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Preparation of TiO_2 Nanolayers via. Sol-Gel Method and Study the Optoelectronic Properties Assolar Cell applications

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Abstract: The aim of this research is to prepare TiO_2 films on Indium Tin Oxid (ITO)-glass substrates with various nano-layers via. sol-gel method and study the properties that make these films suitable for solar cell application. Polycrystalline TiO_2 films are resulting from X-Ray Diffraction (XRD) examination with preferred orientation along (101) plane appear for the films with thickness more than 107 nm (3 layers) at $2\theta = 25.62°$. Other peaks appear (211), (004) and (200) at $2\theta = 30.27$, 35.49 and 48.69, respectively and the crystallite size ranged from 15-32 nm for the prepared films. The homogeneity of the films is appear from the scanning electron microscope in addition of smooth and free of pinholes. UV-Visible spectrophotometer use to recording the transmittance spectra in the range of 360-1000 nm. The energy gaps were determined by Touc Model and from the dispersion parameters which found good comparable to be 3.21 eV for the film thickness 155 nm (5 layers). The energy loss of electrons which travelling through surface and bulk of material also determined. Urbach energy is increase with the increasing of film thickness. Dispersion parameters (E_o, E_d) determined from Wemple and DiDomenco relationship.

Key words: Sol-gel, TiO_2 layers, dispersion parameters, single-oscillator model, surface, comparable

INTRODUCTION

Many purposes for preparing TiO_2 thin films or nanoparticles by sol-gel method; thin layers of (TiO_2) with a high photocatalytic activity and antibacterial properties for use as a self-cleaning transparent coatings for windows in outdoors applications (Haider *et al*., 2017) biosensor (Cui *et al*., 2018) by doping TiO_2 onto CNTs, among applications of CNTs that have optical property to its application in micro electronic and electro-opticindustry (Askari *et al*., 2017) C, N co-doped TiO_2 noticeably increase in the visible-light-photocatalytic activity performance is ascertained mainly due to the improvement of electron-hole separation and charge carrier migration (Mohamed *et al*., 2018) Titanium dioxide (TiO_2) is a cheap, non-toxic and one of the most efficient semi conductor photo catalysts for extensive environmental applications because of its strong oxidizing power, high photochemical corrosive resistance and cost effectiveness (Weast and Selby, 1967). Titanium dioxide occurs in nature as the well-known naturally occurring minerals (Rusu and Rusu, 2005) rutile with energy gap 3.05 eV, anatase with energy gap 3.26 eV (Carp *et al*., 2004) and brookite with energy gap 2.98 eV (Stankova *et al*., 2009). This range of band gap of is suitable for a variety of applications, especially in solar cells (Yalcin and Yakuphanoglu, 2017; Chen *et al*., 2017; Choe and Han, 2017; Murugakoothan *et al*., 2014). Although, preparation is important in a sol-gel method, however, many researchers have been prepared titanium oxide in other methods such as; PLD (Aadim *et al*., 2015) RF magnetron sputtering (Goto *et al*., 2015) spin-coating (Hsieh *et al*., 2010; Mothi *et al*., 2014) e-Beam evaporation (Hossain *et al*., 2015) liquid phase deposition (Begum *et al*., 2008) spray pyrolysis (Patil *et al*., 2014). Due to the special attention focused onthe monolayer to obtain the unique properties that are found in the monolayer, therefore, it is important to study these structures (Jappor, 2017). In this study, layers are prepared from TiO_2 via. sol-gel method and study the structural and optical properties for various layers for solar cell application.

