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Illumination effect on the structural and optical properties of nano meso nickel (II) tetraphenyl-21H, 23H-porphyrin films induces new two hours photo bleached optical sensor

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ABSTRACT

250 nm thickness of meso nickel (II) tetraphenyl-21H, 23H-porphyrin, NiTPP films were prepared by thermal evaporation technique on a quartz substrate. The prepared films were illuminated for 10, 20, 30, 60, 120, 240, 360 and 420 min. Films of 120 and 240 min of illumination time had been affected while others had no response. The as prepared meso NiTPP films are amorphous and the illuminated one are crystalline with amorphous background included within nano scale. The illuminated films were accompanied by photo bleaching effect. Two gaps could be distinguished; indirect optical gap, E_{gi}^{opt} and the fundamental energy gap, E_g. Optical parameters; refractive index, absorption coefficient, single-oscillator energy, dispersion energy, Lattice dielectric constant, the ratio of the carrier concentration to the effective mass, optical conductivity and energy loss function were studied. All mentioned parameters were affected by the illumination time. The response of nano meso NiTPP films to the mention illumination time has pulse shape, so it is recommended to be used as optical sensor.

1. Introduction

There are many parameters that may affect the structural, optical and electrical properties of materials; doping [1], alloying [2], annealing [3,4], available phase and phase change, [5], radiation [6] aging, [7–10] substrate temperature [11], substrate type [12], preparation technique [13], the constituent's ratios and chemical's purity [14], thickness [15], and light illumination [16,17]. The mentioned parameters are used to tune the properties of materials – organic or inorganic– according to the desired applications in different fields. The organic materials have many industrial applications; optical and gas sensor, solar cell and photo voltaic systems, light emission diodes, LEDS [18], optical switching, optical storage media [19,20], light antenna [16], electroluminescent applications [21,22] and biological applications [23]. The most important advantages of organic semiconductors are: low cost materials (low cost solar cell), high absorption coefficients, their organic thin films can be obtained by thermal evaporation on a large area, finally they have the ability to be chemically engineered for new nanotechnologies applications as nano electronic devices [24].

It was mentioned that [25,26] porphyrin is a molecule consists of four pyrroles linked by four methane groups to form large ring. Four nitrogen atoms of porphyrin facing the center of the large ring, such of this design called free base porphyrin. Porphyrin compounds are formed if the free base is occupied with any element or legend. Some of porphyrin compounds can be used as porphyrin dyes. Porphyrin and porphyrin compounds" had much attention as organic semiconducting materials due to their various applications [9,22,27–29].

The origin of porphyrin nomenclature belongs to the word "porphura" from the Greek language and is translated to English as "purple". It was synthesized for the first time in the 1930s. More details about this issue and the structure of porphyrin are available at [22,23,30,31]. Porphyrin is characterized by two absorption regions; Soret or B band (380–500 nm) and Q band (500–750 nm) [23]. There are many classifications of porphyrin; etio, rhodo and oxo-rhodo e phyllo [32]. There are many elements that may join the porphyrin free base to form metalloporphyrins [9,23,25,33] for example; Co, Cu, Ni, Mg, Cd, Zn, Fe, Mn, Ti, Zr and Hf. Other elements can also join porphyrin free base, more details about this issue are available at [26].

Illumination may affect materials in different forms; bulk, thin and thick films, liquid, nano, macro….etc. There is no available literature about the effect of illumination on the structural and the optical properties of meso NiTPP, so this study is important.

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2. Experimental technique

Thermal evaporation technique is used to deposit meso NiTPP films with 250 nm thickness on a quartz substrate using Edwards E-306A coating unit. 6 N purity of meso NiTPP powder ampoule is received from Sigma- Aldrich Company. The mentioned thickness was determined by quartz crystal monitor type Edwards FTM5 as an additional accessory supporting the coating unit. One section of the as-prepared films was used to study the structural and the optical properties of meso NiTPP as un-illuminated films. The other section is illuminated for different times; 10, 20, 30, 60, 120, 240, 360 and 420 min. X-ray diffraction, XRD is used to study the structural properties while the spectrometric measurements of transmittance, T and reflectance, R were measured within the wavelength of (200–1100 nm). More details about the XRD, optical measurements, illumination procedure and the experimental error are available at [3,17].

3. Results and discussions

3.1. Structural properties

The presence of the well known hump which characterizes the amorphous materials confirms the amorphous state of the as prepared meso NiTPP films as depicted in Fig. 1a. The illuminated meso NiTPP films for 240 min have a sharp peak with a broadening background which confirms the presence of crystalline nature with the amorphous matrix of the illuminated films as illustrated in Fig. 1b. The observed preferred orientation at 2θ (25.89°) is (004). Scherrer equation [3,4,34,35] is used to calculate the corresponding crystallite size.

