Electrical and Structural properties of (ZnTiO3)/Epoxy System Nanocomposite Thin films

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Abstract. Spin coating technique using to prepare two layers of epoxy reinforced by weight (0Wt%,1Wt%,2Wt%,3Wt%,4Wt%) nano ZnTiO3 additives uniform thin films with a fixed thickness of (0.7 μm) on glass floors at room temperature, dispersion and magnetic stirring techniques are used to prepare the nanocomposites thin films. The purpose of this study was to produce a new modified polymer (ZnTiO3/Epoxy) nanocomposite thin films then evaluate electrical and structural properties of these thin films. The electrical properties of thin films have a degree effect temperature on the resistance (R) of thin films within the range (303 - 433) K or (30 - 160) °C. Electrical conductivity and activation energy of the thin film was calculated where the results indicate that there is a two activation energy and this means there is two mechanisms connection. It is also shown by measurements of the effect of the whole (ZnTiO3/Epoxy) nanocomposite thin films have a connection from the negative type (n-type). Structural properties include XR-D and SEM. XRD, show crystal structure of zinc titanite (ZnTiO3) nano powder. Scanning electron microscopy SEM, show clearly analysis for different weight ratio affected thin films surfaces.

Keywords. Nanocomposites, Epoxy, nanoZnTiO3, thin film, Spin coating, electrical and structural properties.

1. Introduction
Unique set of properties of polymer such as stiffness, light weight, low cost, and ease of processing and fabrication which med it one of the important type of materials finding their way into the electronic industries [1]. Nanocomposite is a special composite where one of the phases has one, two or three dimensions less than 100 nm [3]. An important parameter for characterizing the effectiveness of reinforcement is the ratio of surface to area (A) of reinforcement to volume of reinforcement (V) [4]. ZnO and TiO2 are the most important nano filler Oxides used in (PV technology) it is used as a transparent conductive oxide (TCOs).Zinc oxide is a direct gap semiconductor 3.4 ev, with a considerable fraction of ionic bonding [5] Spin coating is currently the predominant technique employed to produce uniform thin films of photosensitive organic materials with thickness of the order of micrometers and nanometers. The pioneering analysis of spin coating was performed more than fifty years ago by (Emil et al) who considered the spreading of a thin axsymmetric film of fluid on a planner
substrate rotating with constant angular velocity. Our goal of this work is to develop materials and devices that are capable of making large improvements of electrical and structural properties of polymer solar cells.

2. Theoretical Considerations

Electrical properties of the nano system (ZnTiO3) Thin-films models will be measured electrical Conductivity in crystalline and random semiconductors is due to the release of electrons from the associated atoms. The following equation shows the electrical resistance relationship of semiconductors with temperature [3, 4].

\[ R(T) = R_0 \exp\left(\frac{-B}{T}\right) \quad \text{(1)} \]

Where B and Ro constants depend on semiconductor properties and this equation can be rewritten in terms of conductivity as follows:

\[ \sigma_{d.c} = \sigma_0 \exp\left(\frac{-B}{T}\right) \quad \text{(2)} \]

and by multiplying the span and the base of the KB and placing KBB = Ea

\[ \sigma_{d.c} = \sigma_0 \exp\left(\frac{-E_a}{K_B T}\right) \quad \text{(3)} \]

Whereas:

- Ea: Activation energy Equivalent to (Ec-Ef) and is a characteristic of the semiconductor, which varies depending on the temperature [5-6].
- Ef: Fermi level energy donor.
- \( \sigma \): Continuous electrical connection.
- \( \rho \): Less metal connection.
- KB: Constant Boltzmann.
- T: absolute temperature.

Or

\[ \rho = \frac{R b t}{L} \quad \text{(4) A} \]

and continuous conductivity from the inverted calculation of the resistance value.

\[ \sigma_{d.c} = \frac{1}{\rho} \quad \text{(4) B} \]

Whereas:

Resistivity (cm)
- R: Thin film resistance
- b: pole width (cm)
- t: thickness of the thin film (cm)
- L: Distance between aluminum poles (cm)

The equation above expresses the continuous electrical conductivity obtained from high temperatures through thermal excitation or thermal excitation as charge carriers where the electrons jump to the extended levels at and above the Ec level. [7, 8, and 9]

