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Design and characterization of Bi₂O₃/ZnPc optical interfaces

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Thesis Approval

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Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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Abstract

In this thesis heterojunction devices made by stacking layers of Bi₂O₃ and zinc phthalocyanine (ZnPc) are studied. The Films are coated by the thermal evaporation technique under a vacuum pressure of 10⁻⁴ mbar. The produced Bi₂O₃, ZnPc and Bi₂O₃/ZnPc are structurally and optically characterized. It was observed that coating of ZnPc onto polycrystalline Bi_2O_3 induces the crystallinity of ZnPc. Both of the stacked layers are of polycrystalline nature. The induced crystallization of ZnPc is attributed to the atomic substitutions and completed bonding mechanisms. In general, ZnPc layer decreased the Strain and defect density in Bi₂O₃ leading to larger crystallite sizes. The behavior is probably due lower ionic radii of Zn⁺² as compared to Bi⁺³. On the other hand, optical studies have shown that formation of two stacked layers is accompanied with pronounced free carrier absorption and pronounced interband transition, it is also noted that increasing the thickness of Bi₂O₃ substrate results in indirect allowed photonic transitions at the Bi₂O₃ /ZnPc interfaces. In addition, although both of Bi₂O₃ and ZnPc show the same energy band gaps (2.9 eV), the Bi₂O₃/ZnPc interface displayed narrower band gap (2.15 eV). Bi₂O₃/ZnPc heterojunction devices are also observed showing symmetrical condition and valance band of sets of 1.46 eV and 1.40 eV, respectively. Moreover, the dielectric dispersion studies on the proposed heterojunction devices have shown that Bi₂O₃/ZnPc film can perform as dielectric resonators with critical energies centered at 2.48, 1.73, 2.97 and 3.28 eV. Drude -Lorentz modeling on the imaginary part of the dielectric spectra revealed optical conductivity parameters that show the suitably of devices for optoelectronic application.

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Chapter One

Introduction

Zinc Phthalocyanine (ZnPc) is a promising and organic material that has beneficial properties which qualifies it to be used in medical, technological and industrial applications. It has powerful features including minimal skin photosensitivity due to its great tendency to aggregate in polar solvent, considerable penetrating radiation in tissues due to the strong absorption in the red region of the spectrum in the Q band (674 nm) which appears in the region between 1.4 and 2.6 eV [1,2], high the rapeutic effect with low toxicity and high photochemical stability [3]. It may be have as microwave cavities [4], and also employed for fabricating photodiodes of high responsivity [5]. In the same sector, research studies on Bi_2O_3 have shown that it is highly conductive device and exhibit remarkable current growth at critical biasing voltages [6], a good candidate to be used as wave traps and electronic fast switches [7], other studies of the effect of bismuth oxide (Bi_2O_3) on the optical properties of Bi2O3-Li2O-20ZnO15B2O3 glasses have shown that the prepared glasses have preferable features to apply for radiation shielding applications [8], the addition of Bi2O3 has decreased the optical transmission, increased the optical dielectric constant of the glasses, it's also shown that Bi₂O₃ is suitable elect to be used in radiation shielding application in the range of 30.82 keV -383.9 keV[9].

Many recent studies have focused on the exploration of the physical properties of the ZnPc films and discover the monoclinic crystalline structure [4,2], the electron affinities ($q\chi$), work functions ($q\phi$) and energy band gap values which were $q\chi$ = 3.34 eV, $q\phi$ = 4.54 eV [10, 11], and E_g = 2.70 eV [12], the direct band gaps of ZnPc were found to be 1.99 and 3.09 eV[13]. In spite of the fact that in semiconductor materials

electrical conductivity increases with temperature, it is also true that organic semiconductors like ZnPc may suffer devolution in their internal structure at high temperatures, leading to a decrease in their performance and/or operational failure [2].In the same sector, the Bi₂O₃thin films observed to show a crystallization nature relying on the crystal structure of the substrate, [14] they also found to prefer the monoclinic nature of structure with larger values of microstrain, stacking faults, dislocation density and smaller grain sizes when changing the glass substrate by germanium [15]. For the monoclinic phase of Bi₂O₃ films the value of 2.80 eV is reported [16] with $q\chi = 4.8$ eV [17], $q\phi = 6.33$ eV[18], and Eg = 2.49 eV [19].

ZnPc thin films have been subjected to many different experimental techniques in order to develop their performance. It was shown that topography has a considerable effectiveness on the properties exhibited by the ZnPc-doped films and it relies especially on the experimental parameters that used in the deposition of the films [2]. The results of coating ZnPc onto glass and Yb substrates using thermal evaporating technique showed that structural, electrical and optical properties of the Yb/ZnPc interfaces suggest that it can be used as optoelectronic and/or radio/microwave components [4]. Sol-gel method was used to produce dye sensitized composite catalyst (ZnPc/TiO2) by immobilizing (ZnPc) molecules to TiO2 nano particles, obtained structures were specifically designed to increase the light absorption, shift the light absorption to longer wavelength and harvesting capacity beside facilitate the electron transfer in UVA region photocatalysis [20]. Using the solution processed spin coating method, the capacitive type humidity sensor devices was made-up in a planar geometry of Al/ZnPc/Al with the existence of a microporous template [21]. Furthermore, literature data review various investigations that link the Bi_2O_3 based device performance to the substrate they were deposited onto [6].

The varied applications due to unique properties of the ZnPc, its validity to be used in the fabrication of optoelectronic devices, especially those of interest in photovoltaic applications [2], encourage us to manufacture a ZnPc/Bi₂O₃ thin film by using the thermal evaporation technique. Essentially, the aim of our project is to study the structural and optical properties of ZnPc/Bi₂O₃ thin film using Thermo-Scientific Evolution 300 spectrophotometer equipped with variable angle reflectometer and Miniflex 600 XRD unit for the X Ray Diffraction analytic. Some possible applications of this thin film will be suggested.

Chapter two

Theoretical background

2.1 X-ray Diffraction (XRD):

X-ray diffraction is a powerful technique to get information about the crystalline structure of the material. Its power came from the short range in which they appear in the electromagnetic spectrum $(0.1 - 100 A^{\circ})$ which is based on concept of Bragg's law [22].

Crystals can have one or many of the structural phases. Generally, there are seven crystal systems named cubic, triclinic, monoclinic, orthorhombic, hexagonal, trigonal and tetragonal. These systems can be known in terms of the relationships between lattice angles (α, β, γ) and lattice vectors (a,b,c) [23]. Each system has an interplaner distance or spacing (*d*). This quantity is the perpendicular distance between two successive planes on a family of miller indices (hkl). For the triclinic formula, there is no relationships between the lattice parameters: $(a \neq b \neq c)$ and lattice angles $(\alpha \neq \beta \neq \gamma \neq 90)$.

$$\frac{1}{d^2} = \frac{\begin{bmatrix} \frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma \\ + \frac{2kl}{bc} (\cos\beta \cos\gamma - \cos\alpha) \\ + \frac{2hl}{ac} (\cos\alpha \cos\gamma - \cos\beta) \\ + \frac{2hk}{ab} (\cos\alpha \cos\beta - \cos\gamma) \end{bmatrix}}{[1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos\alpha \cos\beta \cos\gamma]}$$
(2.1)

Using equation 2.1 [24] one may derive all the other structural phases. These important phases are shown in table 2.1. [25]

2.1.1 Bragg's law.

X ray diffraction illustrate how the x ray photons scattered elastically in periodic lattice by atoms, constructive interference produced when the interactions between the sample and the incident rays satisfy the conditions of Bragg's law as shown in Figure 2.1 [26].

$$2d \sin\theta = n\lambda$$
 (2.2)

As shown from Figure 2.1, d is the interplanner spacing between two planes of atoms, θ is the diffraction angle, n is an integer, λ is the wavelength of the x ray 1.5405 Å.

By combining the Bragg's condition with procured interplaner spacing, Miller indices (hkl) according to the cubic crystal system with the lattice parameters of the individual plane revealed by the equation [27]:



Figure 2.1: Bragg scattering on the lattice surface.

The orientation of the crystalline planes Miller indices (hkl) is determined by how the plane intersects the main crystalline axes of the solid.

Table 2.2 shows the interplanar spacing formula for the other six structures than triclinic respectively.

