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Synthesis and Characterization Study of n-Bi_2O_3/p-Si Heterojunction Dependence on Thickness

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Abstract. In this work, Bi2O3 was deposited as a thin film of different thickness (400, 500, and 600 ±20 nm) by using thermal oxidation at 573 K with ambient oxygen of evaporated bismuth (Bi) thin films in a vacuum on glass substrate and on Si wafer to produce n-Bi2O3/p-Si heterojunction. The effect of thickness on the structural, electrical, surface and optical properties of Bi2O3 thin films was studied. XRD analysis reveals that all the as deposited Bi2O3 films show polycrystalline tetragonal structure, with preferential orientation in the (201) direction, without any change in structure due to increase of film thickness. AFM and SEM images are used to investigate the influences of film thickness on surface properties. The optical measurement were taken for the wave length range (400-1100) nm showed that the nature of the optical transition has been direct allowed with average band gap energies varies in the range of (2.9-2.25) eV with change thickness parameter. The extent and nature of transmittance, absorbance, reflectance and optimized band gap of the material assure to utilize it for photovoltaic applications. Hall measurements showed that all the films are n-type. The electrical properties of n-Bi2O3/p-Si heterojunction (HJ) were obtained by I-V (dark and illuminated) and C-V measurement at frequency (10 MHz) at different thickness. The ideality factor saturation current density, depletion width, built-in potential and carrier concentration are characterized under different thickness. The results show these HJ were of abrupt type. The photovoltaic measurements short-circuit current density, open-circuit voltage, fill factor and efficiencies are determined for all samples. Finally thermal oxidation allowed fabrication n-Bi2O3/p-Si heterojunction with different thickness for solar cell application.

Keywords. n-Bi2O3/p-Si, heterojuncion, thin films, solar cell.

INTRODUCTION

Bismuth trioxide (Bi2O3) thin films have received much attention at last years, because the unique values of some their characteristic parameters (photoconductivity, dielectric permittivity, refractive index, energy gap, etc.) are suitable for a large range of applications such as optical coatings, gas sensors, visitors solid oxide fuel cells, photovoltaic cells, microwave integrated circuits, optoelectronics equipment's, electronic ceramics, high temperature superconductors and catalysts. [1-6]. Bi2O3 has five different polymorphic forms denoted as monoclinic, tetragonal, body centered cubic, cubic and triclinic [7,8]. Bi2O3 thin films have been prepared by different deposition techniques on a variety of substrates such as pulsed laser deposition (PLD) were Bi2O3 thin films prepared at different substrate temperatures and O2 pressures onto glass substrates [9], rapid thermal oxidation technique without any post deposition annealing condition were used to fabrication and characteristics of n-Bi2O3/n-Si heterojunction [10]. Shital Patil and Vijaya Puri prepared bismuth oxide thin films by thermal oxidation (in air) of vacuum evaporated bismuth thin film on glass and alumina, using the resonance frequency the permittivity and conductivity of bismuth oxide thin film was also measured [11]. Evan Tariq et al. used reactive pulse laser deposition method to deposited Bi2O3 Nanostructure thin film. Structural, surface morphology and optical properties was investigated and the result showed that Bi2O3 thin film have polycrystalline structure with energy gap of (2.5) eV while the Atomic Force Microscopic Image conformed that these films have Nano crystalline

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structure with average grain size of about (75.42 nm) [12]. Evan Tariq et al. investigated the physical properties of Bi and Bi2O3 thin films prepared by reactive pulse laser deposition technique with different laser flounce ranged from (1.8 J/cm2- 9.8 J/cm2). [13]. Evan Tariq et al. investigate the performance of the fabricated n-Bi2O3/p-Si heterojunction detector used reactive pulse laser deposition technique, detector parameter such as responsively; quantum efficiency, rise time and detectivity was investigated [14]. The aim of this study was focused on the fabrication and characterization of n-Bi2O3 /p-Si heterojunction for solar cells with different thickness utilizing thermal evaporation technique.

EXPERIMENTAL

Thin film preparation

High purity of bismuth film was deposited on glass and silicon substrates by thermal evaporation technique at room temperature from molybdenum boat using the Edward coating unit model (E 306) of 3x10-6Torr. Bi2O3 film was obtained with aid of thermal oxidation in an electrical furnace at 573K with ambient oxygen flow with rate (550 sccm) for one and half hour; the films were left to cool slowly. The thickness of films was determined by using optical interferometer method.

