Effect of substrate types on the structural and optical properties of nickel (II) tetrasulfonated phthalocyanine thin films

تأثيرنوع مادة الأساس في الخواص التركيبية و البصرية لأغشية الثالوسيانين- نيكل الرقيقة

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Abstract

Chemical spray pyrolysis (CSP) technique has been employed to deposit tetrasulfonated nickel phthalocyanine (NiTsPc) thin films on different substrate types. Since substrate type is one of the important parameters in CSP, NiTsPc thin films were deposited on different substrate types in order to investigate their structural and optical properties by using different techniques. The structural properties were investigated by X-ray diffraction (XRD) and atomic force microscope (AFM), the optical properties were investigated by ultraviolet visible (UV-Vis) spectrophotometer and fluorescence spectrophotometer. From XRD results, it was shown that the highest crystallinity of the thin films was when using polymer as substrate. The observed topographical images from showed that the roughest surface was when using micro glass as substrate. The absorption spectra recorded in the wavelength range 190-1100 nm revealed two absorption bands, namely, the Soret and the Q-band and that the highest absorption intensity was when using glass as substrate. In addition, UV-Vis spectra showed that thin films deposited on different substrate types have direct energy gap. The energy gap for the NiTsPc thin films were calculated from Tauc equation and compared with results obtained from fluorescence measurements. The highest energy gap was observed for NiTsPc thin films deposited on glass substrates with . It was observed that preparation conditions affect the properties of the thin films and that the different substrates have high impact on the structural and optical properties of the deposited NiTsPc thin films. The crystallinity, grain size, roughness and the optical constants were strongly affected by the different substrates.

الخلاصة

تم إستعمال تقنية الرش الكيميائي الحراري لترسيب أغشية رقيقة من مادة الثالوسيانين – نيكل. و نظراً لكون نوع مادة الأساس هي عامل مهم في تقنية الرش الكيميائي الحراري، فقد رسبت أغشية الثالوسيانين – نيكل الرقيقة على أنواع مختلفة من طبقات الأساس لدراسة الخواص التركيبية و البصرية لهذه الأغشية باستعمال تقنيات مختلفة. و قد درست الخواص التركيبية باستعمال تقنية حيود الأشعة السينية و مجهر القوى الذرية، أما الخواص البصرية فقد درست باستعمال مطياف الأشعة المرئية و فوق البنفسجية بالإضافة إلى تقنية مطياف الفلورة. و قد تبين من أطياف حيود الأشعة السينية إن أفضل تبلور هو عندما إستعملت مادة البوليمر كمادة أساس. و أظهرت صور مجهر القوى الذرية إن أخشن السطوح المحضرة هي عند إستعمال الزجاج كطبقة أساس. و قد أظهرت أطياف الإمتصاص المسجلة في مدى الأطوال الموجية (190 - 1100) نانومتر وجود حزمتي إمتصاص و المسميتان بحزمة (Soret) و حزمة (Q)، و إن أعلى شدة إمتصاص تحصل عند إستعمال الزجاج كطبقة أساس. بالإضافة إلى ذلك فقد أظهرت أطياف الأشعة المرئية و فوق البنفسجية إن الأغشية المرسبة على مختلف أنواع طبقات الأساس كانت ذات فجوة طاقة مباشرة. و قد حسبت قيم فجوة الطاقة للأغشية المحضرة من معادلة تاوس و قورنت هذه القيم مع القيم المستحصلة من قياسات الفلورة. و وجد إن أعلى قيمة لفجوة الطاقة هي للأغشية المرسبة على الزجاج. و قد لوحظ إن ظروف التحضير تؤثر في خواص الاغشية المحضرة و إن طبقات الأساس المختلفة لها تأثير كبير في الخواص التركيبية و البصرية لأغشية الثالوسيانين – نيكل الرقيقة. إن التبلور و الحجم الحبيبي و الخشونة و الثوابت البصرية قد تأثرت بشكل واضح مع تغير نوع مادة الأساس.

1. 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 planarity, symmetry and electron delocalization [1]. Unlike porphyrins, Pcs do not occur in the nature and are not involved in the biochemical processes; they are completely synthetic organic compounds. They are exhibiting semiconducting properties and hence come under the class of organic semiconductors which are generally p-types characterized by low mobility, low carrier concentration and high extinction coefficient of approximately $10^5 \ M^{-1} cm^{-1}$ [2]. Studies have shown that the extinction coefficient changes by up to 1 order of magnitude depending on the central metal atom, whereas solvent effects cause only smaller variations in different types of solvents [3]. Metal phthalocyanines are interesting macromolecules because of their high coloring property, chemical inertness, very high thermal stability, electrical conductivity, photoconductivity and catalytic activity. They have potential applications in many areas such as in printing inks, catalysis, display devices, data storage, chemical sensors, solar cells, photodynamic cancer therapy, organic light emitting devices and photonic devices [4-8]. Due to their strong and long wavelength absorption, 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 [9].