The scientist Hall, observed that the presence of a regular magnetic field on a sample of conductive material carrying an electric current in a vertical direction on the current direction of the current will generate a voltage difference across the two ends of the connector in a vertical direction on both the current and the magnetic field. The voltage difference generated by Hall Voltage (VH) with electric field called Hall field (EH) [10, 11].
The Hall effect mechanism, depends on a magnetic field (Bz) directed towards the Z axis in a vertical direction on an electric current (X-direction) through a n-type semiconductor, the (FH) generated by the magnetic field and thus the result of the force affecting the carriers in the direction of normal is equal to zero. [12, 13] this can be

\[ J = -qN_D \nu_X \ldots (5) \]

The above equation represents the current resulting from the movement of electrons towards (X) in terms of velocity of deviation and number of electrons [14].

Whereas:
P: Number of charge carriers of gaps in volume unit

MH can be found from the relationship between Hall and conductivity (\( \sigma \))

\[ \mu_H = \frac{\sigma}{N_D q} = \frac{|R_H| \sigma}{...} \ldots (6) \]

Whereas:
MH: Hall mobility and measured by (cm² / V.S)[14].

Structure properties are an important means of studying the crystalline structure of thin films determine the nature of crystalline structure and crystalline phases as well as the trend of thin films prepared under certain conditions. Crystalline size is determined by applying the Scherer equation [15].

\[ D = K \lambda / \beta \cos \theta \ldots \ldots (7) \]

Where k is particle shape factor (0.9), \( \lambda \) the wavelength of Cu kα1 radiation (1.54056Å0), the full-width at half-maximum of the selected diffraction peak (degrees), \( \theta \) the Bragg angle, d the crystalline size (Å) [16-17]. Scanning electron microscope (SEM) is probably the most widely used semiconductor characterization.

Annealing: It is the process of exposing the thin film to a certain temperature and for a period of time. Thickness was calculated using the gravimetric method from the following equation.

\[ t = \frac{m_1 - m_2}{\rho} A \ldots \ldots \ldots (8) \]

t: thickness of the thin film
m1-m2: difference in weight before and after deposition
\( \rho \): density of polymer nanocomposite
A: surface area of substrate

3. Experimental Work
In this work Epoxy resin (105), hardener (3:2 wt%) used as a (matrix material) for the preparation of nanocomposite thin film material by dispersing nano powder (reinforced material) particle size of (ZnTiO3) is (50-80) nm purity,(99%) and proportions by weight (0Wt%,1Wt%,2Wt%,3Wt%) to get (nanocomposite material), spin coating technique using to achieve better state of dispersion. The treated nanoparticles are then added to the Epoxy resin followed by magnetic stirring (100 rpm) for an hour to homogenization followed by spin coating (1500 rpm) for (30 sec) time, one type of glass is used of dimensions (2.5*2.5) cm² (German origin) wash thoroughly with water, then washed with hydrolysis acid diluted (HCl) then it is placed in alcohol Pure ethanol, then in the acetone to remove the residue of the oil impurities for (15) min. The prepared mixture, deposited homogenously in the middle of the glass bases then put into the spin coating 1500 rpm for 30 seconds, then placed in a heat oven for the process of annealing of (50C0) for 2 hours. to be ready for use, then weight the substrates using a sensitive balance (10-4 mg). Spin coating is currently the technique employed to produce uniform thin films of photosensitive organic materials with thickness of the order of micrometers and nanometers.

4. Results and Discussion
The continuous conductivity was calculated by studying the change in resistivity ($\rho$) of thin films with temperature using the following relation

$$\rho = \frac{R d}{L}$$

and

$$\sigma_{d,c} = \frac{1}{\rho}$$

continuous conductivity (\(\Omega\cdot\text{cm}\))-1. By drawing the correlation between (\(\rho\)) and inverted temperature (1000 / T) the slope is calculated and then the activation energy is calculated (Ea = Ec-Ef. By multiplying the slope by Boltzmann constant (KB) with eV units by the following equation: 

$$Ea = 0.08625 \times \text{Slope}.$$ 

Then measured the resistance (R) of the thin films (ZnTiO3) within the temperature range (30 -160) C° and by knowing the dimensions of the thin film were found both resistivity ($\rho$) and conductivity and activation energy and according to the relationships above. Tables (1) and figure (1) illustrate the continuous conductivity values of prepared thin films and the values of the activation energy under atmospheric pressure conditions and the thermal range (30-160) C°.

