Investigate the Structural and Optical Properties of Nickel Phthalocyanine (NiPc) Thin Films Prepared by Chemical Spray Pyrolysis Method.

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Abstract. The technique of the chemical spray pyrolysis has been employed to deposit Nickel Phthalocyanine (NiPc) on different substrate types at temperatures 150 °C to investigate their structural, Scanning Electron Micrographs, X-ray diffractograms and optical properties. The results of X-ray diffraction show that structure of the powder is polycrystalline with monoclinic structure, and the results of XRD for a thin film of NiPc shows polycrystalline with a fairly weak degree of crystallization, SEM revealed that the surface of the film is usually homogeneous, the roughness of NiPc films was evaluated by AFM technique and the results showed that the grain size increases with increasing of concentration. The optical measurement using UV-Visible Spectra showed that the NiPc thin films have an optical constant like the absorption coefficient and have a direct energy gap for all samples.

Key words: Organic semiconductor, Nickel Phthalocyanines, structural and optical properties.

1. Introduction

In 1907, Phthalocyanines was discovered and used as a product in preparation of benzene derivations (ortho disubstituted), it characterized by electron delocalization and high planarity [1]. Nickel Phthalocyanine is semiconductor organic compounds used as an optoelectronic device as thin films. Modules of the thin-film are cheap compounds that have low energy, low costs, and low capital costs. Thin-film technologies are being developed as a means to substantially reduce the cost of electronic systems. The thin films have a future due to there is no energy-needed hardware parts in it. The technology of the memory depended on thin-film electronics for manufacturer PC, servers, mobile phones and digital cameras [2]. In this research, thin-film Nickel Phthalocyanine (NiPc) was deposited using the CSP technique, structural and optical properties were studied.

2. Experimental Work

The Nickel phthalocyanine provided from (Aldrich Chemical-USA) dissolved in ethanol to form a solution at (10:1) concentration. Using of the chemical spray pyrolysis for the accumulation of NiPc thin film at several types such as micro-glass, silicon, and glass at the temperature (150) °C and two bar as pressure and the period was twelve seconds, and the distance was (30) centimetre. The glass has
(75x25x1.35) mm as dimensions while the micro-glass have (20x20x1) mm as dimensions to the preparation of the film by the chemical spray pyrolysis techniques. Results of the X-ray diffraction are confirmed for thin films coated by radiation of Cu Kα of at wavelength 1.54059Å. The previously prepared aqueous solutions are atomized by a special nozzle glass sprayer at heated which are fixed on thermostatic controlled hot plate heater. An air gas is used as a carrier gas and the spray is atomized via an air compressor. The substrate temperature was maintained to be 150±10 oC during spraying to deposition of the thin films at different levels, the distance between the substrate and spray nozzle was kept at 30 ±1 cm.

3. Result & Discussion:

3.1 XRD measurements:

Phthalocyanines have two forms of crystal phases (α and β). The α-phase is getting from thin film or polycrystalline powder at (25) C. the β-phase is getting at thigh temperature [3]. Size of the crystal calculated by [4].

\[
D = \frac{k\lambda}{\beta \cos\theta}
\]

D = crystal size average
k = relates and constant to the dimensionless shape factor
θ = the Bragg angle based on the peak
β = at the half of the maximum intensity (line broadening)

Value of the shape factor was (0.9), however, it different depended on crystallite. Powder and structures of the NiPc films are examined by the XRD system. The voltage was (30) kV, Cu (Kα) is the source of radiation, the current was (20) mA and the wavelength was 1.5405 Å. The range of the scanning angle was (10°–80°).

The interplaner distance d (hkl) for different planes was determined by using Bragg’s law, grain size calculated from Scherrer equation eq. (1). The results compared with standard values for NiPc Powder. Figure (1) shows the results of X-ray diffraction of NiPc powder, the figure showed that the material is polycrystalline. Figure (2) and show NiPc thin films are made by deposition on the glass, Figure (3) show NiPc thin films prepared and deposited on micro and silicon substrate in figure (4). The results showed that the prepared and deposited thin films on glass and micro-glass substrates have a crystalline structure closer to amorphous, or it is possible to say that the films have low crystallization for three conurbations, while the prepared film on the Silicon wafer substrate has a polycrystalline structure. The relation of substrate types and average crystal size is shown in Table (1).

![Figure 1. XRD for NiPc powder](image-url)
Figure 2. show X-ray diffraction for NiPc thin films prepared and deposited on Mica glass.

Figure 3. show X-ray diffraction for NiPc thin films prepared and deposited on glass.
Figure 4. show X-ray diffraction for NiPc thin films prepared and deposited on silicon.