Lattice constant	Angle	# of Bravais lattice
$a_1 \neq a_2 \neq a_3$	$\alpha\neq\beta\neq\gamma\neq90^{o}$	1
$a_1 \neq a_2 \neq a_3$	$\alpha=\beta=90^{o}\!\neq\gamma$	2
$a_1 \neq a_2 \neq a_3$	$\alpha=\beta=\gamma=90^{\rm o}$	4
$a_1 = a_2 \neq a_3$	$\alpha=\beta=\gamma=90^{\rm o}$	2
$a_1 = a_2 = a_3$	$\alpha=\beta=\gamma=90^{\rm o}$	3
$a_1 = a_2 = a_3$	$\alpha=\beta=\gamma<120^{\rm o}\neq90^{\rm o}$	1
$a_1 = a_2 \neq a_3$	$\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$	1
	Lattice constant $a_1 \neq a_2 \neq a_3$ $a_1 \neq a_2 \neq a_3$ $a_1 \neq a_2 \neq a_3$ $a_1 = a_2 \neq a_3$ $a_1 = a_2 = a_3$ $a_1 = a_2 = a_3$ $a_1 = a_2 = a_3$ $a_1 = a_2 \neq a_3$	Lattice constantAngle $a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$ $a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90^\circ \neq \gamma$ $a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$ $a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$ $a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$ $a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$ $a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ \neq 90^\circ$ $a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma < 120^\circ \neq 90^\circ$ $a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

Table 2.1: 3-D crystal structures for solid state materials and their conditions

Table 2.2: The interplanar spacing formula for the other six structures than triclinic [28]

crystal System	Spacing Interplanar
Cubic	$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}$
Trigonal	$\frac{1}{d^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}$
Tetragonal	$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2) + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta}$

2.1.2: Structural parameters

The Structural parameters, microstrain (ϵ), dislocation density (δ), broadening width

(β), crystallite size (D) and stacking faults (SF %) are obtained with the help of maximum peak of the most intensive peak.

Crystallite size and Scherrer's formula

X-ray diffraction is a conventional method for calculating the mean size of crystallites in polycrystalline materials. Crystallite size is determined by Scherrer's equation [29]

$$D = \frac{0.94\,\lambda}{\beta\,\cos\left(\theta\right)} \tag{2.4}$$

Microstrain

Strain is caused by the relative displacements of atoms that affects the lattice constant and make the deformation [30]. It is specified by the relation:

$$\varepsilon = \frac{\beta}{4\tan\left(\theta\right)} \tag{2.5}$$

uniform strain (elastic deformation) and non-uniform strain (plastic deformation) can be found in the crystal as shown in Figure 2.2



Figure 2.2. Effect of lattice strain on diffraction peak position and width.

Dislocation density

The Dislocation density is the total length of dislocation line per unit area or

per unit volume of the crystal (lines/cm²) [31]. It can be determined from the following equation [29]:

$$\delta = \frac{15\,\varepsilon}{aD} \tag{2.6}$$

Where a is the lattice constant at the a - axis.

Stacking faults

Stacking faults is known as a type of planar defect in a crystal structure or defined as a break in the normal sequence of stacking in the crystal [32]. It is calculated by the relation [29]:

$$SF = \frac{2 \pi^2 \beta}{45 \sqrt{3 \tan(\theta)}} \tag{2.7}$$

2.2: Optical properties

Optical properties of materials are very significant in the development of technology. These properties depend on how the electromagnetic radiation interacts with the material. This interaction is relied to the wavelength and frequency of the radiation beam as well the property of the material like refractive index, band gap values, dielectric constant, etc. These optical properties affected by the microscopic and macroscopic properties of the material, like the electronic structure and the nature of its surface and. There are many optical properties, the most important: transmission, absorption reflection and refraction.

2.2.1 Band to band or fundamental absorption:

Band to band or fundamental absorption of radiation returns to the photoexcitation of an electron from the valence band (VB) to the conduction band (CB). There are two types of band to band absorption, which are direct and indirect transitions.

2.2.2 Direct transition:

No phonons are involved in the photo excitation process of a direct transition. Electron excited from VB to CB when the photon of energy (hv) is absorbed, the electron's k vector doesn't change because the photon momentum very little compared with the electron momentum. A direct transition on E - k diagram is a vertical transition from an initial energy E in the VB to a final energy E' in the CB with no change in the wave vector k in the VB and the wave vector k' in the CB, k' = k, as shown in Figure. 2.3. [33]

$$E' - E_{C} = \frac{P^{2}}{2m_{e}^{*}} = \frac{(\hbar k)^{2}}{2m_{e}^{*}}$$
(2.8)
$$E_{v} - E = \frac{(\hbar k)^{2}}{2m_{h}^{*}}$$
(2.9)



Figure 2.3: A direct transition from VB to CB through the absorption of a photon.

The absorption coefficient α can be obtained from the quantum mechanical probability of transition from *E* to *E'*, the occupied and the unoccupied density of states at *E* in the VB and CB from which electrons are excited and at E + hv, respectively. The density of states can be approximated by a parabolic band near the band edges, and α rises with the photon energy as following:

$$\alpha h v = \mathbf{A} \left(h v - E_g \right)^{1/2} \tag{2.10}$$

where A is constant $\approx \left[\frac{e^2}{nch^2 m_e^*}\right] (2\mu^*)^{3/2}$, μ^* is the reduced electron and hole effective masses, E_g is the direct band gap with minimum $E_c - E_v$ at the same k value and n is the refractive index [33].

2.2.3 Indirect transition:

As shown in Figure 2.4, the photon absorption for the photon energies near E_g in indirect band gap solids requires the absorption and emission of phonons during the absorption process. The energy of photon ($E_g - hv'$) corresponds to absorption which represents the phonon absorption with energy $\hbar\omega$. Thus, α is proportional to $[hv' - (E_g - hv')]^2$. When the photon energy reaches $(E_g + hv')$, then the absorption of photon process happens by phonon emission, for which the coefficient of absorption is greater than that for absorption of phonon [14].



Figure 2.4: An indirect transition across the band gap involves photons.

The absorption coefficient relates to the energy gap E_g through the relation [34]:

$$(\alpha E)^{1/p} = B (E - E_g)$$
 (2.11)

Where B is a constant depends on the transition probability, p is an index that characterizes the absorption process and E_g is the energy gap.

Then,

 $P = \frac{1}{2}$ for direct allowed transition.

- P = 2 for indirect allowed transition.
- P = 1/3 for direct forbidden transition.
- P = 3 for indirect forbidden transition.

The common way to calculate the energy gap (E_g) is plotting a graph of $(\alpha E)^{\frac{1}{p}}$ versus photon energy. In suitable value of p is used to get linear plot with the widest range of data, the value of E_g will be obtained by the intercept on the photon energy (E) axes.

2.2.4 Absorption band tail (Urbach energy):

The optical absorption spectra of the materials have an essential role as it gives the fundamental information about its optical band gap and its composition. Three main region can be appeared in the optical absorption spectra, they are:

- (1) Strong absorption region, that determine optical energy gap.
- (2) Weak absorption region, which produce from defects and impurities.
- (3) Absorption edge region, which produced because of the perturbation of structural and disorder of the system.

Urbach tail is an exponential part near the optical band edge and along the absorption curve. This tail appears in low crystalline, the disordered and amorphous materials due to localized states for these materials that extended in the band gap. The following relation represents Urbach rule [34]:

$$\alpha = \alpha_o \exp\left(\frac{E}{E_e}\right) \tag{2.12}$$

Where α_o is a constant, α is the absorption coefficient and E_e represent the energy of the band tail which is weakly dependent upon temperature and called Urbach energy. Taking the logarithm for the two sides of the eq. (2.15), hence we can obtain a straight line equation. It is given as follows:

$$\ln \alpha = \ln \alpha_0 + \frac{E}{E_{\varrho}}$$
(2.13)

So, the energy band tail can be calculated from the slope of the straight line of plotting $\ln \alpha$ versus the incident photon energy (E).

2.2.5 The complex refractive index and dielectric constant

Dielectric constant(ε) is the ratio of permittivity of material relative to the vacuum permittivity. It's a complex property that consists of two parts, real and imaginary. The refractive index (n) which show how fast light propagate through the medium, can be a complex number.

If we consider an eclectic field on the x-axis and propagating on the z direction include the incident and reflected waves [35].

$$\vec{E}_x = \mathbf{E}_0 e^{i(kz - \omega t)} \tag{2.14}$$

Where E_0 is the amplitude at z = 0, ω is the angular frequency and k is the wave vector..