2. Experimental part

The organic material, NiTsPc was purchased from Sigma Aldrich and was used without further purification. The compound was dissolved in purified water to achieve a solution with a concentration of 10^{-4} M. Chemical spray pyrolysis was used to deposit NiTsPc thin film on different substrate types. The substrate types were flexible transparent foil (polymer), glass, quartz, silicon and micro glass. Substrate temperature (T_s) was kept at 140°C, pressure (P) at 2 bar, spray-time (S_1) at 1 s, standby-time (S_2) at 3 s and nozzle to substrate distance at 30 cm. A vessel of 40 ml NiTsPc solution was used for each deposition. The solution was thoroughly mixed using a magnetic hot plate stirrer model L-81 (Labinco, Netherlands). The substrates were cleaned using distilled water and pure alcohol.

Substrate temperature was controlled using temperature controller TE4-RB10 (Saithong Electric Co, Thailand) with temperature accuracy of ± 0.5 percentage of full scale (% FS). The duration of spray time was controlled using a digital display time relay model DH48S-S (Any Electronics Co, China) with an accuracy of ± 0.05 s. Nitrogen gas was used as carrier gas to prevent moisture in the system and deposition process. An air blast atomizer with a gas output diameter of 0.8 mm was used to generate aerosol from precursor solution.

The structures of the NiTsPc powder and deposited thin films have been characterized by using X-ray diffractometer model XRD 6000 (Shimadzu, Japan) which records the intensity as a function of Bragg angle. The radiation source was $Cu(K_\alpha)$ with wavelength of 1.5406 Å, the current was 30 mA and voltage was 40 kV. The data were collected in the 2θ range from 2 to 80 degree, scanning speed at 2 (deg/min) with 0.02 deg step and 0.15 mm slit width.

Surface morphological measurements were carried out using AA3000 Scanning Probe Microscope (Angstrom Advanced, USA) in AFM mode. The contact mode was used with a lateral resolution of 0.26 nm and a vertical resolution of 0.1 nm. The roughness, diameter of grains and topographical images were obtained for each sample.

The absorbance spectra for deposited thin films were measured using double beam UV-Vis spectrophotometer model UV-1800 series (Shimadzu, Japan) in the wavelength range from 190 nm to 1100 nm. A sampling interval of 1 nm was used during the measurements. Fluorescence measurements were obtained using FluoroMate FS-2 (Scinco, Korea). The emission spectrum was recorded in the wavelength range from 340 nm to 600 nm with excitation wavelength of 317 nm and the incident radiation was at 90° angle.

3. Results and discussion
3.1 XRD measurements

Phthalocyanines exist in at least two polymorphic crystal phases, which are designated as α and β phases. The metastable α-phase is obtained either as polycrystalline powder or as thin film deposited at room temperature, while the more stable β-phase can be obtained by increasing the temperature [10]. From diffraction peaks the average crystal size can be calculated using Scherrer equation [11].

$$D = \frac{k\lambda}{(FWHM)cos\theta} \qquad (1)$$

where D is the average crystal size, k is a constant and relates to dimensionless shape factor, ($FWHM$) is the line broadening at the half of the maximum intensity and θ is the Bragg angle corresponding to the peak considered. The shape factor has a typical value of about 0.9, but it varies with the actual shape of the crystallite. The relation of substrate types and average crystal size is shown in Table 1. From Figure 1 the effect of substrate type on the structural properties of deposited NiTsPc thin films is shown. It is clearly observed that the substrates have high impact on the crystallinity. The highest intensity is when using the polymer as substrate (see Figure 1a), indicating that thin films deposited on this substrate have a minimum potential energy of the nuclei on the surface of the substrate which leads to enhanced crystallite size [12]. The XRD pattern in Figure 1b shows a broad band or which corresponds to silica that is part of the glass slide. The broad peak at 2θ range from 17-27 deg. in Figure 1c is related to Quartz-SiO_2. The peak is centered at 2θ equal 22 deg. and similar results were obtained by Tzounis *et al.* [13] and Musić *et al.* [14] with a slight difference in peak position. In Figure 1d silicon was used as substrate and from the XRD pattern a single crystalline structure is shown. The peak centered at 30.9 deg. is related to NiTsPc thin film and the peaks centered at 29.5 deg. and 48.5 deg. are related to Si(111) and Si(220), respectively [15]. The intensity of NiTsPc thin film deposited on silicon substrate gives the lowest intensity value. The sharpest peak with lowest FWHM and highest average crystal size is obtained when using micro glass as a substrate.

Table 1: Variation of FWHM and average crystal size of thin films deposited on different substrate types.

