Renewable Energy and Sustainable Developments

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Preface

The twelve review chapters are collected including properties and applications researches in addition to one important feature: these chapters have presented results obtained from different research groups. The principal objectives are exchanging the information about the fundamental and applied research developments in the area of Renewable Energy and Sustainable Developments. In recent years, the nanoscience has successfully contributed too many interdisciplinary fields. Therefore, transfer of ideas, methods and tools from traditional to nanoscale should be a promising endeavor.

An additional objective is to increase the understanding of the fundamental principles that underlies the problems of nano in the life realms. This is of great relevance to the society and science, in particular for economic endeavors. Objective assessment of risk and quantitative representations of information that support decisions has a vital role to play in many other areas.

The chapters are devoted to thin films and nanostructures principles and applications studies in the field of book title. Chapter one is focused on the nano and micro structures of bismuth oxide thin films preparation by reactive Q-switching pulsed laser deposition was studied using 9 nsec and 1.06 μm of Nd-YAG laser as an ablating tool for Bi target under the O₂ environment on silicon and glass substrates. The optimum conditions are based on different laser fluence, oxygen back ground pressure and substrate temperatures for device preparation, followed by chapter two as devoted to nanocrystalline zinc oxide (ZnO) seeded catalyst layer thin films deposited on glass substrates using a sonicated sol-gel method method at various sol concentrations. To obtain desirable piezoelectric properties, X-ray diffraction analyses were used to investigate the effect of sol concentrations on the crystallinity of the films. Where showed as increasing in sol concentration, the value of the full-width at half-maximum of the (002) peak decreases while the stress initially decreases and then increases. Thin films deposited at high concentrations result in an
increase in crystallite size. The 0.4 M ZnO thin films exhibited lower stress/strain than other films. The lowest stress value was achieved at the highest crystallinity value. Experimental results show that sol concentration has the greatest influence on the crystallinity of the ZnO thin films. A higher degree of crystallinity and large surface area availability was observed for the ZnO nanorod layer compared to the seeded catalyst layer. While, Three-level single phase transformerless photovoltaic inverter (TPVI) is proposed to minimize the current total harmonic distortion (CTHD). The maximum voltage angle will effect on the current total harmonic distortion, the lowest CTHD of 15.448% is obtained when the maximum voltage angle is 134° is presented in chapter three. Also, a dye-sensitized solar cell (DSSC) consists of a pair of glass substrate with transparent conducting oxide (in this case the Indium Tin Oxide or ITO glass), a non toxic nano porous TiO₂ coating which acts as a photo-electrode, sensitizer from dye molecules soaked in the TiO₂ film, redox electrolyte layer and a counter electrode catalyst. Due to their excellent potential to deliver solar electric power at very low cost, the DSSC are referred to as the third generation photovoltaic. This chapter four is focused on the usage of organic substances from fruits and vegetable as a potential dye sensitizer. Fruits such as the Pitaya (Dragon fruit), Keriang’s fruit, Black plum skin, Mangosteen pericarp, Rose syrup and Chlorophyll extracted from Spinach are applied as sensitizer to the fabricated DSSC using the conventional method of oxide electrode smearing method, otherwise known as the Doctor Blading method. Result shows that the photoelectrochemical performance of the DSCs based on these dyes showed that the Voc ranged from 0.432 to 0.787 V, and Jsc was in the range of 0.88 to 2.19mA/cm². The DSC sensitized by Pitaya extract offered the highest conversion efficency of 1.02% among the six extracts. The photoelectrochemical performance of DSSC and the usage of natural sensitizer demonstrate good potential as a sensitizer yet further studies are needed to enhance the DSSC solar cell efficiency.

Otherside, the hybrid organic-inorganic nanocomposites systems are being studied more closely due to its possibility in combining the advantageous characteristics of inorganic and organic components as explained in chapter
five. The nanocomposited photoactive layer thin film which is MEH-PPV: MWCNT were prepared and characterized. The parameters that involved in the optimization are different composition of MWCNT in tetrahydrofuran (THF) and toluene, different composition of Iodine doped Multiwalled Carbon nanotubes (I-MWCNT) with low and high concentration of I-MWCNT. It was found that annealed MWCNT gave the best results in physical, electrical and optical properties. In this work, bulk-heterojunction solar cells based on poly (2-methoxy-5-(2’-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) and a highly conductive multiwalled carbon nanotubes (I-MWCNT) were fabricated and characterized by white light I-V and external quantum efficiency measurements. The influences of different temperature treatment of the nanocomposite layer, the various concentrations of Iodine and different metal contact used as cathode on the solar cell device performance were studied. Following by chapter six to present Magnesium oxide (MgO) that has been prepared by pulsed laser deposition (PLD) as transparent material on silicon (Si) substrate. Structural properties via X-ray diffraction (XRD) for different oxygen pressures, different temperatures and different laser fluencies are elaborated. The particle size is researched. Optical properties of refractive index, transmission, absorption coefficient at different pressures and different temperatures are investigated. Also, the electrical properties to characterize MOS including C-V and I-V for different structures of multi-application and related studies are presented to fit the suitability of MgO device.