Thus, k and ω are related to each other through:

$$k = \frac{2\pi}{(\lambda/n)} = \frac{n\omega}{c}$$
(2.15)

Using complex refractive index and generalized:

$$k = \frac{\omega}{c} \widetilde{N}_{complex} \tag{2.16}$$

$$\vec{E}_x = \mathbf{E}_0 e^{i(\omega z \,\tilde{N}/c - \omega t)} \tag{2.17}$$

$$=E_1 e^{i(\frac{\omega \tilde{N}z}{c}-\omega t)} + E_2 e^{-i(\frac{\omega \tilde{N}z}{c}+\omega t)}$$
(2.18)

$$E_o = E_1 + E_2$$
 (2.19)

Where E_0 , E_1 and E_2 are correlating by the continuity equation for the tangential component of H_y through the boundary of the solid, using Maxwell's equation

$$\nabla \times \vec{E} = -\frac{\mu}{c} \frac{\partial \vec{H}}{\partial t} = \frac{i\omega\mu}{c} \frac{\partial \vec{H}}{\partial t}$$
(2.20)

$$\frac{\partial \vec{E}_x}{\partial z} = \frac{i\omega\mu}{c} \frac{\partial \vec{H}}{\partial t}$$
(2.21)

Derive Eqn. (2.18)

$$E_{o}k = E_{1}\frac{\omega}{c} - E_{2}\frac{\omega}{c} = E_{o}\frac{\omega}{c}\hat{N}_{complex}$$
(2.22)

$$E_1 - E_2 = E_o \hat{N}_{complex} \tag{2.23}$$

Solving the equations (2.27) and (2.23)

$$E_{2} = \frac{1}{2} E_{o} \left(1 - \hat{N}_{complex} \right)$$
(2.24)

$$E_{1} = \frac{1}{2} E_{o} \left(1 + \hat{N}_{complex} \right)$$
(2.25)

The normal incident reflectivity is given by the relation,

$$R = \left| \frac{E_2}{E_1} \right|^2 \tag{2.26}$$

Substituting equations (2.24) and (2.25) we can simplify Eqn. (2.26)

$$R = \left| \frac{(1 - \hat{N}_{complex})}{(1 + \hat{N}_{complex})} \right|^2 = \frac{1 - \hat{n}^2 + \hat{k}^2}{1 + \hat{n}^2 + \hat{k}^2}$$
(2.27)

Where $\widehat{N}_{complex}$ has real and imaginary parts, $\widehat{N}_{complex} = \widehat{n} + i\widehat{k}$

$$R = \frac{1 + \hat{n}^2 - 2\hat{n} + \hat{k}^2}{1 + \hat{n}^2 + 2\hat{n} + \hat{k}^2}$$
(2.28)

For strongly absorbing medium (n = $\hat{k} \gg 1$) [36], the unity terms are cancelled, Eqn.

(2.25) becomes

$$R\hat{n}^{2} + 2\hat{n}R + \hat{k}^{2}R = \hat{n}^{2} - 2\hat{n} + \hat{k}^{2}$$
(2.29)

$$(R-1)\hat{n}^2 + 2\hat{n}(R+1) + \hat{k}^2(R-1) = 0$$
(2.30)

If we use the solution of square root equation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{2.31}$$

we can obtain

$$\widehat{n} = \frac{-2(R+1) \pm \sqrt{(2(R+1))^2 - (4(R-1)(R-1)\widehat{k}^2)}}{2(R-1)}$$
(2.32)

$$\widehat{n} = -\frac{(R+1)}{(R-1)} \pm \sqrt{\left(\frac{(R+1)}{(R-1)}\right)^2 - \widehat{k}^2}$$
(2.33)

Then, the roots are

$$\widehat{n}_{1} = -\left(\frac{R+1}{R-1}\right) + \sqrt{4\left(\frac{R+1}{R-1}\right)^{2} - 4\,\widehat{k}^{2}}$$
$$\widehat{n}_{2} = -\left(\frac{R+1}{R-1}\right) - \sqrt{4\left(\frac{R+1}{R-1}\right)^{2} - 4\,\widehat{k}^{2}}$$

As we know,

$$\widehat{n} = \sqrt{\varepsilon_{eff}}$$
(2.34)

Substitute Eqn. (2.32) in equation (2.31) we get

$$\sqrt{\varepsilon_{eff}} = -\frac{(R+1)}{(R-1)} \pm \sqrt{\left(\frac{(R+1)}{(R-1)}\right)^2 - \hat{k}^2}$$
(2.35)

To derive the dielectric constant equations, it is important to define the complex refractive index [31, 32]

$$\widehat{N}_{complex} = \sqrt{\mu\varepsilon}$$
(2.36)

Where $\hat{N}_{complex}$ consists of real and imaginary parts

$$\widehat{N}_{complex} = \widehat{n} + \mathrm{i}\widehat{k} \tag{2.37}$$

$$K = \frac{\omega}{c} \hat{N}_{complex}$$
(2.38)

Equation (2.32) can be derived from Maxwell's equations [36], *K* is the extinction coefficient and \hat{n} is the refractive index.

For non-magnetic material ($\mu = 1$), Eqn. (2.34)

$$\widehat{N}_{complex} = \sqrt{\varepsilon_{eff}}$$
(2.39)

The dielectric constant equation is given by,

$$\varepsilon_{eff} = \varepsilon_1 + i\varepsilon_2 \tag{2.40}$$

 ε_1 and ε_2 states the real and imaginary parts of dielectric, respectively.

Substitute Eqn. (2.32) in Eqn. (2.30) we get,

$$\hat{N}^{2}_{complex} = \varepsilon_{eff} = (\hat{n} + i\hat{k})^{2}$$
(2.41)

$$\varepsilon_{eff} = \hat{n}^2 - k^2 + i2\hat{n}\hat{k}$$
(2.42)

Matching Eqn. (2.33) with Eqn. (2.35) the real and imaginary parts are

$$\varepsilon_1 = \hat{n}^2 - \hat{k}^2 \tag{2.43}$$

$$\varepsilon_2 = 2\hat{n}\hat{k} \tag{2.44}$$

We consider that the equation of the electric field for an electromagnetic wave propagate in a medium in the z-direction is:

$$E(z,t) = E_o e^{i(kz - \omega t)}$$
(2.45)

Where ω is the angular frequency and k is the wave number, the relation between the extinction coefficient *K* and λ is

$$K = \frac{2\pi}{\lambda/\hat{N}} \tag{2.46}$$

Joining Eqns. (2.30), (2.31), (2.38) and (2.39)

$$E(z,t) = E_o e^{i(\frac{\omega nz}{c} - \omega t)} e^{\frac{-kz\omega}{c}}$$
(2.47)

As we know, I $\propto EE^*$ where I is the optical intensity of the light wave and E is the electric field:

$$I \propto e^{\frac{(-k\omega_z)}{c}}$$
(2.48)

Comparing Beer' equation with (2.42) equation we can find that

$$2\frac{K\omega}{c} = \alpha = \frac{4\pi K}{\lambda} \tag{2.49}$$

Then,
$$K = \frac{\lambda \alpha}{4\pi}$$
 (2.50)

Chapter Three

Experimental Details

3.1 Cleaning glass

The glass is cleaned to get sure no impurity and foreign materials exist in the films. In the cleaning process, we firstly wash a 7.5 cm-length glass (Lime; SiO₂:Na₂: MgO:CaO) by using softening sponge, distilled water and alcohol. Then, the glass was immersed in H₂O₂, covered with aluminum foil, and ultrasonically shacked for 30 minutes at 70°C. Thereafter, they were immersed with 70%-Ethyl-Alcohol and ultrasonically shacked for 30 minutes at 28°C and then dried. In order to begin the evaporation process, cleaned glass was checked by eye to have no scratch on the surface.

3.2 System preparation for thin film evaporating

The evaporation process of the Bi₂O₃/ZnPc thin films onto the cleaned glass was done using Norm VCM-600 vacuum evaporation system (Figure 3.1). Bi₂O₃ boat used for placing a high purity Bi₂O₃. The cleaned glass substrates were put and splice on a substrate holder (metal plate), after that the jar was closed. In order to perform an impurity free environment inside the deposition champer, the vacuum pressure was lowered to 1.3×10^{-4} mbar, then the evaporation process of Bi₂O₃ started to form the first layer. The films were removed from the champer after the champer was cooled to a suitable level. The films of the Bi₂O₃ with different thickness were determined by using surface roughness tester-profilometer (Model SOLID TR-200 plus). The profilometer is shown in Figure 3.3. Then, thin films of ZnPc were prepared from the ZnPc powder by depositing it onto the previously cleaned glass and Bi₂O₃-coated glass substrates. The evaporation boat is supplied with current when the pressure was about 10⁻⁴ mbar and the shutter is opened after 2 minutes. When the boat was heated ZnPc powder started to evaporate and form on the substrates. The thickness of ZnPc thin films was allocated to be 0.5 μm through an INFICON STM-2 thickness monitor linked to the evaporating system. When the requested thickness was achieved, the shutter was closed. The geometrical design of the Bi₂O₃/ZnPc samples is shown in Figure 3.2.



Figure 3.1: The 600 VCM evaporation system.



Figure: 3.2 The geometrical design of $Bi_2O_3/ZnPc$ thin film.



Figure: 3.3 The roughness tester-profilometer (Model SOLID TR-200 plus) system.

3.3 Thin film analysis

The structural and optical properties of the thin film were studied with the help of the X-ray diffraction (XRD), hot probe, and optical spectrophotometry techniques. These techniques are termed in the next sections.

3.3.1 The X-ray Diffraction (XRD) Measurements

The crystallinity, preferred plane orientations, phases, and other structural parameters of Bi₂O₃, ZnPc and Bi₂O₃/ZnPc thin films were determined using Rigaku diffractometer which is shown in Figure 3.4, with K_{α} radiation source of a copper anode which have average wavelength of 1.5405 Å running at 40 KV tube voltage and 15 mA tube current was used. The data was collected by the MiniFlex guidance software linked with the x-ray unit. XRD patterns were recorded with diffraction angle 2 θ between 3°-70° with scanning speed of 0.3 deg/min and scanning step of 0.02 deg.