MATERIALS AND METHODS

Methods of synthesis and preparation of thin film: The three components used in the preparation of the TiO_2 sol-gel films can be explained as follows Titanium

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Isopropoxide (TIP) Ti $[OCH(CH_3)_2]_4$ whose purity is 98%, Acetic acid CH_3COOH whose purity is 99.5% and Ethanol CH_3CH_2OH whose purity is 99.7-100%. All chemicals are as supplied by Aldrich chemicals Ltd. TIP is a metal alkoxide which has the general formula M (OR n where, M = Metal, R = Alkyl group and n is the valence of the metal atom.TiO_2 thin films are prepared by sol-gel spincoating method by using 50 mL of Ethanol and permitting to be mixed for 50 min an amount of 5 mL of acetic acid with a pipette into Ethanol and stir by using a magnetic stirrer it for 5 min and measure 6.3 mL of TIP is added by pipette to a beaker containing a mixture of glacial acetic acid and ethanol that have been mixed for 5 min. The mixture is continually stirred by using a magnetic stirrer addition for further 2 min after adding of the precursor.The effects of altering molar ratios of acid TIP on thickness and absorption properties of the films are investigated. The sols manufactured due to the method described above are immediately used to produce coating on the Indium Tin Oxid (ITO)-glass substrates. Thin films of TiO_2 are deposited by the method of spin coating by using a standard photoresist spinner. Glass plates coated with transparent conducting (ITO) are used as substrates, these have been thoroughly cleaned in Millipore water and neutral detergent for 10 min by using an ultrasonic bath and then propanol has been applied for further 10 min in the ultrasonic bath.The solution is placed into a convenient glass flask and is sealed well. This sealing should keep the solution from contaminated air. Finally the substrates have been rinsed by deionized water and then dried out with nitrogen gas. TiO_2 films are spin coated onto the cleaned (ITO) substrates with a spinning speed 2000 rpm. All samples in the furnace program are put at 550°C

RESULTS AND DISCUSSION

Structural analysis of films: The crystal structure of TiO_2 films that prepared via. sol-gel method at various layers on ITO substrates were investigated using X-Ray Diffraction (XRD). Figure 1 represents the XRD pattern to evaluate the crystallographic properties of TiO_2 film layers that deposited on ITO substrate. The XRD results show that the films with thickness 37, 72 nm (1, 2 layers, respectively) are amorphous and when the thickness increase lead to the polycrystalline films (107, 126, 155 nm (3-5 layers, respectively). The TiO_2 polycrystalline films has anorientation peak along (101) plane at 2θ = 25.62° and the other peaks corresponding to the (211), (004) and (200) at 2θ = 30.27°, 35.49° and 48.69°, respectively. The crystallite size (D) was estimated by scherrer formula (Krawitz, 2001).

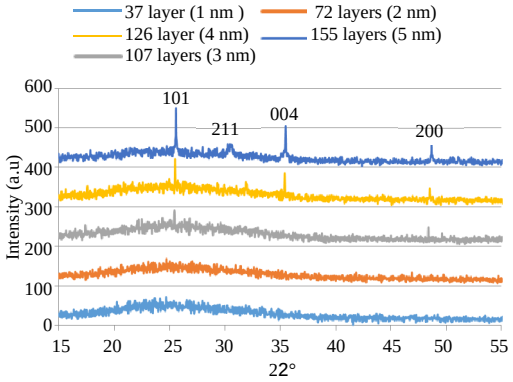

Fig. 1: XRD pattern of TiO_2 films with various layers

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

Where:

K = The Scherrer constant and equal 0.94

λ = The wavelength of X-ray (1.54060 Å)

β = The Full Width at Half Maximum (FWHM) for the peaks and

θ = The Bragg diffraction angle

The crystallite size was calculated from Scherrer formula to be 15 nm (FWHM = 0.224) and increased with the increasing of film thickness to be 33 nm for the film with thickness 155 nm (FWHM = 0.454)

The morphological properties of TiO_2 films can determine from Scanning Electron Microscope (SEM). Figure 2 illustrates the homogeneity and continuous separate coating layersand also it can seen the films are smooth and free of pinholes.

Optical properties: The optical properties of TiO_2 nanoparticle layers are determine from recording the absorbance and transmittance spectra via. UV-Visible spectro photo meter (UV/1800/Shimadzu spectro photo meter) in the wavelength range 360-1000 nm.

