop coating, etc. Phthalocyanines are usually difficult to dissolve in common solvent (de-ionized water, ethanol, methanol etc.). In order to assist the MPcs to dissolve in solvent and to enhance the mobility of the charge carrier in electronic devices, different functional groups have been introduced to the phthalocyanines. Water soluble phthalocyanine can also be synthesized from non-substituted phthalocyanines by attaching sulfonate groups [14]. Copper (II) phthalocyanine tetrasulfonic acid, tetrasodium salt (CuPcTs) is a typical example of water-soluble phthalocyanines. CuPcTs structure is very similar to CuPc except that polar SO_3Na attached to the corners of benzene rings and makes this compound water soluble[14].

Because of the expansion and contraction of the lattice with temperature, the various band parameters, particularly the energy gap is temperature dependent. Although calculations are available to predict and account for the T dependence of the band gap at the fundamental absorption edge, $E_g(T)$ is best found by empirical fits [15].

In this study, an organic compound Nickel (II) phthalocyanine tetrasulfonic acid tetrasodium salt (NiPcTs) is used to investigate its optical properties under the effect of temperature.

Experimental

Nickel (ii) phthalocyanine tetrasulfonic acid tetrasodium salt (NiPcTs) was purchased from Sigma-Aldrich and used without further purification. Its molecular formula is $C_{32}H_{12}N_8Na_4NiO_{12}S_4$ and has 979.4 g/mol molecular weight. Molecular structure of NiPcTs is shown in Fig. 1. To fabricate the Films, a 40 mg/ml NiPcTs was dissolved in deionized water and the result solution spin coated using Laurell WS-650Mz-23NPP Spin coater on pre-cleaned ITO-glass substrates. The thickness of the NiPcTs films which equal to 150nm were measured by KLA-TENCOR P-6 Surface Profiler. The resistivity of the deionized water was ~15 MΩ-cm. The ITO-glass substrates (25mm×25mm) were cleaned using acetone, isopropyl, and deionized water by ultra- sonic bath for ten minutes, subsequently.

To examine the UV-Vis optical properties of the as-deposited and heat treated NiTsPc thin films, a double beam JASCO V-570 UV-Vis-NIR spectrophotometer was used in the range (300–800)nm. Photoluminescence(PL) measurements recorded by Renishaw 2000 system operating at excitation wavelengths of 325nm for as-deposited and heat treated NiPcTs thin films. While Fourier-transformed Infra-red (FTIR) spectrum for as-deposited and annealed NiPcTs thin films were recorded the spectrum over the range of 400-4000 cm^{-1} with resolution 4, the spectra obtained at room temperature and recorded in the transmittance mode using Thermo Scientific™ Nicolet™ iS™10 FTIR Spectrometer. An X-ray diffraction type (SHIMADZU XRD-6000) was used to exam the structure of the as-deposited and heat treated NiPcTs films deposited on corning glass substrate, while the surface morphology of NiPcT tested by FESEM type JSM-7600F produce by JEOL Ltd. Japan.

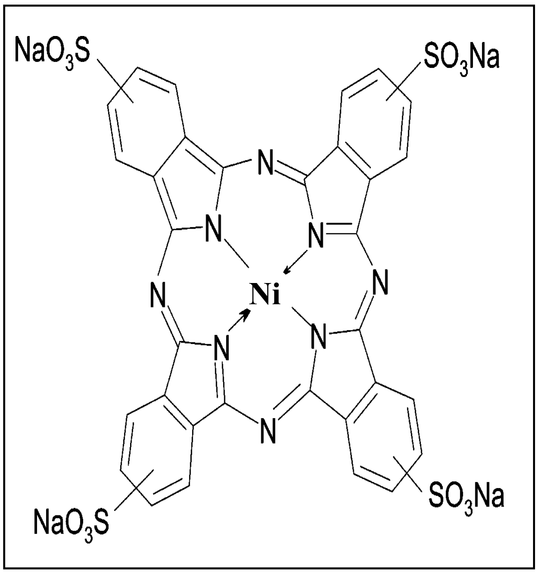

Fig. 1: Molecular structure of nickel (ii) phthalocyanine tetrasulfonic acid tetrasodium salt (NiTsPc z) [14].