Figure: 3.4 X-ray Rigaku diffractometer.

3.3.2 Optical Measurements:

The optical measurements of the Bi_2O_3 , ZnPc and $Bi_2O_3/ZnPc$ thin films were determined by thermo-scientific evolution 350 ultra-violet visible light near infrared (UV-VIS-NIR) spectrophotometer processed with VEE MAX II variable angle reflectometer. The spectrophotometer shown in Figure 3.5, uses a Xenon (Xe) lamp light. The spectral wavelength was in the range of 190-1100 nm with a scanning speed of 1200 nm/min. The transmittance and reflectance of the incident light on the films was identified at normal incidence. For transmittance and reflectance measurements, a baseline of 100 % T and 0% T is set through the process, respectively. The reflectance measurement is set with the help of pike reflectometer. The data is then collected and analyzed by a vision software program attached to the system.



Figure 3.5: The UV-VIS spectrophotometer.

As seen from Figure 3.6, the spectrophotometer contains two instruments: a spectrometer and a photometer in which spectrometer produces light of any wavelength, while the intensity of light is measured with the photometer. The spectrophotometer is layout of a way that the film is set between spectrometer and photometer. The amount of light that passes through the sample is measured by the photometer. Photo meter also provides a voltage signal to the display. The voltage signals change with the changing of the absorbing of light.



Figure. 3.6: The schematic of the spectrophotometer system.[37]

3.3.3The hot-probe technique

The conductivity types of semiconductors (n-type, p-type) are important especially in design the energy band gap diagram. The hot-probe technique is used to define the conductivity type of semiconductors by specifying the majority charged carriers. This method, which consists of a standard digital multimeter (DMM) and a heated probe, allows the recognition of the type of the semiconductor. The DMM reads positive or

negative voltage for the p-type or n-type semiconductor, respectively. It reads positive value (p-type) for the ZnPc film and a negative one (n-type) for the Bi_2O_3 film. Figure. 3.7 displays the set-up of hot-probe technique connecting the positive probe to the hot side.



Figure. 3.7 The set-up of hot-probe technique.

Chapter Four

Results and Discussion

4.1 Structural Analysis

The structural and morphological properties of the Bi_2O_3 , ZnPc and $Bi_2O_3/ZnPc$ thin films were identified by means of X-ray diffraction (XRD). The XRD patterns of the films are shown in Figure 4.1.



Figure 4.1 The X-ray diffraction patterns for Bi₂O₃, ZnPc and Bi₂O₃/ZnPc thin films. Inset.1 shows the shift in the main peak. Inset.2 shows the photo sample.

Three sharp patterns are observed for Bi_2O_3 film. The most intensive peak is centered at a diffraction angle of $2\theta = 22.72^\circ$. The other diffraction patterns are observed at 2θ values of 20.62° and 46.16°. The standard diffraction patterns of Bi_2O_3 appear is at diffraction angles of $2\theta = 20.62^\circ$, 22.72° and 46.16°. Deep analyses using "crystdiff" software backges to explore the structure were carried out. The deviations from the standards of these values are 1.2%, 2.8% and 0.4%, respectively. In accordance with "crystdiff" software packages, the XRD patterns were analyzed and pointed out that the peaks are exhibiting cubic structure of Bi_2O_3 . The first observed reflection peak which is located at $2\theta = 20.62^{\circ}$ is assigned to (112) plane with estimated lattice parameters of $a = b = c = 10.55 \text{ A}^{\circ}$. The lattice parameters of this peak are comparable to those reported in the open crystallography database (COD 9007686) as a=10.25 Å, with space group of I_{23} . The analytical studying of the main peak pointed out that the preferred plane orientation of the planes in the crystal is in the (022) direction. The third peak is indexed along the (044) orientation direction. Ii is also noted from the software analyses that changing the space group to Fm3m reproduce the experimental data of Bi_2O_3 with a = b = c = 11.16 Å. The lattice parameters for the main and third peaks were estimated to be $a = b = c = 11.05 \text{ A}^{\circ}$ and a = b = c = 11.14A°, respectively. The lattice parameters for these peaks are comparable to those reported as 11.20 Å along the axis of the crystalline unit cell, in the open crystallography data base (COD 1528292) with space group of Fm3m. The parameters which were calculated with the help of previously mentioned equations in chapter two are in good agreement with literature data, where a value of a = b = c =11.420 A° were reported [38].

The X-ray diffraction (XRD) pattern of ZnPc thin film shown in Figure 4.1 displayed an amorphous phase of structure for this layer. However, the amorphous or crystal phase of ZnPc relied on the temperature at which the thin film is deposited and the annealing temperature that transforms the amorphous structure into crystalline β -form The volume fraction of β -form increased with increasing the annealing temperature [39]. The ZnPc films that were deposited at substrate temperature (Ts \approx 300K) were found to be of amorphous structure [40]. As appears in the insets of Figure. 4.1, the main peak of Bi_2O_3 shift toward lower values of diffraction angle indicating larger interplanner spacing and longer lattice parameters. Namely, the main and third peaks which are located at diffraction angles of $2\theta = 22.72^{\circ}$ shifts to $2\theta = 22.60^{\circ}$, with new lattice parameters values of 11.19 Å. However, the shift in the major peak and the decrease in the peaks intensity that is associated with larger broadening, necessarily means that a deformation in the structure of Bi_2O_3 have taken place. The impact of deformation usually resulted from the lattice distortions that cause strain due to alteration in shear stresses over the axial directions of the lattice [15].

The XRD patterns of the Bi₂O₃/ZnPc thin film in Figure. 4.1, showed the appearance of new peaks in the curve. Namely, the film had sharp and lowest intensity diffraction peaks at $2\theta = 4.34^{\circ}$ and $2\theta = 27.62^{\circ}$, which are assignable to the ZnPc nanostructure [41], and a body centered cubic phase of Bi₂O₃ [42], respectively. These proposals are in good agreement with literature data, where a values of $2\theta = 4.62^{\circ}$ with a = 12.83Å for ZnPc and $2\theta = 27.50^{\circ}$ with a = 10.25Å for Bi₂O₃ were reported. The crystallization process of ZnPc is induced by the cubic Bi₂O₃ substrate. Induced crystallization process probably resulted from the diffusion of some unbounded Bi or O atoms into the matrix of the ZnPc organic compound [43].

On the other hand, the calculated crystallite size (D), micro strain (ϵ), defect density (δ) and stacking faults (SF%) values for Bi₂O₃ film coated onto glass and recoated with ZnPc thin films are presented in Table 4.1. These structural parameters were calculated with the help of equations reported on chapter 2. In accordance with the table, the presence of ZnPc layer caused an increment in the values of the stacking faults, micro strain and crystallite size. Theses parameters exhibit values of 0.68%,

10.48 and 28 nm, respectively. The defect density decreases due to the reduction in the number of unbounded atoms.

				Mi	ller					
				indi	ices					
			h	k	1	Lattice	D (nm)	ε(X10 ⁻³)	SF%	δ(X10 ¹²
Sample	20 (°)	I (X10 ³ c/s)				constant (Å)				line/cm ²)
Bi ₂ O ₃	22.72	380	0	2	2	11.07	24	10.00	0.65	55.88
Bi ₂ O ₃ /ZnPc	22.6	383	0	2	2	11.19	28	10.48	0.68	50.74

Table 4.1 The structural parameteres for Bi₂O₃ and Bi₂O₃/ZnPc thin films.

Particularly, as can be seen from table 4.2, the increase in the crystallite size could be related to the fact that the effective ionic radius of Zn^{+2} in ZnPc which equals 88 pm [44] is smaller than the effective ionic radius of Bi^{+3} which equals 103 pm [45], as a result, replacement of Zn^{+2} in unoccupied sites of Bi^{+3} is preferable. This contributes to defects which decrease in our new thin film. So, we could assign the increase in the crystallite size to the enhancement of the crystallinity which in result increase the crystallite nucleation. This leads to coalescence and agglomeration of crystallites together producing higher grains. Furthermore, as indicated in table 4.3, every atom in any bond can attract to another atom in another bond. These interaction forces usually cause the strained structure causing the increasing of the crystallite size of Bi₂O₃ over the Bi₂O₃/ZnPc interfacing. The potential barriers at the grain boundaries decrease due to the increase in the crystallite size of the Bi₂O₃, as a result, the conduction band increased due to the decrease of the energy needed for electrons to overcome the barrier [46].

Sample	Ionic radius	Electronic
	(Å)	configuration
Bi	1.17	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^3$
Ο	1.40 ^[47]	[He] 2s ² 2p ⁴
Zn	0.74	[Ar] 3d ¹⁰ 4s ²

Table 4.2 The ionic raduis and electronic configuration of the samples.

If we think that the material composers could create chemical interaction, then in comparisons using the bond length of Bi-Bi, Bi-O, O-O, Zn-Zn and Zn-O in Table 4.3. According to the collected data in the table, the shortest bond length with higher bonding energy is assigned to Bi-O interaction. Therefore, Bi and O atoms can't interact with Zn due to the higher bonding energy needed to break the Bi-O bond. However, it may result in bond weakening that in turn allow unbounded atoms of O to react with excess Zn.