The transmittance spectra was presented in Fig. 3. From the Fig. 3, it can notice the decrease of the transmittance with the increasing of thickness (number of layers) for the TiO_2 nanoparticle films. The values of transmittance spectra are ranged from 60-80% approximately in the visible region, make these films suitable in the solar cell applications. The optical Energy gap (E_g) of nanostructure TiO_2 layers can determine from the following relation (Abass, 2015):

$$(\alpha h\upsilon)^n = B(h\upsilon - E_g) \quad (2)$$

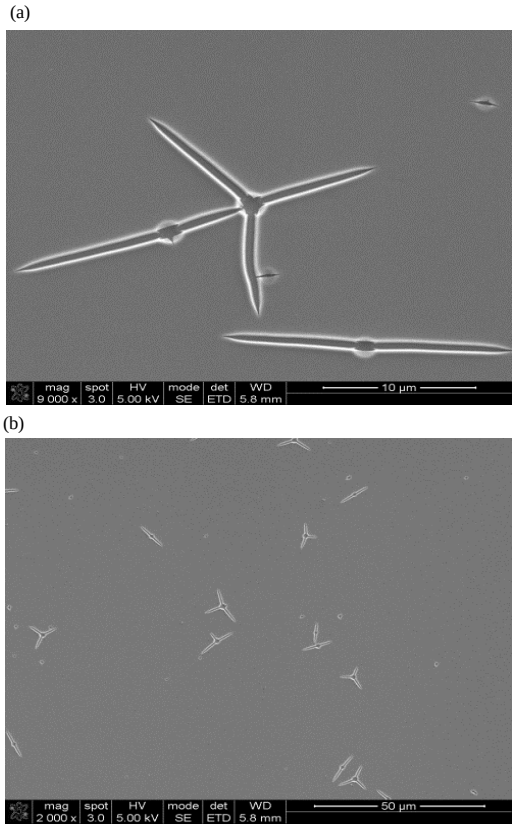

Fig. 2: SEM images of annealed TiO_2 film

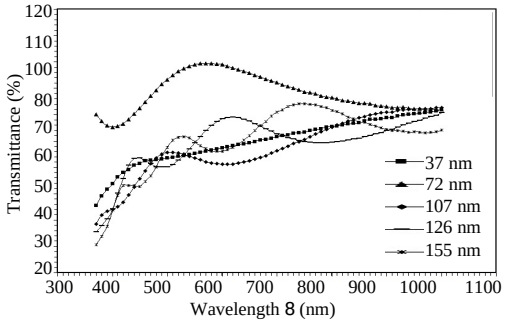

Fig. 3: Transmittance spectra of TiO_2 films for various thickness

Where:
$h\upsilon$ = The photon energy, B is a constant and
n = The allowed transition type (n = 2 for direct transition, n = 1/2 for indirect transition)

To determine the optical energy gap, it can plot the $(\alpha h\upsilon)^2$ on the y-axis versus photon energy on the x-axis, the extrapolation that intercept with x-axis represent the value of energy gap (Abass and Latif, 2016) as shown in Fig. 4. The values of energy gap for TiO_2 films are decreased with the increasing of number of layers from 3.3 eV for one layer (37 nm) to 3.21 eV for five layers (155 nm).

The complex dielectric constant is very important because provides information about electronic structure of the films. There Al part of dielectric constant (ε_r) describes the propagation characteristics while the imaginary part (ε_i) describes the rate of attenuation along the propagation direction were calculated using the formulas (Buet *et al*., 1991):

$$\varepsilon_r = n^2 - k^2 \quad (3)$$

$$\varepsilon_i = 2nk \quad (4)$$

where, k is the extinction coefficient. The real and imaginary dielectric constants are decreased with the increasing the number of layers of TiO_2 films as shown in Fig. 5.

The Surface Energy Loss Function (SELF) and Volume Energy Loss Function (VELF) are represent the energy loss of electrons which travelling through surface and bulk of material, respectively which obtained from complex dielectric constant as the following formulas (Mahmoud, 1987; Park, 2012):

$$SELF = \frac{\varepsilon_i}{(\varepsilon_r+1)^2 + \varepsilon_i^2} \quad (5)$$

$$VELF = \frac{\varepsilon_i}{\varepsilon_r^2 + \varepsilon_i^2} \quad (6)$$

The SELF and VELF versus photon energy are presented in Fig. 6 and 7, respectively. From the Fig. 6 and 7, the SELF and VELF are decreased with the increasing of number of layers (thickness) leads to less loss of electron energy with the increasing of thickness. Also, the values of surface energy loss are less than the volume energy loss, this result is agreement with the researcher Wug-Dong (Park, 2012).