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 the determination is very important for using it in any one of such devices. Optical absorbance (A) spectra were performed over the wavelength (λ) and the of these spectra were used to calculate the absorption coefficient (α) and band gap energy (E_g).

The relation between the intensity of incident light (I_o) and the transmitted intensity (I_T) is represented by an exponential form [16]:

$$I_T = I_o\exp(-\alpha t) \qquad (1)$$

where α being the absorption coefficient and t is the film thickness. According to this equation, the optical absorption coefficient of thin films was evaluated from the absorption data using the relation [16].

$$\alpha=2.303\ A/t \qquad (2)$$

As a result of absorption coefficient data, the nature of transition (direct or indirect) is determined according to Tauc relation [17] given by:

$$\alpha E=B(E-Eg)^r \qquad (3)$$

where B is a constant, r is a constant whose value depends on the type of transition, where r 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 [18]:

$$E\ (eV) = h\upsilon = 1.24/\lambda(\mu m) \qquad (4)$$

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. Extrapolation of the linear portion of the plot to the energy axis (αE=0) yielded the direct optical band gap energy value of deposited thin film.

Results and discussions

Absorption spectra of the as-deposited and annealed NiTsPc thin films are shown in Fig. 2. These absorption spectra exhibits two peaks which are B and Q bands. In the Q band, an intense absorption peak at around 615nm is due to the transition between the bonding and antibonding (π–π^*) at the dimer part of the phthalocyanine molecule. The central metal atom (Nickel) of the phthalocyanine molecule is associated with the d-band. Therefore, within the UV region of the spectrum, a strong absorption peak at around 340nm is attributed to partially occupied d–π^* transitions [19]. The variations in absorption with annealing temperature for B band are greater than the variations in Q band.

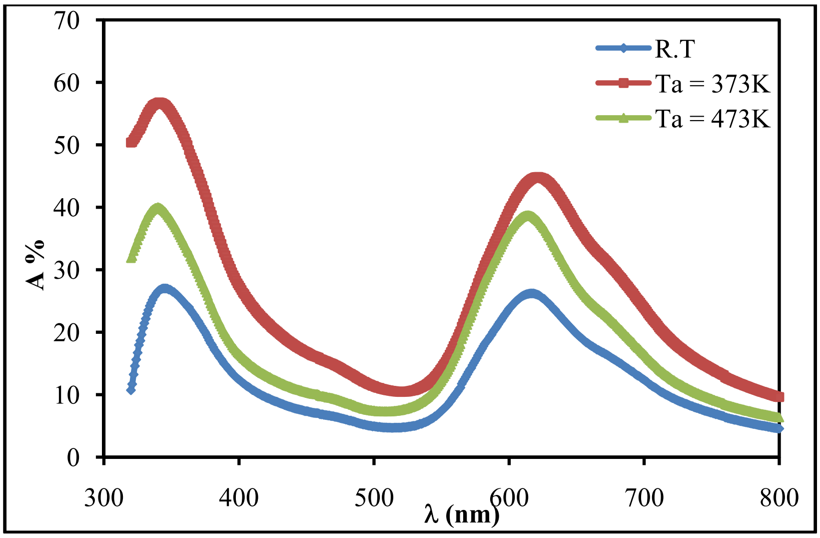

Fig. 2: Absorption spectrum of as-deposited and annealed NiPcTs thin films.

From Fig. 2, one can see that the light absorption is increased as the annealing temperature increases, however it drops at 473K.

The morphology of the film can be modified by thermal treatment which leading to the improvement in the absorption properties. Some researchers utilized similar research work to enhance the absorption capability of the thin films [20, 21]. The absorption features of this spin-coated phthalocyanine derivative film are similar to the reported thermally evaporated phthalocyanine films [20, 22]. The result indicates that the simple spin coating method can be utilized to obtain similar light absorption properties of a soluble phthalocyanine, as provided by the complicated thermal evaporation technique.

Fig. 3 shows the dependence of the absorption coefficient (α) on annealing temperatures as a function of wavelength for NiPcTs films. This absorption coefficient was determined from the region of high absorption i.e. at the fundamental absorption edge of the films.