Sample	Bond length (Å)	Bond energy (kJ/mol)
Bi-Bi	2.82 ^[48]	204.40 ^[49]
Bi-O	1.93 ^[49]	337.2 ^[50]
0-0	2.00 ^[51]	142.0 ^[52]
Zn-Zn	2.33 ^[53]	126.44 ^[54]
Zn-O	1.96 ^[55]	250.4 ^[56]
Zn-N	1.97 ^[57]	160 ^[58]

Table 4.3 The bond length and bond energy of the samples.

4.2 Optical measurements:

The optical transmittance (T%) and reflectance (R%) for the Bi_2O_3 , ZnPc and $Bi_2O_3/ZnPc$ thin films shown in Figure. 4.2 were measured in the wavelength range of 190-1090 nm with the help of an evolution 350 spectrophotometer.

As seen in the figure, the transmittance of ZnPc thin film increased sharply with increasing incident light wavelengths (λ) in the ultraviolet (190-400) and infrared (700-820) nm regions. The film exhibited two high transparent regions, it reached about 90% at 500 nm, which is comparable to that of glass in the visible light region, and about 80% at 820 nm. These two regions are recognizable as B-band and Q-band being dominant in the 340–580 nm and 700–1100 nm, respectively. These bands are believed to originate from the transitions between the ZnPc molecular states a_{1u} to e_g , and a_{2u} to e_g both with b_{2u} to e_g transition, respectively [57]. The transmittance spectra for Bi₂O₃ showed a shoulder at 360 nm and have a maximum transmittance value of 40% at 570 nm.

For Bi₂O₃/ZnPc thin film, a decrease in the transmittance spectra were observed. The maximum value of transmittance was about 40% at 420 nm wavelength. However, the transmittance spectra for both ZnPc and Bi₂O₃/ZnPc have approximately similar trend of variation. The similarity is due to the wider energy band gap of ZnPc which perform as optical window.

The transmittance spectra for Bi_2O_3 , and $Bi_2O_3/ZnPc$ thin films with different thickness of Bi_2O_3 layers are also studied and displayed in Figure 4.3 and Figure 4.4, respectively. For the Bi_2O_3 and $Bi_2O_3/ZnPc$ thin films, the transmittance spectra showed lowering in the transmittance with increasing the thickness of the Bi_2O_3 layer.



Figure 4.2. The transmittance (T%) spectra for the ZnPc, Bi_2O_3 and $Bi_2O_3/ZnPc$ thin film.





Figure 4.3. The transmittance (T%) spectra for Bi_2O_3 thin films.

Figure 4.4. The transmittance (T%) spectra for Bi_2O_3 / ZnPc thin films.

It's obvious from the previous figures that a high transmittance reaching about 70% at 400 nm for sample of thickness 100 nm film. The transmittance increased with increasing λ in the ultra violet region. The thinner the film, the more settled the energy in the region above λ =400 nm. For the Bi₂O₃/ZnPc films, the thinner the film, the more resemble for the ZnPc behavior.

The reflectance spectra of ZnPc, Bi_2O_3 , $Bi_2O_3/ZnPc$ thin films are illustrated in Figure 4.5. As it is obvious from the Figure, the ZnPc spectra showed five peaks at different wavelengths values, the maximum peak value of about 9.5% is observed at 700 nm. The other peaks read a value of 7.0% and 6.5% at 380 and 635 nm, respectively. Furthermore, the reflectance spectra of Bi_2O_3 thin film show two peaks at different wavelengths values. The maximum peak value of about 12.1% at 392 nm.



Figure 4.5. The reflectance spectra of ZnPc, Bi₂O₃ (214 nm), and Bi₂O₃/ZnPc thin films.

The reflectance spectra of $Bi_2O_3/ZnPc$ thin film which are illustrated in the Figure also showed five peaks at different wavelengths values, two maximum peak value of about 9.5% and 10.0% at 500 and 720 nm, respectively. The other peaks read a value of 630 nm. The presence of the peaks at the R spectra is arise from the interfering of waves arriving at film surface and ones reflected from the bottom of the thin films.

Considering the reflectance of Bi_2O_3 thin films with different thickness shown in Figure 4.6, the Bi_2O_3 thin films showed red shift with increasing the reflectance by growing the thickness of the layer. Two peaks at different wavelength values were observed in the spectra, the maximum peak value was about 12.0% at 400 nm. Figure 4.7 also showed five peaks at different wavelength values with two maximum peaks. Five different peaks at different wavelengths values were observed in the spectra.



Fig. 4.6. The reflectance spectra of Bi_2O_3 films.



Fig. 4.7. The reflectance spectra of $Bi_2O_3/ZnPc$ films.

The measured T% and R% spectra are appointed to calculate the absorption coefficients spectra (α) which were calculated with the mentioned equations in chapter two. The absorption coefficient spectra (α) for Bi₂O₃, ZnPc and Bi₂O₃/ZnPc thin films are displayed in Figure 4.8.



Figure. 4.8. The α -E spectra for Bi₂O₃(214nm), ZnPc and Bi₂O₃/ZnPc thin films.

As the figure displayed, the absorption coefficient spectra of both ZnPc and $Bi_2O_3/ZnPc$ films show the same manner with an increase in the values of absorption coefficient for the ZnPc film in all the ranges of incident light wavelength as a result of coating the Bi_2O_3 film with the ZnPc layer. It means that the Bi_2O_3 atoms have considerably altered the electronic transitions of films. The noticeable increasing in light absorbability in the energy range between 1.4-1.8 eV for both ZnPc and $Bi_2O_3/ZnPc$ films results from the interband transitions. The interbands are usually assigned to inhomogeneities and defects which exist in the films [59]. The amorphous

nature of the ZnPc layer deposited onto glass substrate makes such types of transitions favorable [60]. On the other hand, the noticeable decrease in light absorbability in the energy range between 1.9-2.5 eV for both ZnPc and Bi₂O₃/ZnPc films probably due to the free carrier absorption that comes from the existence of lattice distortion [61], free holes and electrons [62] and transitions of carriers between conduction and valence bands [63].

The α -spectra of Bi₂O₃ film showed a different behavior from ZnPc and Bi₂O₃/ZnPc. Its absorption coefficient decreases with increasing incident photon energy (E) until reaching 2.30 eV. In the region above 2.30 eV, the α -spectra of Bi₂O₃ exhibits increasing trends of variation with increasing photon energy.



Figure. 4.9. The α -E spectra for Bi₂O₃/ZnPc thin films.

The α –spectra of the Bi₂O₃/ZnPc films showed that the absorption coefficient values decrease with increasing the thickness of the Bi₂O₃ film which may be appointed to the indirect photon transitions involvement when the thickness increased. It can also

be assigned to the increasing of the surface roughness upon increasing the thickness. The scattering becomes larger with increasing the roughness of the film surface, which in turn results in less ability of light absorption [64].

The optical absorption which is based on the difference between the incident photon and the band gap energy gives us information about the energy band gap by applying Tauc's equation [65]

$$(h\nu)^{1/p} \propto (\mathbf{E} - \mathbf{E}g) \tag{4.1}$$

The substitution of p =1/2, 2, 3, 3/2 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively. Then graphing of $(\alpha E)^2$, $(\alpha E)^{1/2}$, $(\alpha E)^{1/3}$ and $(\alpha E)^{2/3}$ versus E have shown that the graph of $(\alpha E)^2$ provides the most suitable linear fitting of the previous equation. The values of the band gaps were determined from the values of intercepting of the most suitable plots. The $(\alpha E)^2$ – E variations is shown in Figure 4.10.

As the figure show, the indirect electronic allowed transition is the most appropriate one, because it linearize most of the experimental data. The E-axis crossing for the Bi_2O_3 , ZnPc and $Bi_2O_3/ZnPc$ absorption coefficient spectra reveal energy band gap values of 2.90 eV, 2.90 eV and 2.15 eV, respectively. The value of the indirect energy bandgap for the Bi_2O_3 matches with the value of 2.85 eV reported for orthorhombic Bi_2O_3 in the handbook of semiconductors [66]. Furthermore, ZnPc is determined to have an indirect band gap of 2.90 eV similar to the value we specified [67].

Recalling that the electron affinity in Bi_2O_3 is 4.8 eV and that of ZnPc is 3.34 eV, then the conduction band offset is 1.46 eV. Since the band gaps are well aligned then the valance band offset is $\Delta E_v = \Delta E_g - \Delta E_c = 1.4$ eV. Symmetrical band offsets are obtained for this heterojunction device



. Figure 4.10 The (αE) ^{1/p}-E for Bi₂O₃, ZnPc and Bi₂O₃/ZnPc thin films with p values of (a) 1/2 (b) 2 (c) 3/2and (d)

3

The effective dielectric constant (ε_{eff}) is also determined with the help of T, R and α spectral data. The real part of the dielectric constant (ε_r) was calculated from ε_{eff} and plotted in Figure. 4.11.