**Table 1.** Activation energy values for Epoxy /ZnTiO3 nanocomposite with deference w% 

| Activation energy | Epoxy (pure) | 1W% Epoxy/ZnTiO3 nanocomposite | 2W% Epoxy/ZnTiO3 nanocomposite | 3W% Epoxy/ZnTiO3 nanocomposite | 4W% Epoxy/ZnTiO3 nanocomposite |
|-------------------|--------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Ea(eV)            | 0.003        | 0.0307                         | 0.321                         | 0.26                           | 0.17                           |
| Ea(eV)            |              | 0.190                          | 0.182                         | 0.035                          | 0.1                            |

**Figure 1.** Relation between ln ((\(\sigma_{d,c}\))) and 1000/T for (ZnTiO3/Epoxy) thin films with (1%, 2%, 3%, 4%) additives.

Hall Effect Results (Table 2) from the results between I&V the results shows that there is inversely relation between them which voltage decrease with increase the field applied on the two side of thin film of ZnTiO3/Epoxy nanocomposite (n-type). Hall Effect coefficient calculated by using relation:

$$E_{H} = \frac{V_{H}}{W_{r}} = -\frac{1}{qN_{D}} \frac{I_{x}}{W_{r}B_{z}}$$

The limit is known as Hall Coefficient (RH) Thus, the previous equivalent shall be as follows:

$$V_{H} = -E_{H} \frac{B_{z}I_{x}}{r}$$

is by semiconductor type, which is negative for the n-type Semiconductor and is positive for the p-type semiconductor. Using the two links:
Table 2. Hall measurements results for ZnTiO3/Epoxy nanocomposite.

| Sample                          | Conductivity (Ω cm) | Average Hall Coefficient (cm²) | Resistivity (Ω cm) | Mobility (cm²/Vs) | Carrier Concentration cm⁻³ |
|---------------------------------|---------------------|-------------------------------|---------------------|-------------------|---------------------------|
| Epoxy(pure)                     | 2.519E-5            | -5.09E+7                      | 3.969E+3           | 1.284E+3          | -1.225E+11                |
| 1W% Epoxy/ZnTiO₃ nanocomposite  | 9.091E-8            | -6.091E+10                    | 1.100E+7           | 6.111E+3          | -9.286E+7                 |
| 2W% Epoxy/ZnTiO₃ nanocomposite  | 1.241E-7            | -2.142E+9                     | 8.059E+6           | 2.658E+2          | -2.914E+9                 |
| 3W% Epoxy/ZnTiO₃ nanocomposite  | 1.074E-7            | -4.211E+10                    | 9.315E+6           | 4.934E+3          | -1.483E+8                 |
| 4W% Epoxy/ZnTiO₃ nanocomposite  | 9.304E+8            | -4.211E+10                    | 1.075E+7           | 3.91E+3           | -1.483E+8                 |

Through the results of X-ray diffraction of the pure and reinforced with nanoZnTiO₃ and epoxy (nanocomposite) showed Epoxy resin thin film is amorphous as it is shown in Figure 2 but [ZnTiO₃] nano powder are crystalline, cubic type as it is shown in the Fig. 3 multi-gelling materials Figure 4 XRD-of (ZnTiO₃)/Epoxy nanocomposite thin films with (1%, 2%, 3%, 4%) additives. Figure 5 showed Result of (SEM) measurement for pure epoxy and epoxy reinforced with nano(ZnTiO₃) respectively thin films the picture showed that increase in homogeneous of ZnTiO₃ thin films and holes are reduced which appear clearly the complete of crystal growth and reduced defects and this results was agreement with increasing grain size which get it from XR-D results [17, 18].

Figure 4. XRD- of (ZnTiO₃)/Epoxy nanocomposite thin films with (1%, 2%, 3%, 4%) additives.
Figure 5. SEM images magnification (10^-m) (a) pure epoxy resin.(b)1% ZnTiO3/Epoxy nano composite (c) 3% ZnTiO3/Epoxy nano composite

5. Conclusions
The (ZnTiO3/Epoxy) nanocomposite thin films have a connection from the negative type (n-type). They can be used in solar cells, sensors and batteries as negative.

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