The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing represent the Urbach Energy (E_U) and given by the following formula (Urbach, 1953):

$$\alpha = \alpha_o \exp(h\upsilon/E_U) \quad (7)$$

Where:
α_o = The α constant and
$h\upsilon$ = The photon energy

To determine the value of Urbach energy, it can plotting ln α as a function of photon energy as shown in the Fig. 8

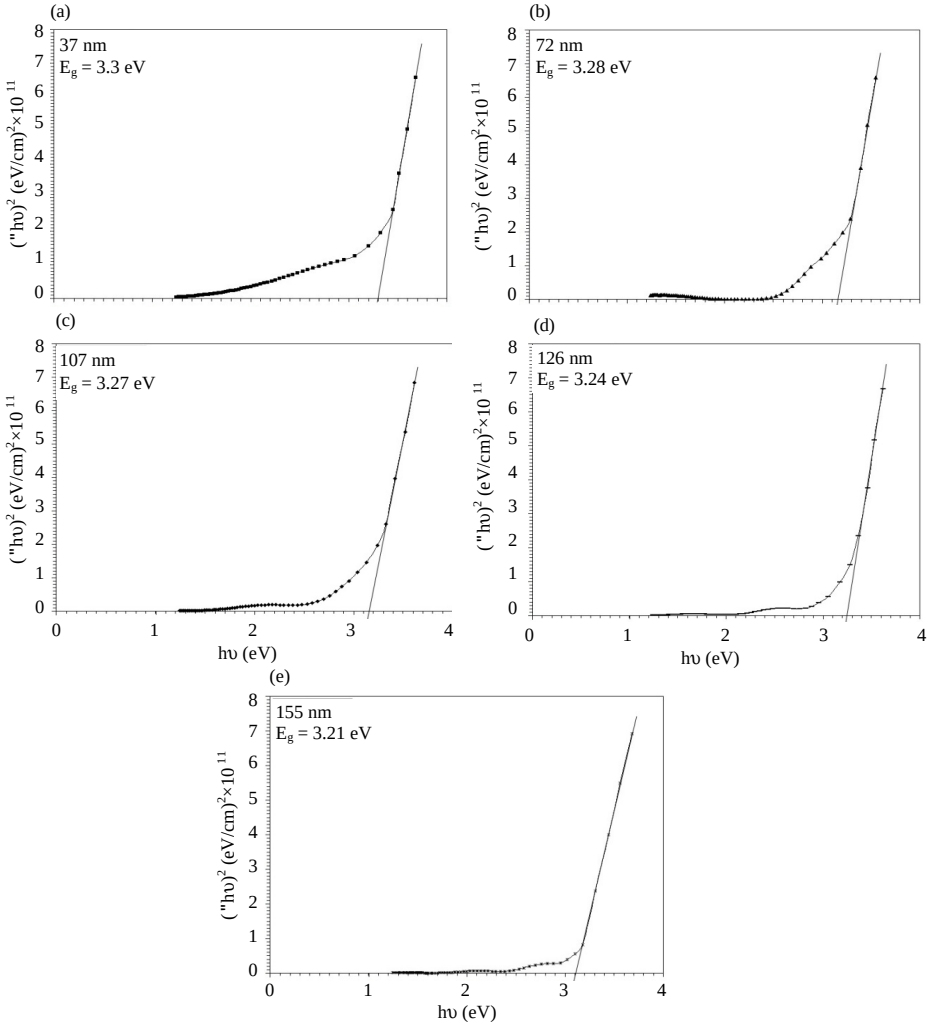

Fig. 4: Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for TiO_2 films; a) 37 nm; b) 72 nm; c) 107 nm; d) 126 nm and e) 155 nm

The values of E_U are increase with the increasing of number of layers for the prepared TiO_2 films which listed in the Table 1, refer to the broadening of tails inside the energy gap