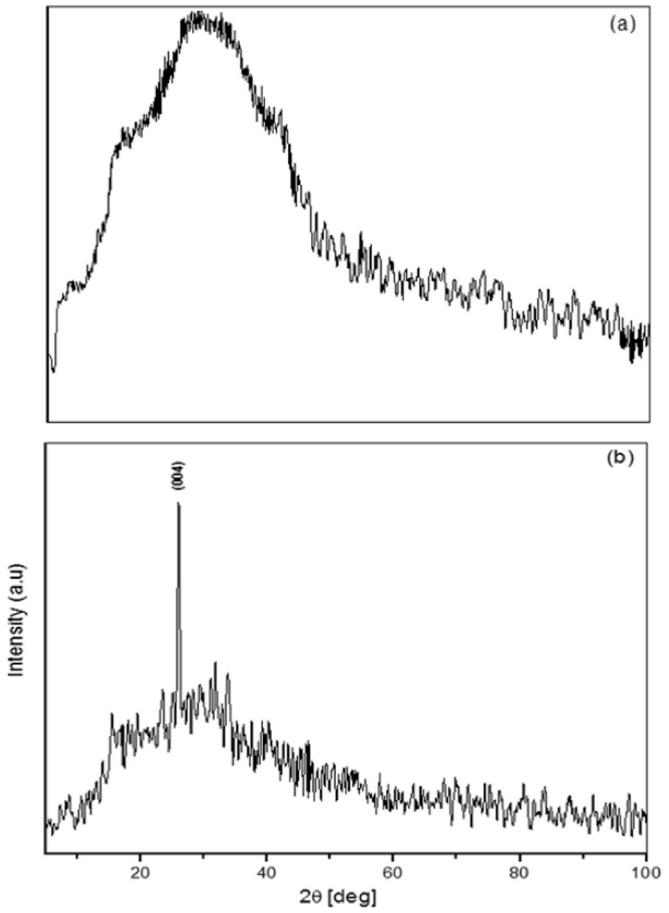

Fig. 1. XRD of (a) the as prepared and (b) 240 min ill. Nano meso NiTPP films.

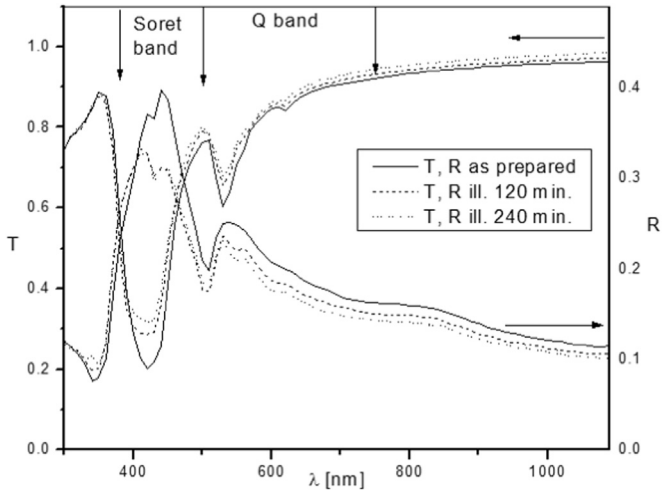

Fig. 2. T and R of the as prepared and illuminated nano meso NiTPP films.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

D is the mean crystallite dimension (Å), K is a constant (typically assumed to be 1), β is the full width half maximum, FWHM of the peak in radians of 2θ and λ is the wavelength of X-ray used (CuKα radiation) equal to 1.54056 Å. The obtained crystallite size of (004) preferred orientation is 29 nm which included within the nano scale. The value of the crystallite size of the illuminated films recommends the increasing of arrangement of the illuminated meso NiTPP films by the increasing of illumination time.

3.2. Optical properties

3.2.1. Spectral distribution of T and R

The variation of the spectral distribution of T and R are shown in Fig. 2.

Both T and R show two regions; the absorbing region λ ≤ 800 nm, the other one is called non absorbing region at λ > 800 nm. The first one has drastic changes of both T and R and contains two absorption peaks; Soret band or B band within (380–500 nm), the other peak at (500–750 nm) is called Q band [36,37] as illustrated in Fig. 2. At this region, absorption coefficient, α extinction coefficient, k and the optical gap, E_g^{opt}; direct, E_{gd}^{opt} or indirect, E_{gi}^{opt} can be calculated. Refractive index, n and the dielectric constant and their derivatives were calculated through the second region. Illumination induces photo changes in meso NiTPP films; the values of T increase as a function of the illumination time and shift to shorter wavelength while the values of R decrease. Illuminations may induce structural changes through the illuminated material [38] followed by two phenomena; photo bleaching, PB and/or photo darkening, PD.

According to [17,38,39], the displacement of E_g^{opt}; E_{gd}^{opt} or E_{gi}^{opt} to high energy values or lower wave length is called PB or blue shift. The reverse behavior is called PD or red shift. Our obtained data follow PB effect; T has a displacement to shorter wavelength. The increasing of T by the increasing of the illumination time is a result of photo bleaching effect. Such this effect was attributed to the structural changes from disorder or amorphous nature to more ordered material or crystalline nature and the improvement of surface morphology [8,10,40].

3.2.2. Optical gap calculations

To calculate E_{gd}^{opt} or E_{gi}^{opt}, absorption and extinction coefficient, α and k should be calculated first according to the following procedure using both T and R [41,42];

$$T = (1 - R)^2 e^{-\alpha d} \quad (2)$$