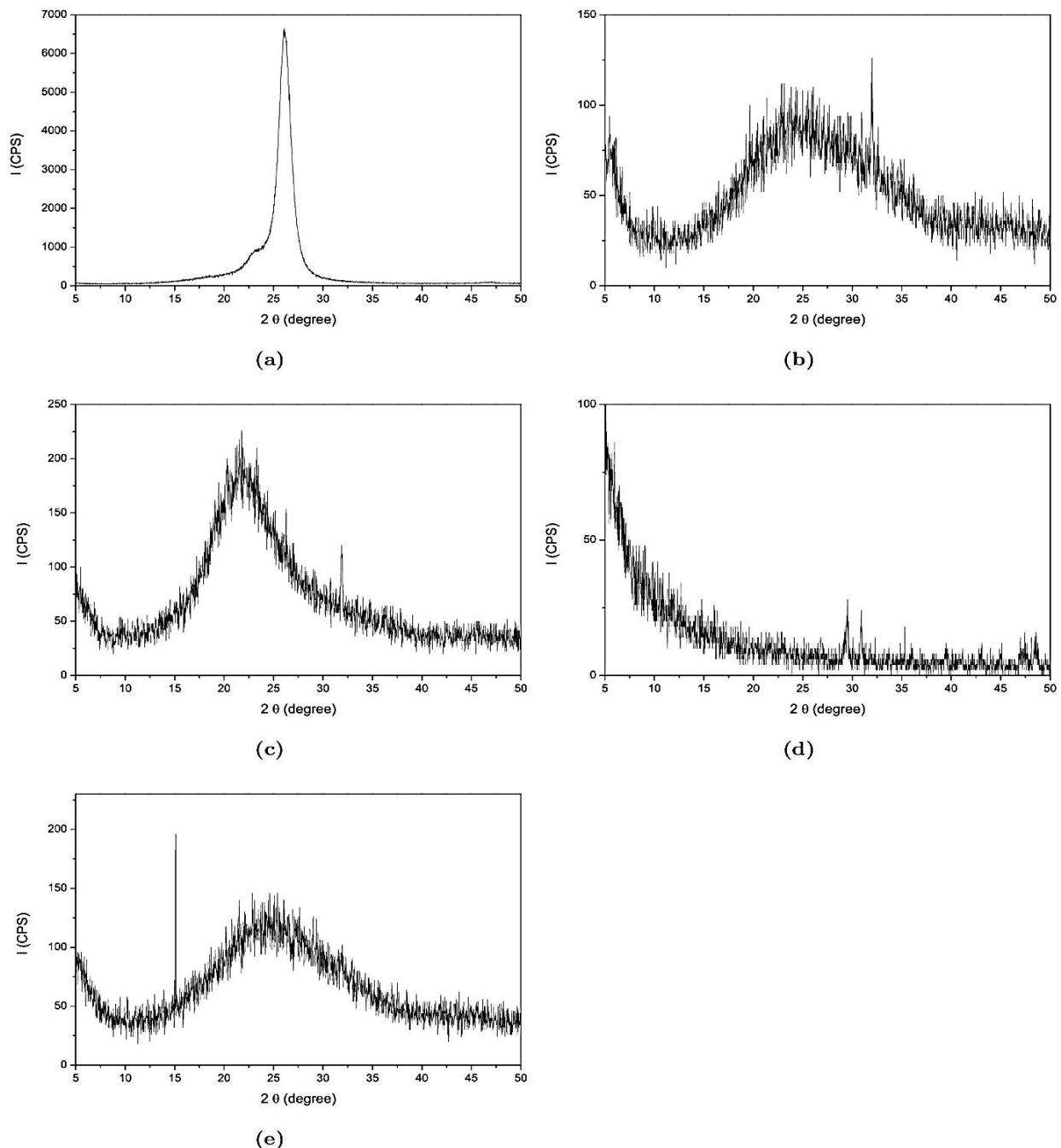| Substrate type	2θ (degree)	FWHM (degree)	D (nm)
Polymer	26.15	0.2388	40.8
Glass	31.98	0.1747	55.8
Quartz	31.89	0.0481	203
Silicon	30.92	0.1568	61.6
Micro glass	15.1	0.026	330.5

Figure 1. XRD patterns obtained for the deposited thin films on (a) Polymer (b) Glass (c) Quartz (d) Silicon and (e) Micro glass.

3.2 AFM measurements

The effect of substrate types on the surface morphology is shown in Table 2 and Figure 2. As noticed from the table, different substrates affect the surface roughness and grain size. The quartz substrate has higher adhesion of the NiTsPc molecules then polymer, which results in smoother surface with smaller grain size. When the adhesion of the NiTsPc molecules on the substrate becomes smaller, the aggregation rate increases and as a results rougher thin films with bigger grain size are fabricated. Using glass or silicon as substrate results in small variation in both roughness and grain size. Using micro glass as substrate results in roughest surface with highest grain size which can be explained by the fact that the improvement of crystallinity due to the coalescence of small grains to form large ones increases grain boundaries and then increases the roughness. The NiTsPc thin films deposited by CSP technique are smoother than those deposited by laser deposition technique [16] and layer-by-layer technique [17].

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Table 2: Surface morphology of NiTsPc thin films deposited on different substrate types.