The dispersion energy is an important for opticalmaterials because it is asignificant factor in optical communication and in designing devices for spectral dispersion. The dispersion of refractiveindexof TiO_2 nanoparticle layers are determinedusing the single oscillator that expressed by Wemple and DiDomenco relationship as following (Wemple and DiDomenico Jr., 1969):

$$n^2-1=\frac{E_dE_0}{E_0^2E^2} \quad (8)$$

Where:

E_o = The single oscillator energy of the electronic transitions

E_d = The dispersion energy, E = hυ is the photon energy

n = The refractive index

Figure 9 represent the plot of $(n^2-1)^{-1}$ versus $(h\upsilon)^2$ which used to determine the values of E_o and E_d from the slop $(E_oE_d)^{-1}$ and intercept (E_o/E_d) (Mishjil *et al.*, 2016).

From Wemple and DiDomenco relationship can determine the value of energy gap from a close approximation $E_o \approx 2E_g$ (Wemple and DiDomenico, 1971). The values of zero frequency refractive index (n_o) can be determine from the Eq. 8 and the zero frequency dielectric constant can be determine from $\varepsilon_o = n_o^2$ (Guler and Gasanly, 2007). The values of ε_o and n_o are decreased with the increasing of number of layers as listed in Table 1.

The moments of the optical spectra (M_{-1} and M_{-3}) of TiO_2 films were calculated from the following equation (Abass and Latif, 2016; Yakuphanoglu *et al*., 2004):

$$E_0^2 = \frac{M\text{-}1}{M\text{-}3} \quad (9)$$

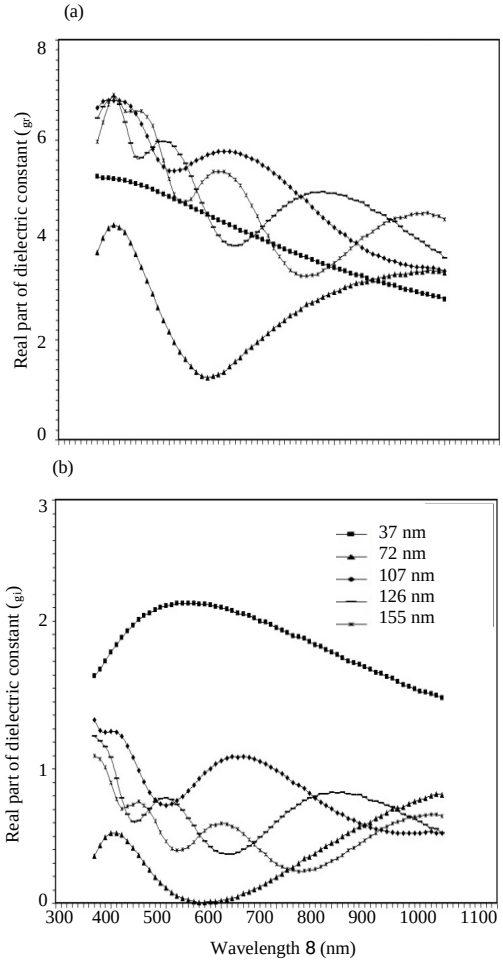

Fig. 5: Dielectric constant of TiO_2 film for various thickness; a) Real and b) Imaginary parts

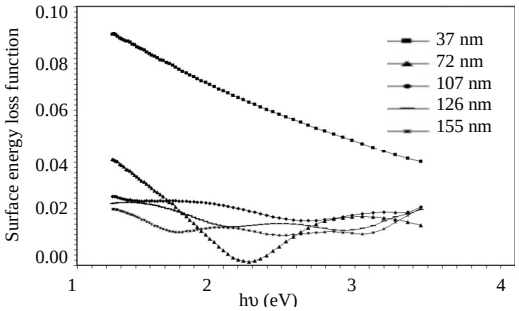

Fig. 6: Surface energy loss function of TiO_2 film for various thickness

$$E_d^2 = \frac{M^3_{-1}}{M_{-3}} \quad (10)$$

The values of M_{-1} and M_{-3} are decreased with the increasing of number of layers as shown in Table 1.