The dielectric constant spectra and the reflectance spectra has shown the same behavior. While the $Bi_2O_3/ZnPc$ included four peaks in its spectra.



Figure. 4.11: The real part of dielectric constant for Bi₂O₃/ZnPc thin films.

For the Bi₂O₃/ZnPc thin film, the new peak (2.48 eV) is assigned to the optical bandgap of Bi₂O₃ [68]. While the fourth peak (3.72 eV), the direct band gap for ZnO [69]. Formation of ZnO layer is due to the weaking of the Bi-O bonds.

Figure 4.12 shows the imaginary part spectra for $Bi_2O_3/ZnPc$ interfaces. The spectra display a peak centered at 0.52 eV, followed by smooth decay. In the ultraviolet range of light, the imaginary part spectra. The imaginary part provides information about the optical conductivity of the proposed interface. The optical conductivity gain importance as it is the key for using $Bi_2O_3/ZnPc$ as optical receivers. Substituting the effective mass value as 0.65 m₀ (m* = (1/ m_{n ZnPc} +1/ m_{e Bi2O3})⁻¹, it was possible to determine the values of the plasmon frequency, the free charge carrier density, the drift mobility and the oscillator energy.



Figure 4.12 The imaginary part of the dielectric spectra for Bi₂O₃/ZnPc thin films

The results are shown in table 4.4. In accordance with the table except for the ultra violet oscillator which is dominate at 4.07 eV. All other oscillators display comparable values of plasmon frequency (2.55-2.33 GHz) regardless of the value of τ and P. This value means waves of frequency larger than (2.33-2.55GHz) can pass while those of lower frequency are rejected. On the other hand, when excited with UV led light the plasmon frequency can reach 4.66 GHz.

In general, the features of the $Bi_2O_3/ZnPc$ nominate it for use in optical communications.

In order to understand and discover information about the Plasmon-electron interaction in the $Bi_2O_3/ZnPc$ thin film and its composers, the imaginary part of the dielectric constant spectra is modeled in accordance with Drude-Lorantz approach through the relation [70],

$$\varepsilon_{im} = \sum_{i=1}^{k} \frac{w_{pei}^2 w}{((w_{ei}^2 - w^2)^2 + w^2 \tau_i^{-2})}$$
(4.2)

Where, k is the number of dominant linear oscillators, $w = 2\pi f$ is the angular frequency of the incident light, $w_p = \sqrt{4\pi ne^2/m^*}$ is the electron bounded Plasmon frequency, w_e is the reduced resonant frequency. m^* is the free carrier effective mass, n is the free electron density and τ is the average scattering time and represents the inverse of the damping coefficient. The free-carrier mobility is also determined by the formula $\mu = e\tau/m^*$. The experimental data was reproduced by fitting the Equation (4.2) through inserting the value of the effective masses as $15 m_0$ [71] and 0.68 m_0 [72], for p-ZnPc and n-Bi₂O₃, respectively. The effective mass of the Bi₂O₃/ZnPc double layers was estimated to be 0.65 m. The black colored curve which represents the theoretical fitting data of the ε_{im} spectra is illustrated in Figure 4.13. The figure indicates that the experimental data values of imaginary dielectric constant are significantly consistence with the fitted ones. The fitting parameters are tabulated in Table 4.4. The scattering time (τ) for the double junction for the first oscillator (τ_1) was 1.0 fs, when we reached the last oscillators (τ_6) it becomes 0.8 fs. In addition, increasing the oscillator energy $(\hbar w_e)$ increases the kinetic energy of electrons which intern enhances the scattering mechanism setting the electrons free. Thus, shorter scattering time and Frier electrons are achieved. Moreover, the drift mobility decreased as the number of oscillation increased; this is probably because the number of electrons that can drift in the direction of the propagation decreased. The higher the number of free electrons, the less the drift mobility and the larger the Plasmon frequency. The bounded Plasmon frequency (w_{pel}) is the cut off frequency in which

all frequencies are less than the Plasmon frequency will reject and all frequencies greater than the Plasmon frequency will transmit,



Figure 4.13 The imaginary part of the dielectric spectra for Bi_2O_3 (214 nm)/ZnPc(500 nm) thin film. The black colored plots represent the fitting which is achieved by Eqn. (4.1).

Table 4.4 The optical conduction parameteres for electron-plasmon interactions at the $Bi_2O_3/ZnPc$ interface.

k	1	2	3	4	5
τ(fs)	1.0	1.7	0.6	0.6	0.8
E _e (eV)	0.98	1.77	2.36	3.61	4.07
$p(x10^{19} \text{ cm}^{-3})$	1.2	1.0	1.2	1.0	4.0
ω _p (GHz)	2.55	2.33	2.55	2.33	4.66
μ (cm²/Vs)	2.70	4.60	1.62	1.62	2.16

Chapter Five

Conclusion

In the current work we have fabricated a new class of heterojunctions that can perform as an optoelectronic device. The device which is prepared by the thermal evaporation technique under a vacuum pressure of 10⁻⁴ mbar is composed of stacked layers of Bi₂O₃ and ZnPc thin films. The effect of Bi₂O₃ substrates on the performance of the device is also explored. Various characterization techniques including X-ray diffraction and optical spectrophotometry were employed. It is observed that Bi₂O₃ substrates induces the crystallization of ZnPc. The crystallinity of Bi_2O_3 is also improved when coated with ZnPc optically transmittance and reflectance spectra of ZnPc are modulated by the substrates thickness. Particularly, thicker films result in less transmittance in narrower transmission edge and larger reflectance. In addition, deep analyses of the absorption coefficient spectra shown that the interfaces exhibit free carrier absorption phenomena in the visible range of light. The infrared range is associated with interband transitions. It is also noted that the light absorption in ZnPc is increased when coated onto Bi₂O₃. Moreover, the prepared interfaces showed enhanced dielectric properties nominating the device for use as dielectric resonators. The computed optical conductivity parameter for Bi₂O₃ /ZnPc interfaces are found to be suitable for optical receiver applications. However, the computed data also suggests that future works must be carried out to enhance the drift mobility value in $Bi_2O_3/2npc$ so that it fit well with this film transistor technology. Some of those works could be post annealing and plasma etching.

References:

 Cacioppo, M., Scharl, T., Đorđević, L., Cadranel, A., Arcudi, F., Guldi, D. M., & Prato, M. (2020). Symmetry-Breaking Charge-Transfer Chromophore Interactions Supported by Carbon Nanodots. *AngewandteChemie*, *132*(31), 12879-12884.

[2]. Sánchez-Vergara, M. E., Gómez-Gómez, M., Hamui, L., Álvarez-Bada, J. R., & Jiménez-Sandoval, O. (2021). Optoelectronic behaviour of zinc phthalocyanines

[3]. Roguin, L. P., Chiarante, N., Vior, M. C. G., & Marino, J. (2019). Zinc (II) phthalocyanines as photosensitizers for antitumor photodynamic therapy. *The international journal of biochemistry & cell biology*, *114*, 105575.

[4].Qasrawi, A. F., &Zyoud, H. M. (2020). Ytterbium induced structural phase transitions and their effects on the optical and electrical properties of ZnPc thin films. *Optical and Quantum Electronics*, *52*(11), 1-12.

[5] Ding, R., Xu, Z., Zheng, T., Huang, F., Peng, Y., Lv, W., ...& Sun, L. (2019). Realizing high-responsive superlattice organic photodiodes by C 60 and zinc phthalocyanine. *Journal of Materials Science*, *54*(4), 3187-3195.

[6] Khusayfan N M, Qasrawi A F and Khanfar H K 2017 Materials Science in Semiconductor Processing 63-70 64

[7]. Al Garni, S. E., &Qasrawi, A. F. (2018). Characterization of Bi2O3/ZnS heterojunctions designed for visible light communications. *Materials Research Express*, 6(3), 036205.

[8]. Boukhris, I., Kebaili, I., Al-Buriahi, M. S., Tonguc, B., AlShammari, M. M., &Sayyed, M. I. (2020). Effect of bismuth oxide on the optical features and gamma shielding efficiency of lithium zinc borate glasses. *Ceramics International*, *46*(14), 22883-22888.

[9]. Abdalsalam, A. H., Şakar, E., Kaky, K. M., Mhareb, M. H. A., Şakar, B. C., Sayyed, M. I., &Gürol, A. (2020). Investigation of gamma ray attenuation features of bismuth oxide nano powder reinforced high-density polyethylene matrix composites. *Radiation Physics and Chemistry*, *168*, 108537.

[10]. R. J. Zou, Y. S. Zhang, D. X. Wang, X. Y. Cui, Y. Zhang, Y. Yuan, in Proc. of the 3rd Int. Conf. of Electronic Engineering and Information Science (ICEEIS 2016), CRC Press, Harbin, China 2016, p. 19.