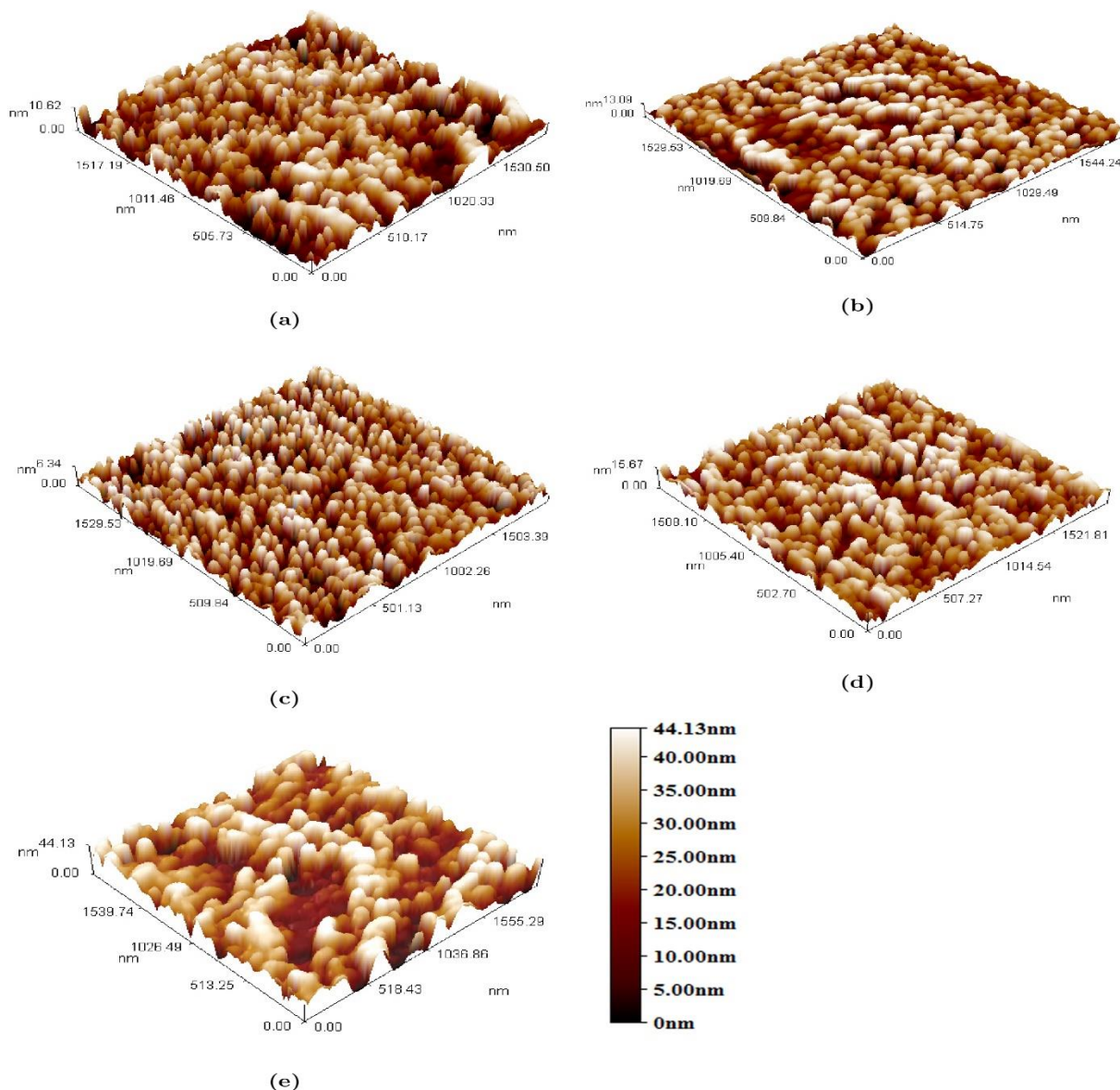| Substrate type	Roughness average (nm)	RMS (nm)	Grain size (nm)
Polymer	2.61	3.01	70.74
Glass	3.05	3.55	79.72
Quartz	1.62	1.86	70
Silicon	3.46	4.06	77.33
Micro glass	9.42	11.1	125.6

Figure 2. AFM topographical image of deposited thin films on (a) Polymer (b) Glass (c) Quartz (d) Silicon and (e) Micro glass

3.3 UV-visible measurements

The UV-Vis spectrum observed for metal phthalocyanines (MPcs) originates from the molecular orbitals within the aromatic 18-π electron system overlapping on central metallic ions [18]. The optical absorption spectrum is one of the most important properties, and is especially important in solar cells fabrication. From absorption spectrum in Figure 3 two different bands, Soret and Q-band, are observed due to the direct electronic transitions between orbitals in the UV-Vis