Thin film Characterization

X-ray diffraction (XRD) with copper target radiation (λ = 1.5418 Å) was used in order to identify the structural of the deposited Bi2O3 films. The average crystallite size (CS) of Bi2O3 thin films was calculated from the Scherrer's formula.

$$C_S = 0.94\,\lambda / \beta \cos\theta$$

Where β is full width half maximum (FWHM) of the preferential plane. Atomic Force Microscopic (AFM) was used to study the surface morphology and roughness. The Scanning Electron Microscope used to obtained Microscopic images with different Nano scale structures of different shapes and sizes were with a magnification (1,000,000) using the Nano LAB-MOST model. The UV–VIS Spectrophotometer was used to investigate the transmittance of the deposited films; the energy gap and the absorption coefficient were determined by equations: [15], [16]

$$\alpha h\upsilon = D\,(h\upsilon - E_g)^r \text{…………… …………………(1)}$$

$$\alpha = 2.303\ A/t \text{ ………..……………………..……. (2)}$$

Where hυ is the energy of the incident photon, D is a parameter inversely proportional to amorphousity, r is an index that characterizes the optical absorption process and is equal to 2, 3, 1/2, 3/2 reliant on the material and the type of the optical transition for indirect and direct transitions, respectively. Eg is determined by extrapolating the straight line portion ($\alpha h\upsilon$)r = 0, α: is the absorption coefficient, A is the absorbance and t is the film thickness.

The Van der Pauw (Ecopia HMS -3000) used to determining majority carrier concentrations, type of carrier and their mobility in Bi2O3 thin films for Hall Effect measurements.

Use study the capacitance–voltage (C–V) distinguishing in reverse bias of n-Bi2O3/p-Si heterojunction for the purpose to calculating built-in potential, junction capacitance, and carrier concentration and depletion width was obtained using LCR meter at a fixed frequency of (10 MHz). [17]:

$$C = \left[\frac{q\,\varepsilon_n\,\varepsilon_p\,N_n\,N_p}{2\left(\varepsilon_n N_n + \varepsilon_p N_p\right)}\right]^{1/2} \left(V_{bi} - V\right)^{-1/2} \qquad \text{...............(3)}$$

Where C: Capacity, Nn and Nρ are the carriers concentration donor in n- Bi2O3 and the accepter concentrations in p-Si, εn and εp are the dielectric constants of n- Bi2O3 and p-Si, respectively , V is the total applied voltage, and Vbi is the built-in potential. The depletion regains width is calculated by the equation (4):

$$W = \frac{\varepsilon_S}{C_0} \text{...(4)}$$

$$\varepsilon_S = \frac{\varepsilon_n \varepsilon_p}{\varepsilon_n + \varepsilon_p} \text{...(5)}$$

Where Co is the capacitance at zero bias voltage and εs is the dielectric constant of heterojunction.

The I-V of n- Bi2O3 /p-Si heterojunction was measured. The amounts were performed in dark and under standardized illumination that simulates the sunlight. The most main PV parameters are open circuit voltage Voc and short circuit current Isc were also measured. Current – Voltage characteristics in illumination and dark is description by the equation [18].

$$I = I_S\left(\exp\left(\frac{qV}{\beta K_B T}\right) - 1\right) - I_L \text{..(6)}$$

Where Is: Saturation current, IL: Illumination current, I: The total current (Solar cell current), V: applied voltage (positive forward bias and negative for reverse bias), T: Temperature in Kelvin, KB: Boltzmann constant, q: electron charge, β: is the ideality factor related to the many physical properties of the heterojunction having a value between (1 and 2) and can calculated from equation: [18].

$$\beta = \frac{q}{K_B T}\frac{dV}{d(\ln I)} \text{...(7)}$$

The photovoltaic conversion efficiency and Fill Factor is given by [18]:

$$\eta = \frac{P_m}{P_{in}} x100\% = \frac{I_m V_m}{P_{in}} x100\% \text{..................................(8)}$$

$$F.F = \frac{J_m V_m}{J_{sc} V_{oc}} \text{..(9)}$$

RESULTS AND DISCUSSION

Figure 1, shows the XRD spectrum of different thickness 400, 500, and 600 nm of Bi2O3 thin films deposited on glass. The patterns show that all the films have four main crystalline peaks, the first peak located at 2θ ≈27.94o with the (201)preferred orientation, while the second peak appeared at 2θ ≈31.76o with the (002), the third peak appeared at 2θ ≈32.69o with the (220) and the forth peak appeared at 2θ ≈46.2177o with the (222). Table 1, show all the peaks observed in all films. The intensities of the peaks increases with increasing- the film thickness but the locations of the measured diffraction peaks do not change significantly. This increase can mainly related to improvement of crystalline of the films due to decrease in defects like dangling bonds and vacancy sites in the film structure the crystallite size become larger from (32.686 to 56.212) nm when increased the film thickness, this result is in agreement with [19]. It is known, that the density of oxide film strongly depends on the oxidation conditions, the oxidation of polycrystalline bismuth caused increase of crystallite size and film structure becomes more compact because the thickness of bismuth oxide layer formed by thermal oxidation is approximately two times the thickness of the consumed bismuthx [20].