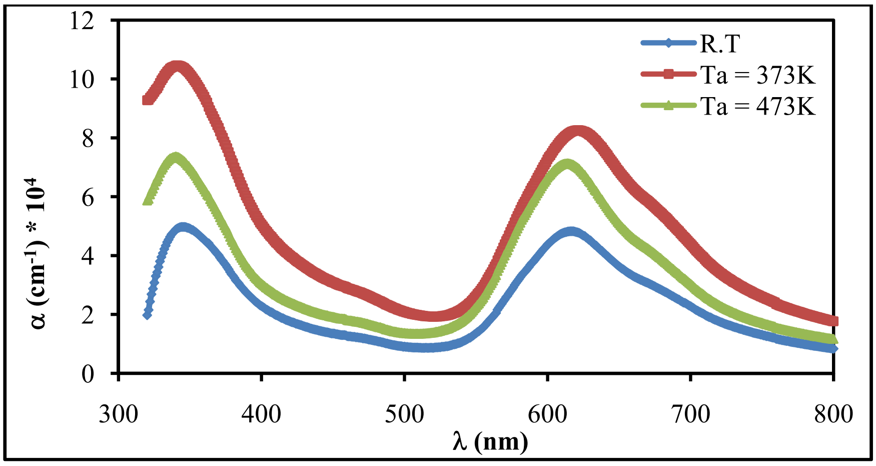

Fig. 3: Absorption Coefficient of as-deposited and annealed NiPcTs thin films.

Two absorption edges in the absorption spectra suggest the existence of two different energy gaps for the NiTsPc film.

The optical energy gap values (E_g^{opt}) for NiPcTs films have been determined by using Tauc Eq. (3) which is used to find the type of the optical transition by plotting the relations $(\alpha h\nu)^2$, $(\alpha h\nu)^{2/3}$, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ versus photon energy (hν) and select the optimum linear part. It is found that the first relation yields linear dependence, which describes the allowed direct transition. E_g^{opt} is then determined by the extrapolation of the portion at (α=0) as shown in Figs. 4 and 5.

The optical energy gap for B-band decreased from 1.7eV to 1.68eV when the film annealed at 373K whereas, its values increased to 1.72eV with increasing annealing temperature to Ta=473K. The same behavior observed in Q-band, the optical energy gap decreased from 3.08eV to 3.04eV when the temperature increases from room temperature to 373K, while the optical energy gap return to increase to 3.12eV after increasing the temperature to 473K.

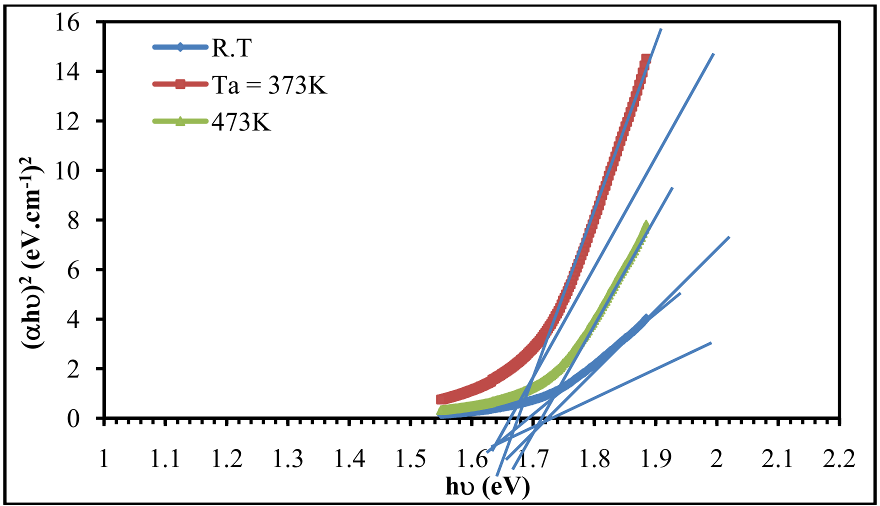

Fig. 4: $(\alpha h\nu)^2$ versus photon energy of incident radiation for as-deposited and annealed NiPcTs thin films (Q-band).