regions. The Q-band (540-700 nm) is the result of $\pi-\pi^*$ transition from allowed highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of the phthalocyanine rings. The peak at 601 nm corresponds to the $\pi - \pi^*$ transition of dimers and higher order of phthalocyanine molecular aggregation, where the shoulder peak with low absorption intensity at 670 nm arises due to monomer part for the second $\pi - \pi^*$ transition [19]. These transitions are responsible for the indigo color of the solution [20]. In Figure 4, the intensity of the absorbance spectra of NiTsPc thin films deposited on different substrate types are visualized. Using glass as substrate type results in highest intensity in the absorption spectrum. When polymer is used as substrate, Soret and Q-band peaks become broader. This may be due to rare J-type aggregation and a slight lowering in symmetry. The absorbance spectra of NiTsPc thin films deposited on quartz or micro glass are almost identical, except a slight difference in the absorption intensity. The absorption spectrum of NiTsPc thin films are similar to those observed in literature [21, 22].
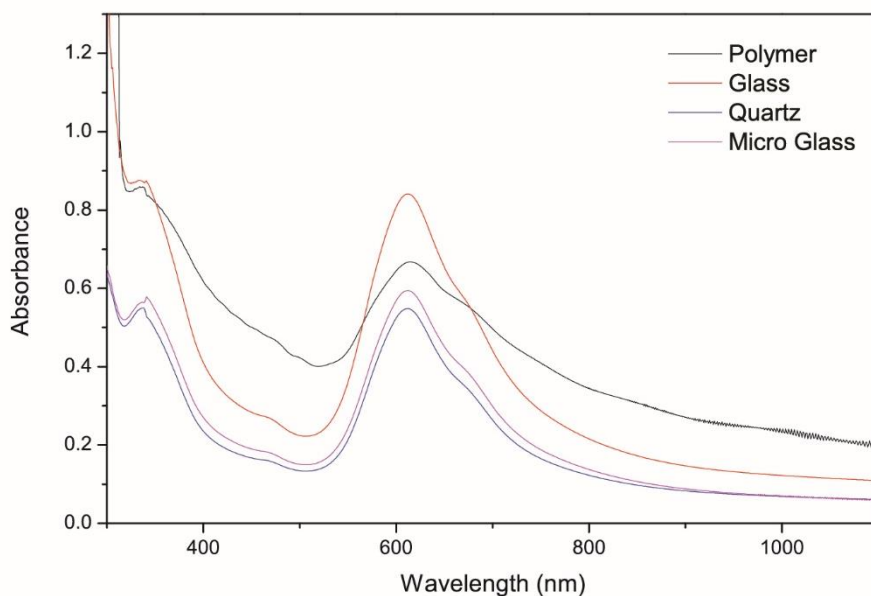

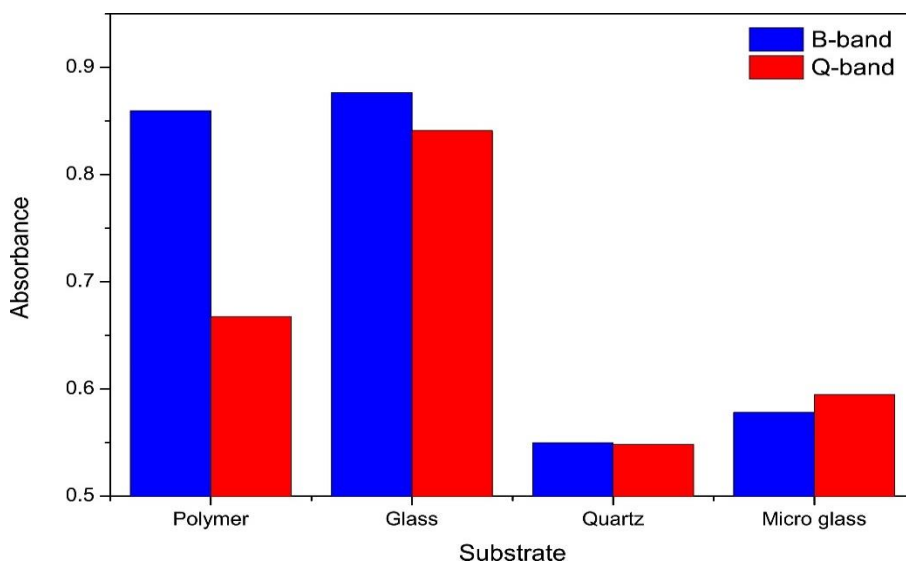Figure 3. Optical absorption spectra of NiTsPc thin films deposited on different substrate types.

Figure 4. Absorption intensity for Soret and Q-band of NiTsPc thin films deposited on different substrate types.

The dependence of the absorption coefficient (α) on the wavelength for thin films deposited on different substrate types is shown in Figure 5. The absorption coefficient was calculated using the equation [23]:

$$\alpha = \frac{2.303A}{t} \qquad (2)$$

where A is the absorbance and t is the thin film thickness.