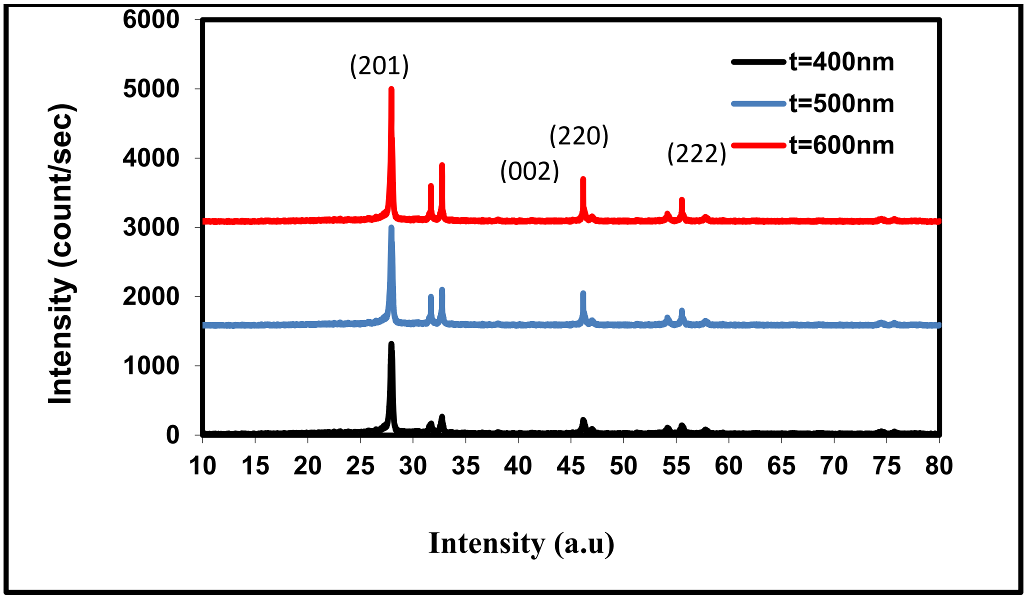

FIGURE 1. XRD patterns for Bi_2O_3 thin films deposited on glass with different thicknesses (400,500,600) nm.

TABLE 1. Structural parameters of Bi_2O_3 thin films at different thicknesses.

Thickness (nm)	**2θ (Std.) (Deg.)**	**2θ (Exp.) (Deg.)**	**d_{hkl} (Std.) (Å)**	**d_{hkl} (Exp.) (Å)**	**hkl**	**FWHM (Deg.)**	**C_S (nm)**
400	27.9463	27.9721	3.19000	3.18720	(201)	0.26160	32.686
	31.7613	31.6873	2.81500	2.82148	(002)		
	32.6914	32.7526	2.73700	2.73210	(220)		
	46.2177	46.2029	1.962600	1.96325	(222)		
500	27.9463	27.9651	3.19000		(201)	0.2041	41.89
	31.7613	31.6173	2.81500		(002)		
	32.6914	32.7011	2.73700		(220)		
	46.2177	46.1991	1.962600		(222)		
600	27.9463	27.9503	3.19000		(201)	0.1551	56.212
	31.7613	31.5773	2.81500		(002)		
	32.6914	32.6741	2.73700		(220)		
	46.2177	46.1792	1.962600		(222)		

Figure 2, shows the AFM images of three-dimensional (3D) surface morphology of Bi2O3 thin films with different thickness. The grain sizes and surface roughness values are evaluated with various thicknesses (400, 500, and 600 nm), take the values (199, 201 and 250 nm) for grain size while a surface roughness equal to (15.96, 21.9 and 28.9). It is clear that both surface roughness and grain size were increased with increasing film thickness this attributed to enhanced the crystallinity of films structure with decrease in grain boundary scattering. This is also supported by the X-ray diffraction data. Therefore, the film with high thickness 600 nm showed higher average diameter (see Figure 2- c) than that (400 and 500 nm) (Figure 2- a, b).