Table 1. Represents the results of X-ray diffraction of thin films NiPc.

| Compound       | substrate | 2 (deg) | (hkl) | d(A°) (Observed) | d(A°) Standard | FWHM (deg) | Grain size (nm) |
|----------------|-----------|---------|-------|------------------|----------------|------------|-----------------|
| NiPc 10⁻³ M    | Micro     | 15.673  | 102   | 5.6495           | 5.5700         | 0.6300     | 14.69           |
|                | Glass     | 15.857  | 102   | 5.5842           | 5.5700         | 0.5300     | 15.53           |
|                | Silicon   | 25.803  | 211   | 3.4499           | 5.5700         | 0.0920     | 90.91           |
| NiPc 10⁻⁴ M    | Micro     | 15.832  | 102   | 5.5929           | 5.5700         | 0.4000     | 20.77           |
|                | Glass     | 15.902  | 102   | 5.5685           | 5.5700         | 0.5000     | 16.46           |
|                | Silicon   | 25.638  | 211   | 3.4717           | 5.5700         | 0.06250    | 133.78          |
| NiPc 10⁻⁵ M    | Micro     | Amorphous |      |                  |                |            |                 |
|                | Glass     | Amorphous |      |                  |                |            |                 |
|                | Silicon   | Amorphous |      |                  |                |            |                 |

3.2 UV-visible measurements:

The UV-Vis spectrum finds the Nickel Phthalocyanine emerge from the orbits of the molecules on central elements ions [5]. The optical absorption spectrum is very necessary for solar cells fabrication with different thickness of Nickel Phthalocyanine as Figure (4).

Q-band and Soret bands are shown in electronic transitions in the UV-Vis. The Q-band was showed (540-700) nanometres due to π-π* transition from highest orbital (occupied) to the lowest orbital (unoccupied) of the phthalocyanine. The peak (601) nanometres of π − π* transition of phthalocyanine where the shoulder peak with low absorption was (670) nanometres increase for monomer part for the second π − π* transition [6]and[2].

The absorption spectrum depends largely on the amount of energy of the levels, which in turn are related to the crystalline and chemical composition of the substance absorption was measured as a function of wavelengths (300-1100) nm. It is noted that absorption increases when concentration increases[7]was found that there was consistent with the international card and published research and it was at a rate of value equal to (aₒ = 3.792 Å, co = 16.34 Å). The absorption spectrum was measured depending on the wavelength. By the study of the absorbance spectrum, we can find many optical constants. The measurements were made at the wavelength range (300-1100) nm for all (CuS) thin film. The results of the UV-VIS measurements are shown in figure (4) which represents the change of the absorbance spectrum of the wavelength. The figure showed that the absorbance would increase with an increase in the number of pulses and this leads to an increase in thickness. In another means, the incident photon can stimulate the electron and transfer to the conduction come from the valence because the photon energy is more than the semiconductor energy gap, therefore, the absorbance increases with increasing wavelength and that similar to the previous studies [8]and [9].
Figure 5. shows The absorption spectrum for (NiPc)

Dependence of wavelength absorption coefficient of thin films deposited at different concentrations. Absorption coefficient was calculated using equation : [23]

\[ \alpha = 2.303 \frac{A}{t} \]  

\( \alpha \) = average of the absorbance  
\( t \) = thickness of the thin [10]

The variations in absorption coefficient with wavelengths variations at different molar concentration are shown in figure (6), we can see that the high value of absorption coefficient (up to 10^4 cm\(^{-1}\)) that represent high chance to direct transition due to traps inside energy gap, and these traps decreasing with increasing of concentrations [11]

Figure 6. Shows Absorption coefficient as a function of wavelength for NiPc.
Value of the optical energy gap of NiPc thin films determine by Tauc equation for determining the optical energy gap by the plotting the relations of $(\alpha hv)^2$ versus photon energy and establishment of the optimum linear as followed formula $(\alpha hv)^2 = 0$ as Figure (7). The optical energy gap become high with increasing concentration as Table (2) due to decreasing of the defect states near the bands[8]and[9].

![Figure 7. Shows the Optical power gap value of radiation for NiPc thin films.](image)

**Table 2.** The value of the optical energy gap for different molar concentration

| Sample  | $E_g$ (eV) |
|---------|------------|
| NiPc $10^{-3}$ M | 2 eV |
| NiPc $10^{-4}$ M | 2.2 eV |
| NiPc $10^{-5}$ M | 2.4 eV |

### 3.3 Scan Electronic Microscope( Surface Morphology)

Analysis of SEM is active sufficient tool that applied for focusing electrons beam for formed high resolution, complex images of the surface of the sample. This subject is very interest in the evaluation of SEM. The results of NiPc thin films show that the crystallized metal, precipitated on glass substrates was consistent and XRD patterns produce the results. Analysis of crystal morphology from Figure (8) illustrates this. It forms a penile-like morphology of varying lengths that increases with increasing concentration. The penile shape and elongated is due to the interaction of the molecules leading to produce stacked layers of the Pc [12].
3.4 Atomic Force microscope (AFM)

To study the topography of film surfaces and the effect of changing the proportions of materials involved in film composition. The surface morphology of NiPc thin films was determined by Atomic Force Microscope, average roughness was tabulated in Table (3) which shows the roughness increase with Concentrations increase.

Table 3. shows surface roughness and thin film (RMS) values

| Compound     | Roughness Average (nm) | Root Mean Square (nm) |
|--------------|------------------------|-----------------------|
| NiPc:10⁻³M   | 2.1                    | 2.4                   |
| NiPc:10⁻⁴M   | 2.78                   | 3.34                  |
| NiPc:10⁻⁵M   | 3.49                   | 4.2                   |
Figure 9. AFM images of NiPc thin films with different Concentrations.

4. Conclusions.
The properties of the prepared material depend on the substrates, where the synthetics have a more amorphous composition on the glass substrates, micro glass and a polycrystalline composition on the silicon substrates. It was also found that the material with properties depends largely on the molar concentration of the prepared material. The energy gap changes markedly as concentration changes.
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