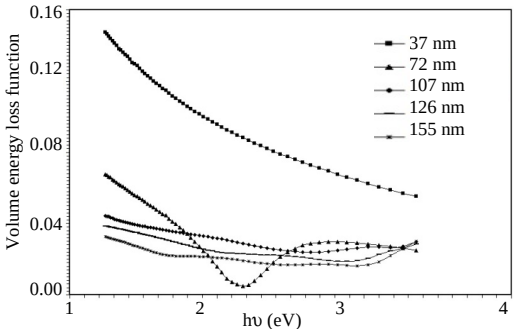

Fig. 7: Volume energy loss function of TiO_2 film for various thickness

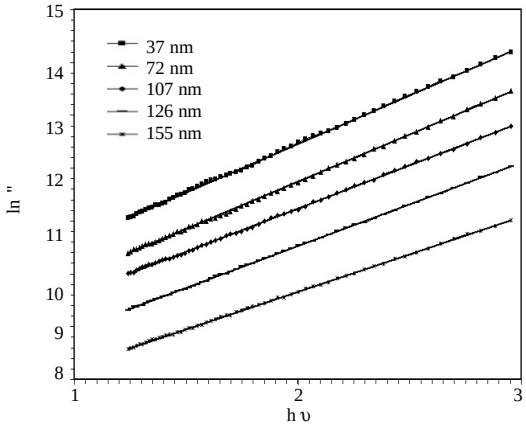

Fig. 8: Plot of ln α versus hυ of TiO_2 films with various thickness

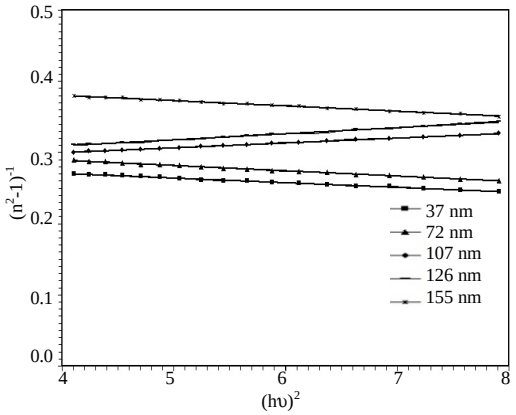

Fig. 9: Plot of $(n^2\text{-}1)^{-1}$ versus $(h\upsilon)^2$ of TiO_2 films with various thickness

Table 1: The urbach energy and dispersion parameters of nanostructure TiO_2 films

TiO_2 thickness (nm)	E_{tl} (meV)	E_d (eV)	E_o (eV)	E_g (eV)	n(o)	ε_o	M_{-1} (eV^{-2})	M_{-3} (eV^{-2})×10^{-2}
37	549	24.40	6.83	3.41	2.13	4.57	3.571	7.653
72	568	23.21	6.73	3.36	2.11	4.44	3.448	7.610
107	609	22.85	6.62	3.34	2.10	4.38	3.440	7.580
126	657	19.29	6.56	3.28	1.99	3.94	2.940	6.834
155	699	17.97	6.46	3.23	1.95	3.78	2.780	6.636

CONCLUSION

In this resaearch, nano-layers of TiO_2 were prepared by sol-gel method onto ITO substrates and annealed at 550°C. Structural and optical properties are investigated to use these films in solar cell application. The nanostructure TiO_2 films have been characterized using XRD which reveal the preferred orientation along (101) plane and other peaks that refer to the TiO_2 anatase phase. Crystallite size ranged from 15-32 nm that estimated from Scherrer formula. The SEM analysis showed the films are smooth, homogeneous and free of pinholes. From recording the transmittance spectra, the optical parameters are determined and the energy gap that calculated via. Touc model and from dispersion parameters. The energy gap was decreased with the increasing of film thickness while the Urbach energy increased. The energy loss of electrons which travelling through surface and bulk of material are decreased with the increasing of thickness. Dispersion parameters (E_d, E_o) are decreased with the increasing of film thickness and the moments of the optical spectra (M_{-1} and M_{-3}) also decreased.

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