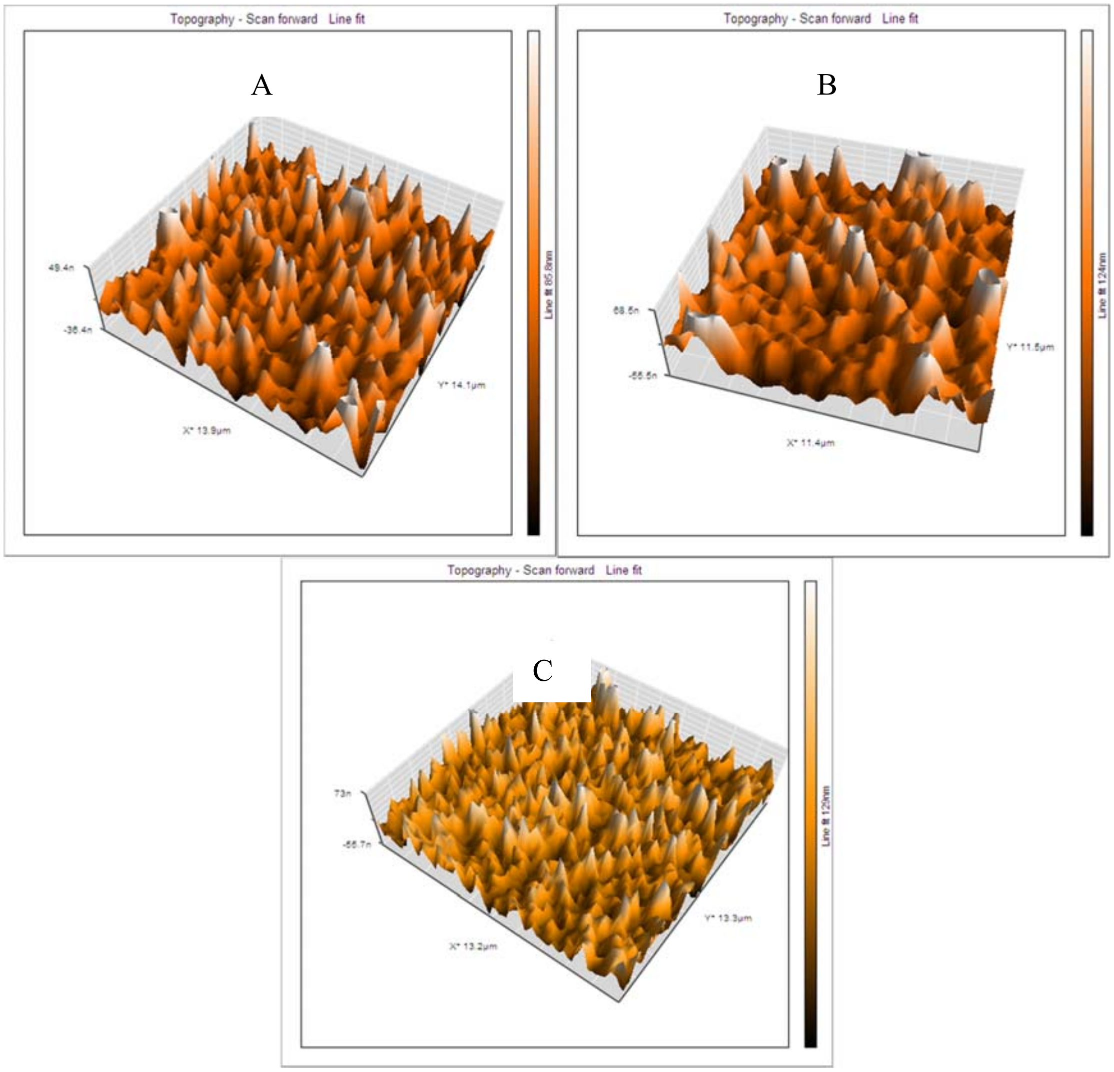

FIGURE 2. 3D Atomic force microscopy of Bi_2O_3 as a function of thickness: (a) 400 nm, (b) 500 nm, and (c) 600 nm

All samples of Bi2O3 with different-thickness were examined using SEM technique with a magnification (1,000,000) to identifying the nature of the films surfaces and observing the variation of particle size with increasing film thickness. It is clear from the images shown in Figure 3 that the change of Bi2O3 thickness has had impact significant on the composition of the surface structure of the prepared films. And all prepared films have regular distribution granules. By increasing the thickness, the surface of the Bi2O3 films becomes more homogeneous and uniform, thus improving the quality of the prepared films. The increase of thickness led to an increase in grain size and this corresponds to the results of X-ray diffraction tests (XRD) and AFM tests.