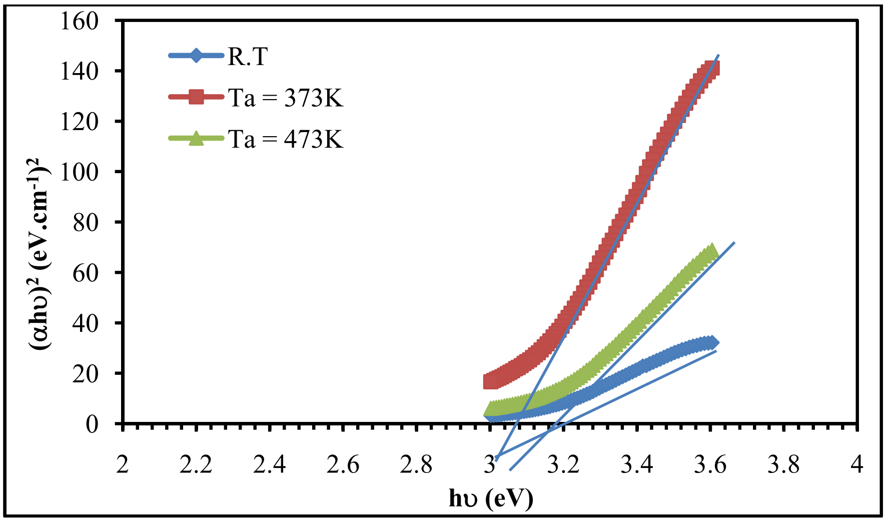

Fig. 5: $(\alpha h\nu)^2$ versus photon energy of incident radiation for as-deposited and annealed NiPcTs thin films (B-band).

The optical energy gap was found to decrease after heat treatment at 373K, this decreasing is attributed to existence of a localized states inside the gap due to amorphous structure of NiPcTs at this temperature. The observed localized states due to change the structure to amorphous because of annealing (see Fig. 6), which is a characteristic of most of the optical data on amorphous semiconductors which is considered to be determined mainly to the structural disorder existing at the grain boundaries, but after the second annealing temperature at Ta=473K the energy gap increased due to structure change to nanofiber as shown in Fig. 7.

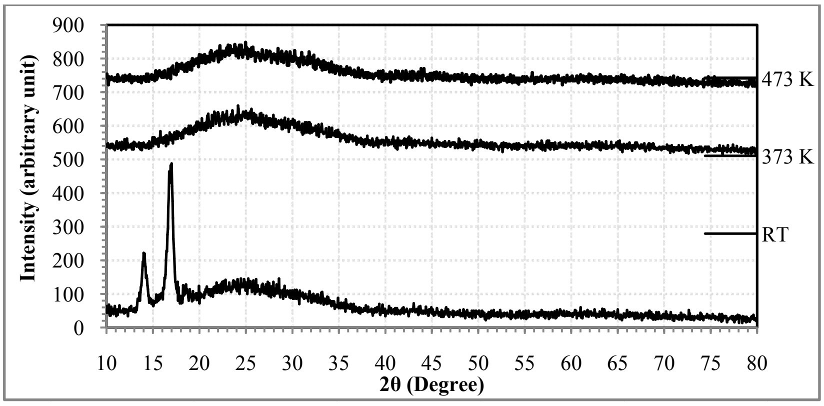

Fig. 6: XRD pattern of as-deposited and annealed NiPcTs Thin Films.

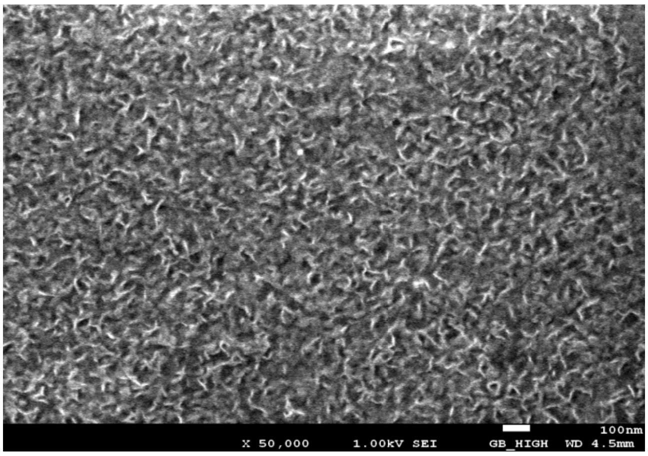

Fig. 7: FESEM pictures ×50 magnification for annealed NiPcTs film at 473K.