High absorption intensity in Soret and Q-band characterizes the absorption coefficient. From the extinction coefficient values it can be concluded that the thin films deposited on different substrate types are direct transition types. It can be seen that deposition of NiTsPc thin films on glass substrate gives highest absorption coefficient value. The lowest absorption coefficient is when using quartz as substrate. The high absorption coefficient in Q-band is due to traps inside energy gap. Fakir (2013) obtained similar results from NiTsPc thin films deposited by spin-coating technique [24].
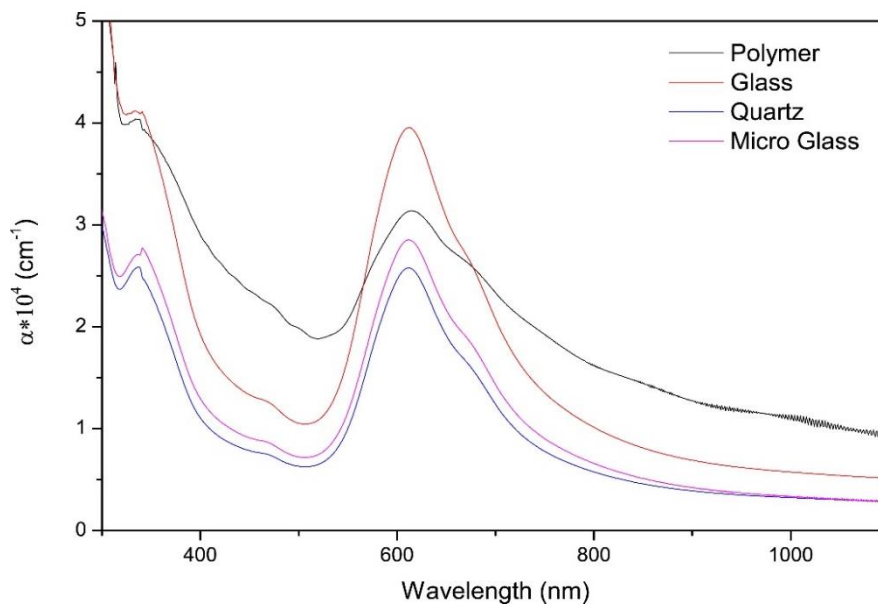

Figure 5. Absorption coefficient as a function of wavelength for NiTsPc thin films deposited on different substrate types.

The optical energy gap values E_g for NiTsPc thin films have been determined by using Tauc equation which is used to determine the optical transition type by plotting the relations of $(h\upsilon)^{1/2}$, $(h\upsilon)^{3/2}$, $(h\upsilon)^2$ and $(h\upsilon)^3$ versus photon energy $(h\upsilon)$ and selecting the optimum linear part [25].

$$\alpha h\upsilon = B\left(h\upsilon - E_g\right)^{r} \qquad (3)$$

Where h is Planck's constant, υ is the frequency, B is a constant and depends on the type of material, r depends on the type of transition and E_g is the optical energy gap. Because of the exponential behavior of the tail of the graph shows the presence of localized states, the exponential value r=1/2 will be used in order to obtain a linear dependence. This indicates that NiTsPc has an allowed direct transition [22].

The extrapolation i.e. E_g, of the portion at $(\alpha h\upsilon)^2 = 0$ is shown in Figure6 for NiTsPc thin films deposited on different substrate types. Ahmad *et al.* (2012) obtained similar results from NiTsPc thin films deposited on glass substrate using spin coating technique [22].
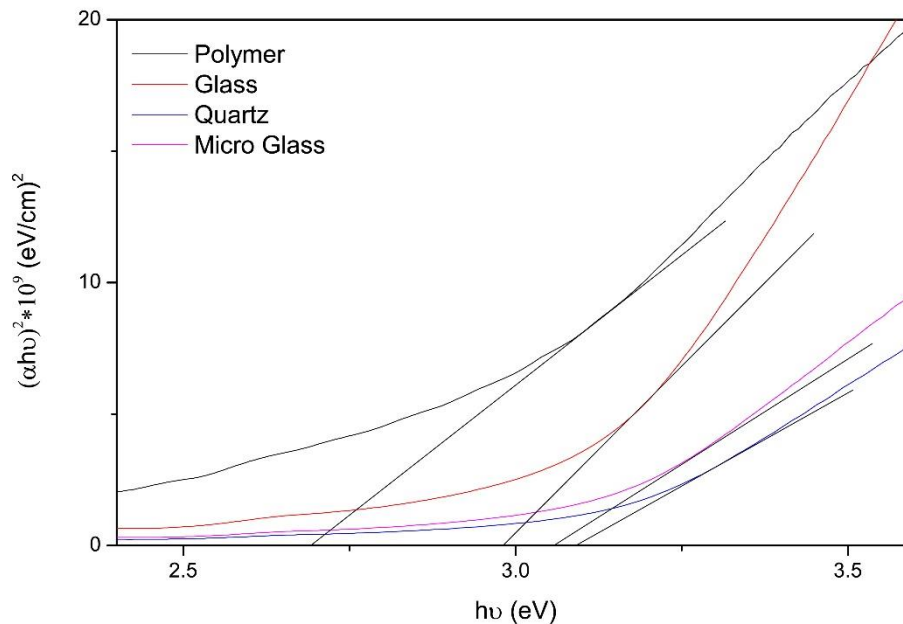
Figure 6. $(\alpha h\upsilon)^2$ as a function of photon energy for NiTsPc thin films deposited on different substrate types.