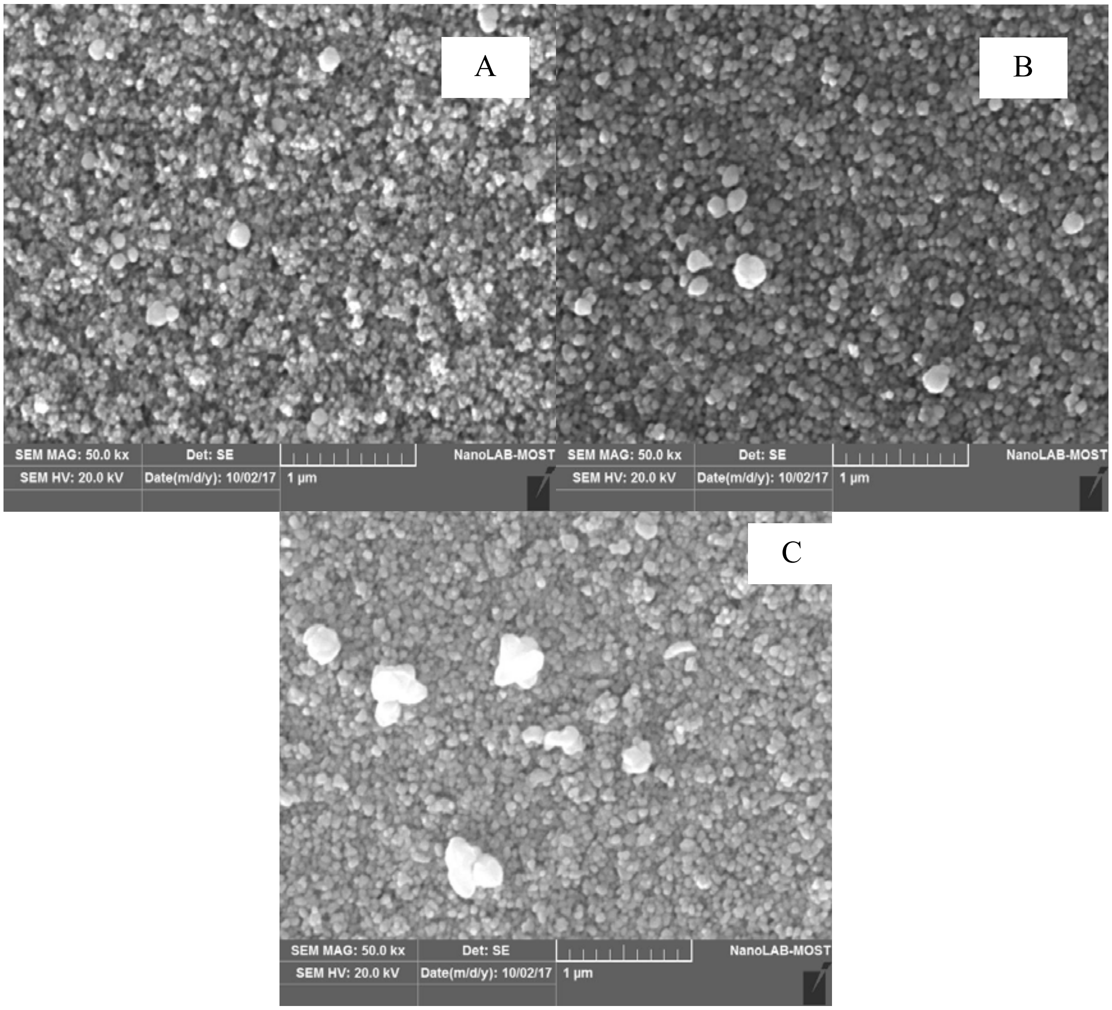

FIGURE 3. The Scanning Electron Microscope (SEM) of Bi_2O_3 thin films with different thickness: (a) 400 nm, (b) 500 nm, and (c) 600 nm

To determine the effect of film thicknesses (400,500,and 600 nm) on the optical properties of Bi2O3 thin films, the transmittance spectrum of Bi2O3 thin films were recorded as a function of wavelength in the range (400-1100) nm as shown in figure 4(a). It is clear from this figure that these films have high values; all samples demonstrate (40-95) % transmittance at wavelengths range (550-1100) nm which makes these films suitable for solar cell window. Also the average transmittance values decrease when film thickness increases which means the absorbance value for Bi2O3 thin film increase with the increase of film thickness, similar effect behavior has been reported by other researchers [19, 21]. Figure 4(b) shows the reflectance spectra for Bi2O3 thin films, it is clear that the average reflectance values of these films are below 20% in the range of wavelength (400-1100) nm, these low values of deposited film at different thickness makes it a desired material for photovoltaic application.

From figure (5) we can observe that the (α) values, which has been calculated using equation (2), indeed, own high amount reached above (105) cm-1. It was pointed that the α values in general increases as film thickness increases, which is attributed to an increase in absorbance of used films, we found that the value of α increases from (0.43-1.22) ×105cm-1 with the increase of thickness. While Egopt values decreases (from 2.9 to 2.25) eV with increase of thickness, as shown in figure 5. The decrease in the band gap (Egopt) values may be attributed to the changes of the quality of Bi2O3 thin films with increasing thickness ,this result is in agreement with [9,12,19].

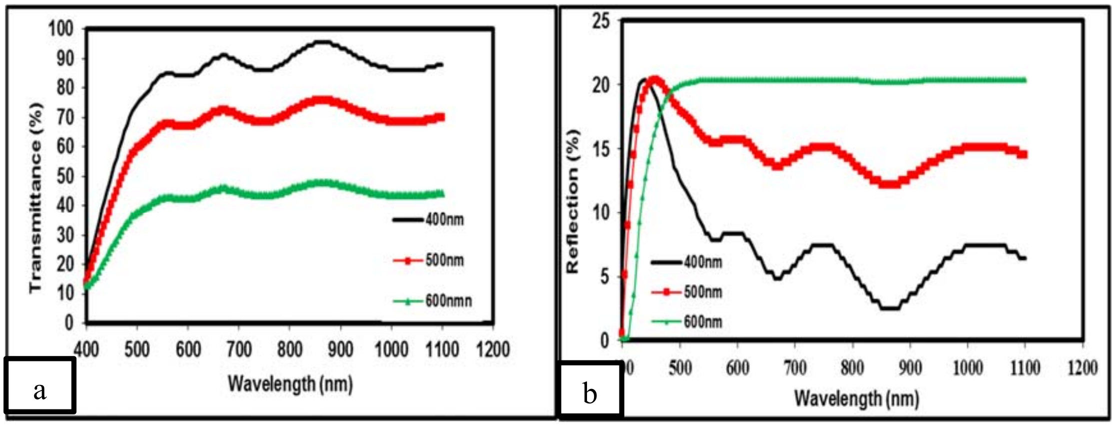

FIGURE 4. The Transmittance and Reflection spectrum of Bi_2O_3 with different thickness 400 nm, 500 nm, and 600 nm.