[11] Y. S. Zhang, D. X. Wang, Z. Y. Wang, Y. Y. Wang, Opt. Quant. Electron. 2016, 48, 18.

[12]. Qasrawi, A. F., &Khanfar, H. K. (2020). Al/MoO 3/ZnPc/Al broken gap tunneling hybrid devices design for IR laser sensing and microwave filtering. *IEEE Sensors Journal*, 20(24), 14772-14779.

[13] El Amin, A. A., & Mahmoud, M. M. (2021, February). Study of dark electrical properties and photoelectric performance of organic/inorganic (ZnPc/p-Si) Solar cells.
In *IOP Conference Series: Materials Science and Engineering* (Vol. 1046, No. 1, p. 012010). IOP Publishing.

[14]. Khusayfan, N. M., Qasrawi, A. F., &Khanfar, H. K. (2017). Impact of Yb, In, Ag and Au thin film substrates on the crystalline nature, Schottky barrier formation and microwave trapping properties of Bi2O3 films. *Materials Science in Semiconductor Processing*, *64*, 63-70.

[15]. Alharbi, S. R., &Qasrawi, A. F. (2019). Effects of Ge substrate on the structural and optical conductivity parameters of Bi2O3 thin films. *Optik*, *181*, 714-720.

[16]. Wang J, Chen Z, Zhai G, He R, Jia X, Sun Q and Men Y 2018 Micro & Nano Letters.

[17]. Xian, T., Sun, X., Di, L., Li, H., & Yang, H. (2021). Improved photocatalytic degradation and reduction performance of Bi2O3 by the decoration of AuPt alloy nanoparticles. *Optical Materials*, *111*, 110614

[18]. Khusayfan NM, Qasrawi AF, Khanfar HK. Impact of Yb, In, Ag and Au thin film substrates on the crystalline nature, Schottky barrier formation and microwave trapping properties of Bi2 O3 films. Materials Science in Semiconductor Processing. 2017;64:63-70. DOI: doi.org/10.1016/j.mssp.2017.02.028

[19]. N.M. Khusayfan, H.K. Khanfar, thickness on the performance of the Mg/Bi2O3 plasmonicinterfaces, Thin Solid Films 651 (2018) 71–76.

[20]. Keşir, M. K., Dilber, G. Ü. L. S. E. V., Sökmen, M., &Durmuş, M. (2020). Assessing photoreductive performance of TiO2 nanocomposites sensitized with zwitterionic and quaternernized Zn-phthalocyanines. *Journal of Molecular Structure*, *1220*, 128722.

[21] Safian, N. A. M., Anuar, A., Omar, A. Z., Bawazeer, T. M., Alsenany, N., Alsoufi, M. S., ...&Roslan, N. A. (2021). Enhanced Sensitivity of Zinc Phthalocyanine-based Microporous Humidity Sensors by varying size of Electrode Gaps. *Sensors and Actuators B: Chemical*, 130158.

doped with anthraquinone derivatives and their potential use in flexible devices. *Materials Technology*, *36*(4), 250-259.

[22] Harris, W. I. L. I. E. (2008). X-ray Diffraction Techniques. *Methods of Soil Analysis: Mineralogical methods. Part 5*, *9*, 8

[23] (Aschroft, 1976) Neil W. Ashcroft and N. David Merman, Solid State Physics (Saunders College Publishing, Harcourt Brace Publishers, Fort Worth, Philadelphia, San Diego, New York, Orlando, Austin, San Antoniao, Toronto, Montral, London, Sydney, Toyko, 1976). [24] T. Hahn, ed. International Tables for Crystallography Volume A: Space-Group Symmetry.

5th ed. Springer, 2005. isbn: 978-0-470-68575-4 (see pp. 32, 33)

[25] C. Kittel, and M.E. Pau. (1996) *Introduction to solid state physics*, New York: Wiley, 8.

[26] [Bunaciu, A. A., UdriȘTioiu, E. G., &Aboul-Enein, H. Y. (2015). X-ray diffraction: instrumentation and applications. *Critical reviews in analytical chemistry*, *45*(4), 289-299.]

[27] Waseda, Y., Matsubara, E., &Shinoda, K. (2011). X-ray diffraction crystallography: introduction, examples and solved problems. Springer Science & Business Media.

[28] Ladd, Mark; Palmer, Rex (2013). Structure Determination by X-ray Crystallography

[29] Peng, W., Li, L., Yu, S., Zheng, H., & Yang, P. (2020). Structure, binding energy and optoelectrical properties of p-type CuI thin films: The effects of thickness. Applied Surface Science, 502, 144424.

[30] Al Garni, S. E., &Qasrawi, A. F. (2017). Effect of Indium nano-sandwiching on the structural and optical performance of ZnSe films. Results in physics, 7, 4168-4173.

[31] Shetty, M. N. (2013). Dislocations and mechanical behaviour of materials. PHI Learning Pvt. Ltd..

[32] Kuzel, R., Mittemeijer, E. J., &Welzel, U. (2006). Proceedings of the Ninth European Powder Diffraction Conference (EPDIC 9). In EPDIC 9. Oldenbourg Wissenschaftsverlag.

[33] Springer handbook of Electric and Photonic Materials, Safa Kasap, Peter CapperEditors. 2nd edition. Page 56-58.

[34] AlGarni, S. E., & Qasrawi, A. F. (2020). Nonlinear optical performance of CdO/InSe Interfaces. *Physica Scripta*, *95*(6), 065801.

[35] Dresselhaus, Mildred, Gene Dresselhaus, Stephen B. Cronin, and A. Gomes Souza Filho,(2018). Solid State Properties. Springer-Verlag Berlin Heidelberg.

[36] Fox, M. (2001). Optical Properties of Solids. New York: Oxford University Press.

[37] Cheung, E. (2010). Evolution of optical gain properties through three generations of electroluminescent fluorene-based polymers.

[38]. Khusayfan, N. M., & Khanfar, H. K. (2018). Impact of Mg layer thickness on the performance of the Mg/Bi2O3 plasmonic interfaces. *Thin Solid Films*, *651*, 71-76.

[39]. El-Nahass, M.M.; Zeyada, H.M.; Aziz, M.S.; El-Ghamaz, N.A. Structural and optical properties of thermally evaporated zinc phthalocyanine thin films. Opt. Mater. 2004, 27, 491–498

[41]. Islam, Z. U., Tahir, M., Syed, W. A., Aziz, F., Wahab, F., Said, S. M., ... & Sabri, M. F. M. (2020). Fabrication and photovoltaic properties of organic solar cell based on zinc ph[40]. Ahn, H., Liou, W. H., Chen, H. M. P., & Hsu, C. H. (2015). Anisotropic exciton relaxation in nanostructured metal (Zn and F 16 Zn)-phthalocyanine. *Optics Express*, 23(3), 3230-3235.

thalocyanine. *Energies*, 13(4), 962.

[42]. Khusayfan, N. M., Qasrawi, A.F., & Khanfar, H. K. (2017). Impact of Yb, In, Ag and Au thin film substrates on the crystalline nature, Shottcky barrier formation

and microwave traooing properties of Bi2O3 films. *Journal of Alloys and Compounds*, 64, 63-70.

[43] Qasrawi, A. F., & Zyoud, H. M. (2020). Fabrication of (Au, Mn)/ZnPc/Ag interfaces as radiowave/microwave band filters. *physica status solidi* (*a*), 217(22), 2000171.

[44]. Anwar, M. S., & Koo, B. H. (2022). Observation of the magnetic entropy change in Zn doped MnFe2O4 common ceramic: Be cool being environmental friendly. *Current Applied Physics*, *39*, 77-83

[45]. Yang, D., Lan, Y., Yuan, C., Lai, H., Wu, J., Feng, Q., ... & Rao, G. (2022). Enhanced energy storage density of antiferroelectric AgNbO3-based ceramics by Bi/Ta modification at A/B sites. *Journal of Materials Science: Materials in Electronics*, 1-10.

[46]. Louis, J., Padmanabhan, N. T., Jayaraj, M. K., & John, H. (2022). Crystal lattice engineering in a screw-dislocated ZnO nanocone.

[47]. Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. Sect. A. 32, 751–767 (1976).

[48]. Ho, L. P., & Tamm, M. (2021). Stabilization of a bismuth–bismuth double bond by anionic N-heterocyclic carbenes. *Dalton Transactions*, *50*(4), 1202-1205.

[49]. Guo, S., Li, H., Lu, Y., Liu, Z., & Hu, X. (2020). Lattice softening enables highly reversible sodium storage in anti-pulverization Bi–Sb alloy/carbon nanofibers. *Energy Storage Materials*, 27, 270-278.

[50]. Qin, H., Zhang, Y., He, S., Guan, Z., Shi, Y., Xie, X., ... & Xu, H. (2021). Increasing the migration and separation efficiencies of photogenerated carriers in CQDs/BiOC1 through the point discharge effect. *Applied Surface Science*, 562, 150214.