Photoluminescence spectrum or emission spectrum has great importance since it gives information about the optical energy band gap, excitons and traps energy levels. The energy gap value that has been obtained from photoluminescence spectrum is more accurate than that calculated by Tauce equation. The behaviour of variation of optical energy gap obtained from photoluminescence spectrum is similar to the behavior of optical energy gap obtained from UV-VIS spectrum, i.e. the energy gap also decreases when the film of NiPcTs annealed to 373K and when the annealing temperature increase to 473K, the energy gap go to increase. The values of optical energy gap using photoluminescence spectrum are 2.92, 2.9 and 2.94 respectively as shown in Fig. 8, these values represent the B-band because the excitation wave length of laser used in this photoluminescence spectrum was 325nm that is mean it have energy of 3.8eV which is higher than the B-band energy gap of NiPcTs.

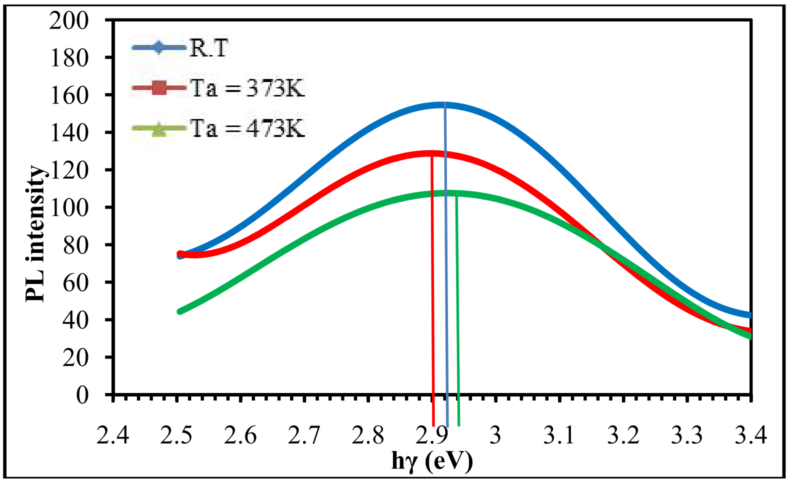

Fig. 8: Photoluminescence spectra of as-deposited and annealed NiPcTs thin films.

Fig. 9 shows the FT-IR spectrum for as-deposited and annealed NiPcTc thin films which was measured at room temperature and compared with H_2Pc spectrum. FT-IR for NiPcTc thin films shows the bond bending represented by the range (400-2000) cm^{-1} while the bond stretching represented by the range (2000-4000) cm^{-1}. One can see a weak peak in the range (600-400) cm^{-1} which indicate the presence of (metal-Nitrogen) bond vibration at (508-578) cm^{-1} have been assigned for (Nickel – Nitrogen). The band at (1334-1320) cm^{-1} is for bond of C-N and the peak (1612) cm^{-1} indicates C=C bond and the peak at (1533) cm^{-1} indicates Benzene ring band, also the spectrum shows the absent of stretching band N-H which is appears in H_2Pc spectrum.

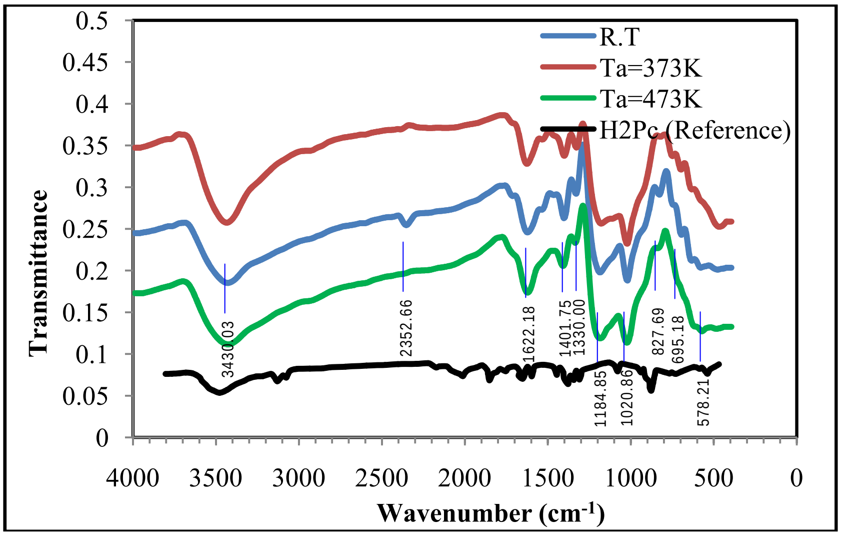

Fig. 9: FTIR spectra for as-deposited and annealed NiPcTc Thin Films.