3.4 Fluorescence measurements

Figure 7 shows the emission spectra of NiTsPc thin films deposited at different substrate temperatures. The fluorescence is used to determine the optical energy gap and compare it with results obtained from Tauc equation. The results obtained from fluorescence emission are more accurate than those obtained from Tauc relation. Table 3 shows the optical band gap determined by fluorescence and Tauc method and compares the results with the error ratio. It is noted that different substrate types influence the optical energy gap.

Table 3: Optical energy gap determined by fluorescence emission and by Tauc relation for NiTsPc thin films deposited on different substrate types.

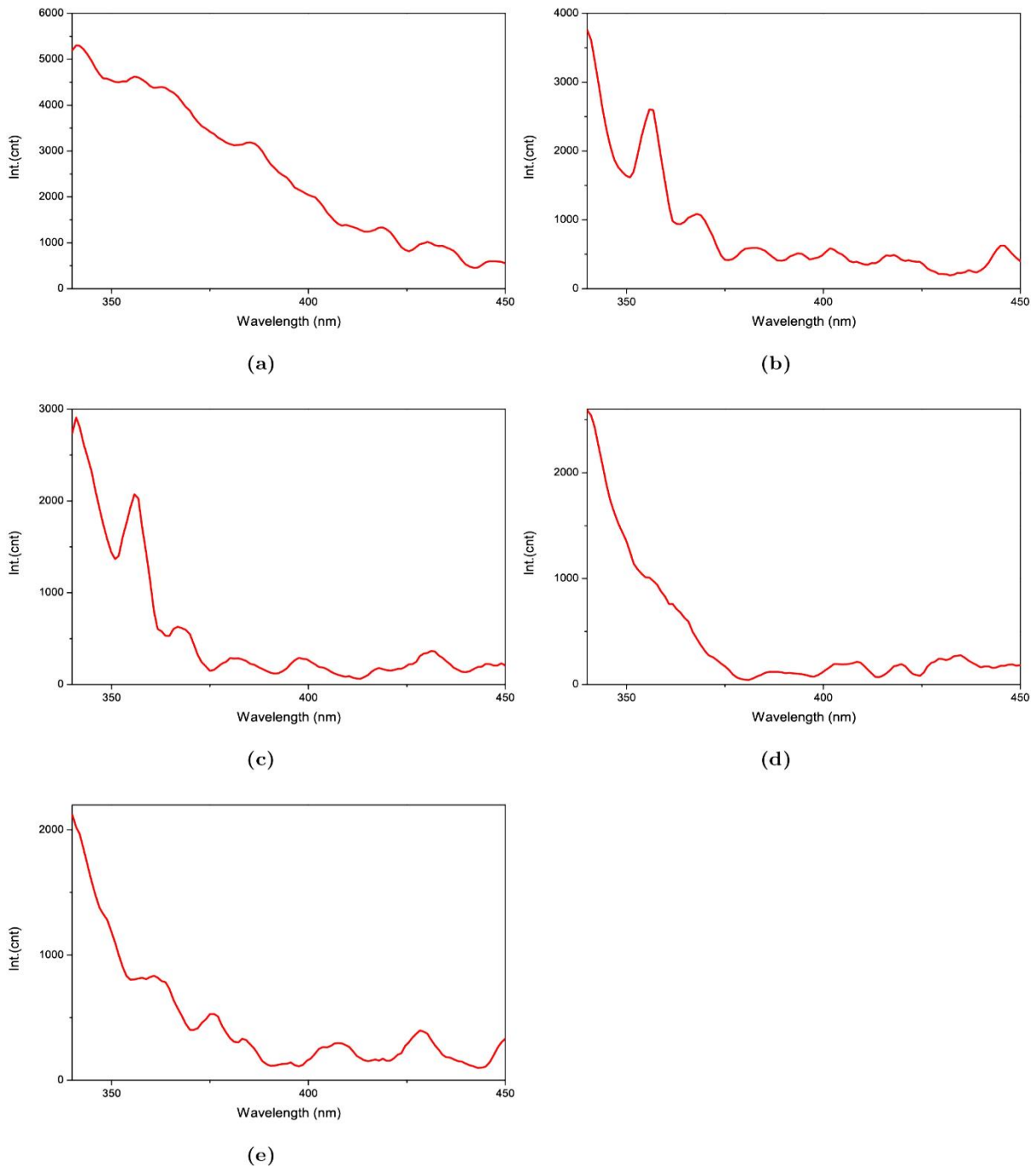| Substrate type	E_g (FL) (eV)	E_g Tauc) (eV)	Error ratio %
Polymer	3.4753	2.6936	23
Glass	3.6364	2.9827	18
Quartz	3.4851	3.0937	11
Silicon	3.4651	—	—
Micro glass	3.4368	3.0574	11

Figure 7. Fluorescence results obtained for the deposited thin films on (a) Polymer (b) Glass (c) Quartz (d) Silicon and (e) Micro glass.