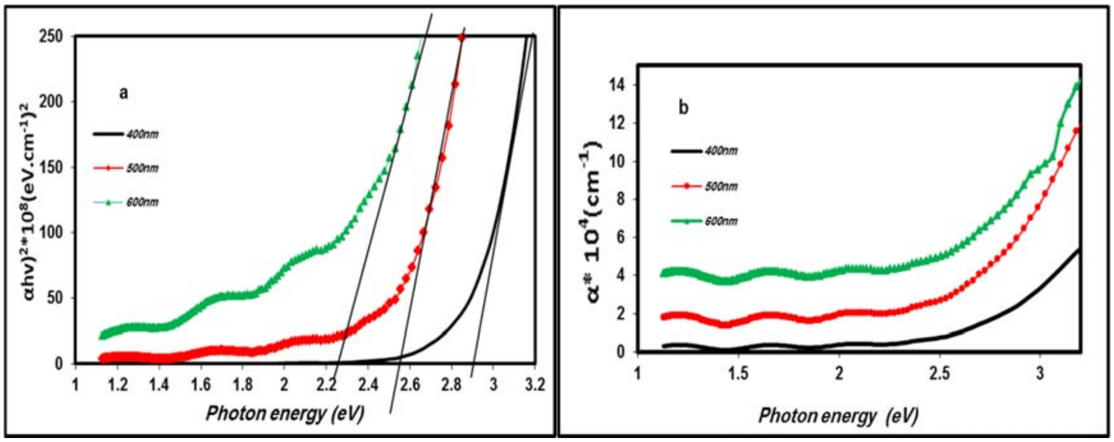

FIGURE 5. (a) Variation $(\alpha h\upsilon)^2$ verse photon energy, **(b)** absorption coefficient verse photon energy of Bi_2O_3 with different thickness 400 nm, 500 nm, and 600 nm.

The electric properties for Bi2O3 thin films can be determined by studying Hall effect, these measurement shows that the Hall voltage decreasing with the increasing of the current . The negative sign of the Hall coefficient indicates that the conductive nature of the film is n.-type, i.e. electrons are the majority charge carriers. The type of charge carriers, concentration (n) and Hall mobility (μHh) has been estimated from Hall measurements. These values are listed in Table 2. The carrier concentration of the order 1015cm-3 is in a good agreement with reference [1, 22]. We can notice from Table 2, that the carrier concentration and mobility increases with increasing of thickness this indicate that the improvement in the films structure.

TABLE 2. Hall Parameters for Bi_2O_3 thin films at different thickness.

Thickness(nm)	$R_{(H)}$	$\mu_H (cm^2/V.S)$	n (cm^{-3})	ρ(Ω.cm)
400	-844.5946	49.68203	7.4E+15	17
500	-726.7442	726.7442	8.6E+15	1
600	-644.3299	4295.533	9.7E+15	0.15

The capacitance-voltage (C-V) measurements led to calculate different parameters such as junction capacitance, depletion width, built -in potential and carrier concentration. Figure 6 shows the relation between the voltage of reverse bias and inverted square capacitance (1/C2-V) measurements for Bi2O3/Si heterojunction at different thickness. From these results, it can be seen that the capacitance decrease as the reverse bias voltage increasing for all films prepared , which can be explained by the expansion of depletion layer with the built-in potential. It is clear from figure 6 and Table 3 that the capacitance values at zero bias voltage (Co) for Bi2O3 thin film were decreases with increasing film thickness. This observations was attributed to the improvement of (Vbi) due to increase in depletion region width (W).Also the carrier concentration (NDd) increases with increasing film thickness as shown in Table 3 and this result is comparable with our result for Hall effect measurements. The C-V measurements show that the heterojunction of abrupt type, because the relationship between inverted square amplitude (1/C2) with a voltage (voltage) of reverse bias is linear relationship.