Conclusions

The NiTsPc thin films deposited successfully using a spin-coating technique and modified the optical properties of the films by heat treatment. The *B* and *Q* indicate the presence of two energy gaps, which have been obtained by manipulating the Tauc relationship. In addition, the absorption intensity at both regions has also been varies with the treatment temperature.

The behaviour of variation of optical energy gap obtained from photoluminescence spectrum is more accurate than the optical energy gap obtained from UV-VIS spectrum, but both have similar behavior under the effect of heat treatment.

References

[1] P. Turek, P. Petit, J.J. Andre, J. Simon, R. Even, B. Boudjema, G. Guillaud, M. Maitrot, Journal of the American Chemical Society, 109, 17 (1987) 5119-5122.

[2] N. Beaumont, I. Hancox, P. Sullivan, R.A. Hatton, T.S. Jones, Energy and Environmental Science, 4, 5 (2011) 1708-1711.

[3] Y. Jian-Fei, W. Zhi-Ming, T. Hui-Ling, L. Xian, W. Yao, S. Yuan-Jie, P. Cong. The investigation of the formaldehyde gas sensor based on organic thin-film-transistors. in 2010 International Conference on Apperceiving Computing and Intelligence Analysis (ICACIA 2010). 2010. Chengdu, China: IEEE.

[4] R.L. Van Ewyk, A.V. Chadwick, J.D. Wright, Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 77, 1 (1981) 73-79.

[5] Madru, M., G. Guillaud, M.A. Sadoun, M. Maitrot, C. Clarisse, M.L. Contellec, J.J. André, J. Simon, Chemical Physics Letters,. 142, 1-2 (1987) 103-105.

[6] C. Schunemann, C. Elschner, A.A. Levin, M. Levichkova, K. Leo, M. Riede, Thin Solid Films, 519, 11 (2011) 3939-3945.

[7] Gu, D., Q. Chen, J. Shu, X. Tang, F. Gan, S. Shen, K. Liu, H. Xu, Thin Solid Films, 257, 1 (1995) 88-93.

[8] K.M. Kadish, K.M. Smith, R. Guilard, The Porphyrin Handbook: Applications of phthalocyanines. 2003: Academic Press.

[9] C.E. Dent, R.P. Linstead, Journal of the Chemical Society, (1934) 1027-1031.

[10] D. Wöhrle, D. Meissner, Advanced Materials,. 3, 3 (1991) 129-138.

[11] T.L. Benanti, D. Venkataraman, Photosynthesis Research, 87 (2006) 73-81.

[12] S.R. Forrest, Nature, 428, 6986 (2004) 911-918.

[13] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, Nature Materials, 4 (2005) 864-868.

[14] A.C. Tedesco, J.C.G. Rotta, C.N. Lunardi, Curr. Org. Chem. 7 (2003) 187.

[15] M. S. Dresselhaus, "Solid State Physics Part II Optical Properties of Solids", MIT Solid State Physics course, 2001.

[16] R. Elliot, A.I.Gibson "An Introduction to Solid State Physics and Application", 1st edition, Macillian Inc. (1974).

[17] T. Moss, "Optical Properties of Semiconductors", London Butter Worthes Scientific Puplications (1959).

[18] J. Millman "Microelectronics" Murray – Hill, Book Company Kogakusha, (1979).

[19] M. El-Nahass, K. Abd-El-Rahman, A. Farag, A. Darwish, International Journal of Modern Physics B, 18, 3 (2004) 421-434.

[20] S. Karan, B. Mallik, Solid State Communications, 143, 6–7 (2007) 289-294.

[21] B. E. Schuster, T. V. Basova, V. A. Plyashkevich, H. Peisert, T. Chassé, Thin Solid Films, 518, 23 (2010) 7161-7166.

[22] G. Park, I. Heo, I. Ryu, S. Yim, Bull. Korean Chem. Soc, 32, 3 (2011) 943.