[51]. Kono, Y., Ohara, K., Kondo, N. M., Yamada, H., Hiroi, S., Noritake, F., ... & Yabashi, M. (2022). Experimental evidence of tetrahedral symmetry breaking in SiO2 glass under pressure. *Nature communications*, *13*(1), 1-8.

[52]. Cheng, X., Guo, H., Zhang, Y., Korshin, G. V., & Yang, B. (2019). Insights into the mechanism of nonradical reactions of persulfate activated by carbon nanotubes: Activation performance and structure-function relationship. *Water research*, *157*, 406-414.

[53]. Zhang, N., Hussain, M. I., Xia, M., & Ge, C. (2021). Graphitic Carbon Nitride Nanosheets-Immobilized Single-Atom Zn Towards Efficient Electroreduction of CO2. *Nano*, *16*(02), 2150016.

[54]. Mondal, R., Singh, Y. B., Das, A. S., Kabi, S., Singh, L. S., & Biswas, D.
(2021). Effect of Zn incorporation on physical properties of quaternary 0.7 Se–0.2
Ge–(0.1-x) Sb–xZn chalcogenide system: A theoretical prediction. *Physica B: Condensed Matter*, 612, 412896.

[55]. Pandarinath, M. A., Muralikrishna, P., Babu, D. S., Kumar, B. V., & Upender, G. (2021). Vibrational, thermal and optical studies of 30TeO2-39.5 B2O3-(30-x) ZnO-xLi2O-0.5 V2O5 ($0 \le x \le 30 \mod \%$) glass system. *Journal of Non-Crystalline Solids*, 566, 120875.

[56] Yu, Z., Cao, X., Wang, S., Cui, H., Li, C., & Zhu, G. (2021). Research Progress on the Water Stability of a Metal-Organic Framework in Advanced Oxidation Processes. *Water, Air, & Soil Pollution, 232*(1), 1-19.

[57]. Qasrawi, A. F., & Zyoud, H. M. (2020). Ytterbium induced structural phase transitions and their effects on the optical and electrical properties of ZnPc thin films. *Optical and Quantum Electronics*, *52*(11), 1-12

[58]. Patiño, R., Campos, M., & Torres, L. A. (2007). Strength of the Zn– N Coordination Bond in Zinc Porphyrins on the Basis of Experimental Thermochemistry. *Inorganic chemistry*, *46*(22), 9332-9336.

[59]. Senthilarasu, S., Sathyamoorthy, R., Lalitha, S.U.B.B.A.R.A.Y.A.N.K.,

Subbarayan, A., Natarajan, K.: Thermally evaporated ZnPc thin flms—band gap dependence on thickness. Sol. Energy Mater. Sol. Cells 82(1–2), 179–186 (2004)

[60] M. Dresselhaus, G. Dresselhaus, S.B. Cronin, A.G.S. Filho, Interband transitions,in: Solid State Properties, Springer, Berlin, Heidelberg, 2018, pp. 345–364.

[61] Skaistys, E., & Sugakov, V. I. (1971). The free-carrier absorption in polycrystals. *physica status solidi* (*b*), 48(2), K99-K101.

[62] Sivakumar, T., Anbarasan, R., Sundar, J. K., & Lakshmi, M. A. (2020). Enhancing the SHG effect of zinc chloride-doped DAST single crystals: new potential materials for nonlinear optical device applications. *Journal of Materials Science: Materials in Electronics*, *31*(15), 12943-12954.

[63] Dell'Olio, F., Ciminelli, C., & Armenise, M. N. (2013). Theoretical investigation of indium phosphide buried ring resonators for new angular velocity sensors. *Optical Engineering*, *52*(2), 024601.

[64]. Qasrawi, A., Alharbi, S., & KJhusayfan, N. (2020). Thickness and annealing effects on the structural and optical conductivity parameters of zinc phthalocyanine thin films.

[65] Wager, J. F. (2017). Real-and reciprocal-space attributes of band tail states. *AIP Advances*, 7(12), 125321.

[66] Dolocan, V. handbook of semiconductors: Appl. Phys. 16 (1978) 405.

[67]. Benhaliliba, M. (2022). The effect of Zn metal on the linear and nonlinear optical properties of Organic Phthalocyanine (Pc) material-Electrical characterization

[68]. Akazawa, H. (2021). Characterization of Bi2O3 thin films for doping photoluminescent Er3+ ions. *Ceramics International*, 47(3), 3292-3298.

[69]. Lakshmi, R. R., Sruthi, D., Prithiv, K., Harippriya, S., & Aranganayagam, K. R. (2018). Synthesis of ZnO and Ag/ZnO Nanorods: Characterization and Synergistic In Vitro Biocidal Studies. *Advanced Science Letters*, *24*(8), 5490-5495.

[70] Kayed, T. S., & Qasrawi, A. F. (2020). Pseudodielectric Dispersion in As2Se3 Thin Films. *physica status solidi* (*b*), 257(3), 1900548.

[71] Qasrawi, A. F., & Zyoud, H. M. (2020). Dielectric dispersion at the Mn/ZnPc interfaces. physica status solidi (b), 257(6), 2000089.

[72] Chitrada, K. C., Raja, K. S., Gakhar, R., & Chidambaram, D. (2015). Enhanced photoelectrochemical performance of anodic nanoporous β-Bi2O3. *Journal of The Electrochemical Society*, *162*(6), H380.

الملخص

في هذه الأطروحة تمت دراسة الأجهزة غير المتجانسة المصنوعة عن طريق تكديس طبقات من البزموث أوكسايد Bi₂O₃ والزنك فثالوسيانين (ZnPc). تم تغليف العينات بتقنية التبخير الحراري تحت ضغط تفريغ

⁴⁻10 ملي بار و دراسة Bi₂O₃ و ZnPc و ZnPc المنتجة من الناحية الهيكلية Bi₂O₃ المنتجة من الناحية الهيكلية والبصرية. لوحظ أن طلاء ZnPc على Bi₂O₃ متعدد البلورات يؤدي إلى تبلور ZnPc. كلا الطبقتين المكدستين ذات طبيعة متعددة الكريستالات. يُعزى التبلور المستحث لـ ZnPc إلى تبديل الذرات وآليات تكامل الروابط.

بشكل عام، قللت طبقة ZnPc من الإجهاد وكثافة الخلل في Bi₂O₃ مما أدى إلى أحجام بلورية أكبر. ربما يرجع هذا السلوك إلى أنصاف الأقطار الأيونية المنخفضة لـ 2 + R مقارنةً بـ Bi 3 + ، ومن ناحية أخرى، أظهرت الدراسات البصرية أن تكوين طبقتين مكدستين مصحوب بامتصاص الشحنات الحرة للطاقة وانتقالها بين النطاق المسموح، ويلاحظ أيضًا أن زيادة سمك طبقة Bi₂O₃ ينتج عنها انتقالات فوتونية غير مباشرة مسموح بها في واجهات / Bi₂O₃ Bi₂O₃. بالإضافة إلى ذلك، على الرغم من أن كلا من Bi₂O₃ وPC يظهران نفس فجوات نطاق الطاقة (2.2 \u03)، فإن واجهة ZnPc / Bi₂O₃ Bi₂O₃ تعرض فجوة نطاق أضيق (2.15 فولت). لوحظ أيضًا أن الأجهزة غير المتجانسة Bi₂O₃ / ZnPc يظهران نفس فجوات فولت). لوحظ أيضًا أن الأجهزة غير المتجانسة Bi₂O₃ / ZnPc تظهر حالة تماثل وقيم لنطاق تكافؤ 1.46 ve و1.40 ve، على التوالي. علاوة على ذلك، أظهرت در اسات تتشتت العازل معلى الأجهزة غير المتجانسة المقترحة أن فيلم ZnPc / Bi₂O₃ وBi₂O₃ ونعال وقيم لنطاق معلى الأجهزة غير المتجانسة 2.40 من أن كلا من والوري تظهر حالة تماثل وقيم لنطاق نطاق الطاقة (2.5 ve) معلى التوالي. علاوة على ذلك، أظهرت در اسات تتشت العازل فولت). وحظ أيضًا أن الأجهزة غير المتجانسة Bi₂O₃ / ZnPc وقيم لنطاق تطهر حالة تماثل وقيم لنطاق تحافز على المجزة غير المتجانسة 2.40 مو 2.50 وقيم لنواي معلى الأجهزة غير المتجانسة المقترحة أن فيلم 2.50 و 3.20 وقيرة فولت. كشفت نمذجة درود-مع طاقات حرجة تتركز عند 2.48 و1.70 و 2.90 و3.20 وقيم فولت. كشفت نمذجة درود-مع طاقات حرجة تتركز عند 2.48 و1.70 و 2.90 و3.20 وقيم وفولت. كشفت نمذجة درود-مع طاقات حرجة تتركز عند 2.48 و1.70 و 2.90 و3.20 وقيم فولت. كشفت نمذجة درود-مع طاقات حرجة التخيلي من أطياف العزل الكهربائي عن معلمات الموصلية الضوئية التي توضح ملاءمة الأجهزة للتطبيقات الإلكترونية الضوئية.