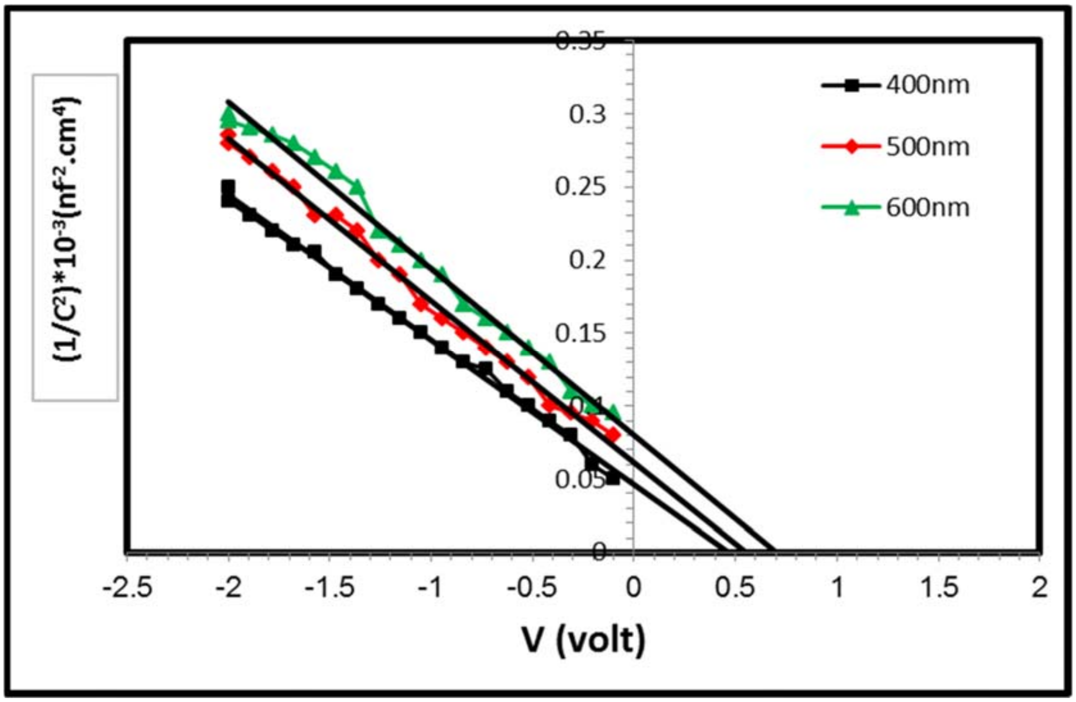

FIGURE 6. variation of $1/C^2$ with reverse bias voltage for Bi_2O_3/Si heterojunction at different thickness.

TABLE 3. Value of C_o, W, N_D, and V_{bi} for Bi_2O_3 /Si heterojunction with different thickness.

Thickness(nm)	**C_o(nf/cm^2)**	**W=$\varepsilon_{(s)}/C_0$ (nm)**	**V_{bi}(Volt)**	**N_D (cm^{-3})**
400	147.1224716	44.35080467	0.4	2.29952E+16
500	127.6191402	51.12869424	0.5	2.30014E+16
600	111.5943553	58.47069939	0.7	2.30463E+16

Figure 7 show the current-voltage (I-V) characteristics of manufactured Bi2O3/Si heterojunction with various thickness. (400, 500 and 600) nm under illumination and dark conditions in the forward and reverse directions. The conversion efficiency and Fill Factor were calculated using equations (8, 9) respectively, all results obtained from this test shown in Table 4. It is clear decrease in the value of the open. circuit voltage (Voc) and increased in the value of short. circuit current density. (Jsc) maximum for both the current and the voltage value (Vm, Jm) and the value of efficiency solar cell, in terms of efficiency increases in general with increasing thickness and this goes back as we have already increase the surface roughness, the absorption coefficient and charge carriers, the increase in film thickness cause rearrangement in interface atoms and reduce the surface states, dangling bond and dislocation at interface layer which leads to enhance of the junction characteristics.