4. Conclusion

Nickel (II) tetrasulfonated phthalocyanine thin films were deposited by chemical spray pyrolysis system. The structural and optical studies of NiTsPc thin films deposited on different substrate types were investigated and from the obtained results it was observed that the different substrate types had high impact on the optical and structural properties of the thin films. The NiTsPc thin films deposited on micro glass had the highest roughness value which makes it compatible for high efficiency devices. From the recorded absorption spectra, two bands named Soret and Q-band were shown. The absorption intensity changed with different substrate types. From the plot obtained from Tauc relation, the fundamental energy gap was between 2.6936 eV and 3.0937 eV depending on the different substrate types.

References

1. Rodriguez-Morgade, M.S., G. De La Torre, and T. Torres, Design and Synthesis of 99 Low-Symmetry Phthalocyanines and Related Systems. The porphyrin handbook, 2003. 11: p. 125.
2. Kadish, K.M., K.M. Smith, and R. Guilard, The Porphyrin Handbook: Inorganic, organometallic and coordination chemistry. Vol. 3. 2000: Elsevier.
3. Ghani,F.,J.Kristen, and H. Riegler,Solubility properties of unsubstituted metal phthalocyanines in different types of solvents.Journal of Chemical & Engineering Data, 2012. 57(2): p. 439-449.
4. El-Bosaty, A., et al., Surface plasmon-cobalt phthalocyanine sensor for NO2 gas. Egypt.J. Solids, 2006. 29(1): p. 121-129.
5. Shah, M., K.S. Karimov, and M. Sayyad, Organic semiconductor nickel phthalocyanine-based photocapacitive and photoresistive detector. Semiconductor Science and Technology, 2010. 25(7): p. 075014.
6. Li, L., et al., Organic thin-film transistors of phthalocyanines. Pure and applied chemistry, 2008. 80(11): p. 2231-2240.
7. Do Kim, Y., et al., The synthesis and application of thermally stable dyes for ink-jet printed LCD color filters. Dyes and pigments, 2009. 81(1): p. 45-52.
8. Carpi, F. and D. De Rossi, Colours from electroactive polymers: Electrochromic, electroluminescent and laser devices based on organic materials. Optics & Laser Technology, 2006. 38(4): p. 292-305.
9. Camp, P.J., et al., Aggregation of copper (II) tetrasulfonated phthalocyanine in aqueous salt solutions. The Journal of Physical Chemistry A, 2002. 106(44): p. 10725-10732.
10. Lever, A.P., The phthalocyanines. Advances in Inorganic Chemistry and Radiochemistry, 1965. 7: p. 27-114.
11. Langford, J.I. and A. Wilson, Scherrer after sixty years: a survey and some new results in the determination of crystallite size. Journal of Applied Crystallography, 1978. 11(2): p. 102-113.
12. Reddy, N.K., et al., Synthesis and characterisation of co-evaporated tin sulphide thin films. Applied Physics A, 2006. 83(1): p. 133-138.
13. Tzounis, L., et al., Controlled growth of Ag nanoparticles decorated onto the surface of SiO 2 spheres: a nanohybrid system with combined SERS and catalytic properties. Rsc Advances, 2014. 4(34): p. 17846-17855.
14. Musić, S., N. Filipović-Vinceković, and L. Sekovanić, Precipitation of amorphous SiO2 particles and their properties. Brazilian journal of chemical engineering, 2011. 28(1): p. 89-94.
15. Zhao, Q., et al., Field emission from AlN nanoneedle arrays. Applied physics letters, 2004. 85(22): p. 5331-5333.
16. Fitl, P., et al., Laser deposition of sulfonated phthalocyanines for gas sensors. Applied Surface Science, 2014. 302: p. 37-41.
17. Santos, C.S., et al., The influence of organization of LbL films containing a silsesquioxane polymer on the electrochemical response of dopamine. Journal of Applied Electrochemistry, 2014. 44(9): p. 1047-1058.
18. Stillman,M.,et al.,Phthalocyanines: properties and applications. VCH, New York, 1989: p. 133.
19. Davidson, A., The effect of the metal atom on the absorption spectra of phthalocyanine films. The Journal of Chemical Physics, 1982. 77(1): p. 168-172.
20. Ureta-Zanartu, M., et al., Electrooxidation of 2-chlorophenol on polyNiTSPc-modified glassy carbon electrodes. Journal of electroanalytical chemistry, 2003. 553: p. 147-156.
21. Zhong, J.-P., et al., Highly active Pt nanoparticles on nickel phthalocyanine functionalized graphene nanosheets for methanol electrooxidation.Electrochimica Acta,2013. 113: p. 653-660.
22. Fakir, M.S., Z. Ahmad, and K. Sulaiman, Modification of optical band gap and surface morphology of NiTsPc thin films. Chinese Physics Letters, 2012. 29(12): p. 126802.
23. Slyom, J., Fundamentals of the Physics of Solids. 2008: Springer.
24. Fakir, M.S., Preparation and characterization of Nickel (II) phthalocyanine tetrasulfonic acid tetrasodium salt for organic solar cells/Muhamad Saipul bin Fakir. 2013, University of Malaya.
25. Tauc, J., R. Grigorovici, and A. Vancu, Optical properties and electronic structure of amorphous germanium. physica status solidi (b), 1966. 15(2): p. 627-637.