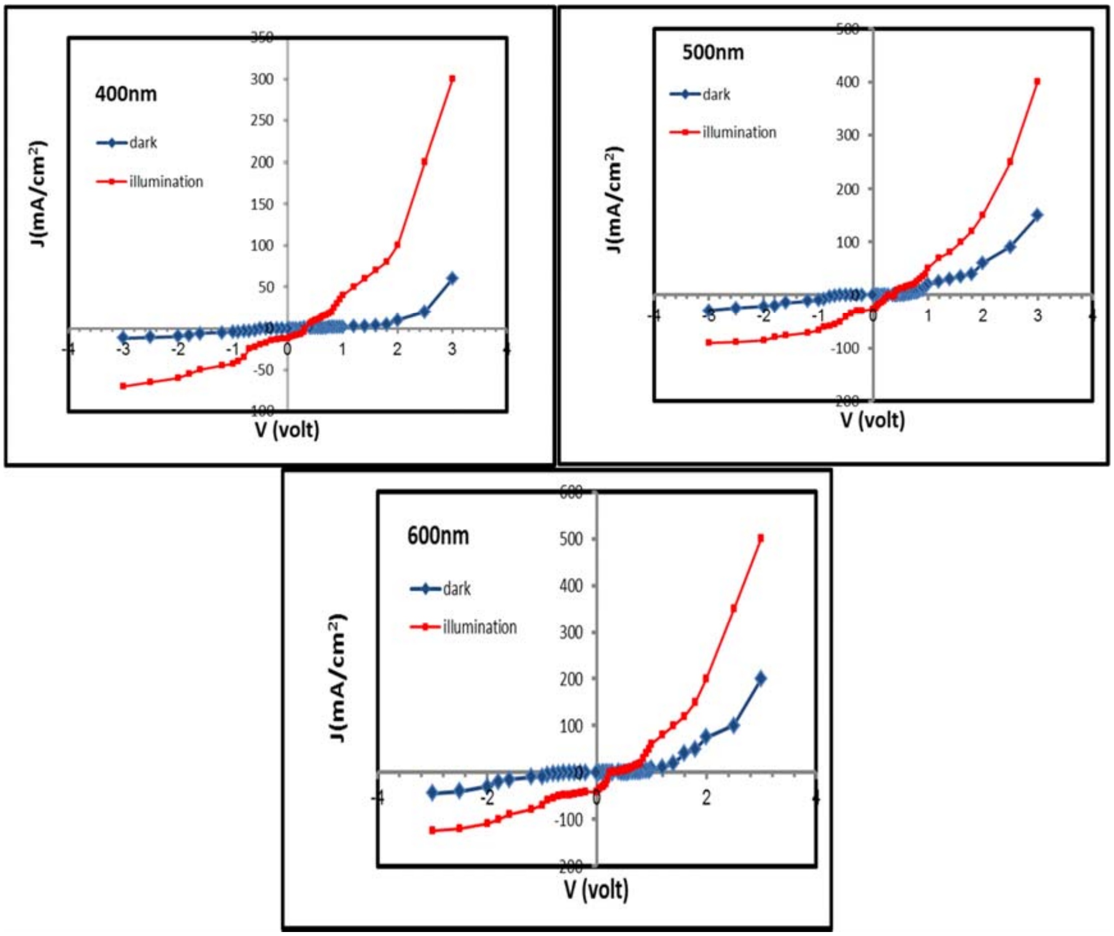

FIGURE 7. I-V Characteristics Of Bi_2O_3/Si solar cell at different thickness in dark and under Illumination

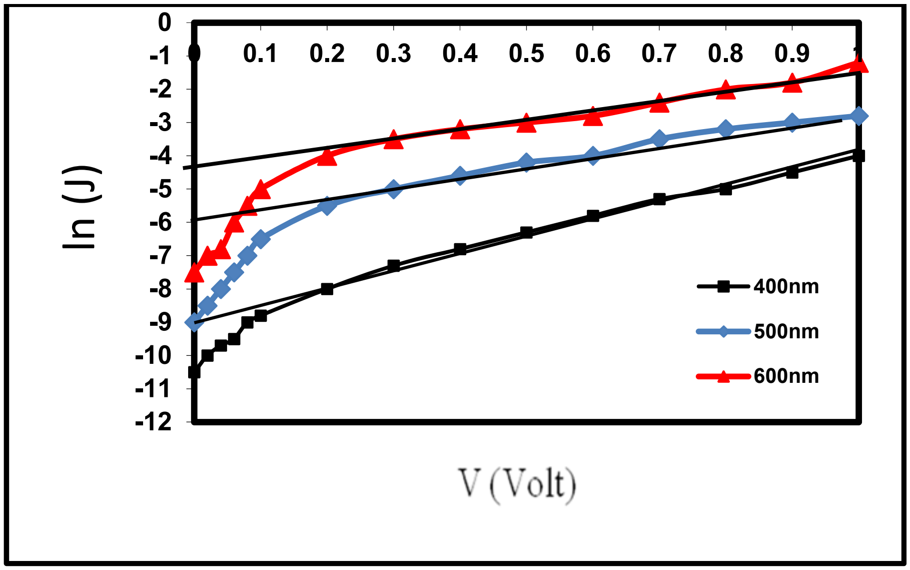

FIGURE 8. ln (J) versus *V* for forward bias of dark for Bi_2O_3/Si junction at different thicknesses.

TABLE 4. The parameter for Bi_2O_3 /Si heterojunction solar cell with different thicknesses.

Thickness (nm)	V_{oc} (Volt)	J_{sc} (mA/cm^2)	V_{max} (Volt)	J_{max} (mA/cm^2)	FF	η %
400	0.31	13	0.22	7	0.382134	1.54
500	0.27	27	0.19	12	0.312757	2.28
600	0.24	41	0.17	24	0.414634	4.08

The value of the barrier height (Φb) , saturation current density and the ideality factor measurement of the Bi2O3 /Si heterojunction solar. cell. are gained from the relation between the bias voltage at dark condition and the logarithm initial part of forward current as show in figure 8 and Table 5. The saturation current can be calculated by using equation (7) from intercepting the straight line with the current axis at zero voltage bias. It can be observed from figure 8 that the current value differs exponentially with voltage at low voltage ($V < 0.2$ V). Table 5 indicate that both values of the ideality factor and the barrier height (Φb) decrease while the saturation current density values increase with increasing film thickness.

TABLE 5. Ideality Factor saturation current density and barrier height values for Bi_2O_3 /Si junction at various thicknesses**.**

Thickness* (nm)	Ideality Factor	Saturation Current Density(J_S) (mA/cm^2)	Barrier* Height (Φb) (eV)
400	2.311978	0.00012341	0.65255
500	1.544402	0.002478752	0.57485
600	1.485001	0.013568559	0.53082

CONCLUSIONS

In the this work, thin films of n-Bi2O3/ p-Si heterojunction solar cell is fabricated successfully by thermal oxidation method, the effect of film thickness on the structural, optical and electrical properties of Bi2O3 films deposited on glass substrate are observed. It was found that the increase film thickness leads to higher growth rate, better crystallinity, increased of electron carrier concentration, smaller resistivity and decreasing the band gap energy.

C-V measurements of n-Bi2O3/ p-Si heterojunction at fixed frequency (10 MHz) deduce that the depletion region width and built in potential increase with the increase of film thickness, also it is found that the junction was an abrupt type. I-V characteristic under dark case shows both identity factor (β) and potential barrier height (Φb) values decrease with the increase of film thickness, the open. circuit voltage2 (Vocd) , short. circuit current density. (Jsc) ,Vm, Jm, conversion efficiency and Fill Factor are seen to be dependent on the film thickness. We should mention that the poor efficiency for solar cell because high recombination centers that lead to excess of leakage current.

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