Chapter seven is devoted to artificial neural networks (ANN) that have been widely used for monitoring, control and optimization of various processes because of their ability to understand a function from observations. In the last two decades, the application of neural networks has grown tremendously in the field of bioprocess control. This chapter provides a review of different applications of ANN based controllers for use in bioprocess control. Different types of controller algorithms, their structures and the results are discussed. A brief description of ANN history and its applications in bioprocess control is also presented. It is observed that majority of the ANN applications presented are based on simulations and that most of the neural network structures
possesses a single layer of hidden neurons. Also, chapter eight discusses serious environmental pollution and energy crisis are the most threatening problems to human kinds. Therefore, executing research for generating clean energy has been the passion for scientists, which can provide energy in sustainable manner. In this manner, solar-driven water electrolysis for hydrogen-based fuel cell is one of the most innovative solutions to supply clean and recyclable hydrogen (H₂) energy. Since the introduction of titanium dioxide (TiO₂) as a photoelectrode in water electrolysis, TiO₂ has attracted considerable scientific interest due to its unique chemical and physical properties. Then, design and development of TiO₂-based nanostructure assemblies has gained significant interest in order to maximize specific surface area for harvesting more photons. The high efficiency H₂ generation system using solar energy for low cost and high efficient fuel cell is getting more scientific attention recently. However, an obvious hindrance to the widespread use of TiO₂-based photoelectrode is its poor visible light response and rapid recombination of electron/hole pairs after photoexcitation.

Lastly, a novel approach for improving the performance of metal-semiconductor-metal (MSM)–type aluminium (Al)-doped zinc oxide (ZnO) nanorod array-based ultraviolet (UV) photoconductive sensors involving sonicating the precursor solution is discussed in chapter nine. The Al-doped ZnO nanorod arrays were deposited onto a glass substrate coated with an Al-doped ZnO thin film as a seed layer using precursor solutions that were sonicated for various amounts of time between 0 to 50 min. The average diameter of the nanorod decreased with increasing sonication time, decreasing from 59 without sonication to 42 nm after 50 min of sonication is observed. The UV photoconductive sensor using Al-doped ZnO nanorod arrays prepared using the 30 min sonicated precursor solution presents the highest responsivity (4.26 A/W) under 365 nm UV illuminations. Chapter ten is considered a pair of electrodes with a nanometer gap (namely, nanogap electrodes) in the fabrication of nanometer-scale devices. Nanogap electrodes have stimulated the development of the field of nanotechnology for their various applications in the study of transport phenomenon in molecular, electronic, and...
nano-electronic devices. This review deals with the topic of the techniques for the fabrication and discusses possible applications of these nanodevices. The history, the prospects, and the research status of nanogap electrodes are also discussed. Chapter eleven submits serious environmental pollution and energy crisis that are the most threatening problems to human kinds. Therefore, executing research for generating clean energy has been the interest of the global community. One of the prospective ways to produce clean energy is to convert lignocellulosic biomass into bio oil that has energy density up to 20MJ/M³ through fast pyrolysis or hydrothermal treatments. The main focus of this review article is to elucidate the state-of-the-art in eliminating these challenges using two of the applauded techniques of upgrading bio oil such as Hydrodeoxyxygenation (HDO), and one step hydrogenation-esterification (OHE). These processes are all high pressure operations employing a wide range of heterogeneous catalysts. Critical information has been shown on how hydrogen is used to remove oxygen from bio-oil in the former route and also used to upgrade the unstable bio oil in the later to more stable bio oil in form of bio-esters. Importantly, catalyst development which is a black art, understanding the mechanism of carbon formation and kinetics, elucidating all possible poison to the catalyst and evaluating the constraint for high pressure and sustainable sources for hydrogen are all grey area of research attention prior to commercialization of these processes.

The amperometric enzyme electrodes, based on glucose oxidase (GOx) have played a leading role in the move to simple easy-to-use blood sugar testing and are expected to play a similar role in the move toward continuous glucose monitoring in chapter twelve. Carbon nanotubes (CNTs) exhibit a unique combination of prefrect electrical properties, which has confirmed increasing interest in glucose biosensors based on CNTs. In this contribution recent advances in the development of reliable methods for the functionalization of the carbon nanotubes for direct electron transfer in glucose biosensors are highlighted. Moreover, growth mechanism and mass production of carbon nanotubes by chemical vapor deposition was discussed and growth-control
aspects such as the effects of temperature, flow rate and catalyst concentration on CNTs production are discussed.

Interactions between authors within their review chapters can be described as links between nodes. In addition to the topology of these works, the link capacity plays a considerable role, for example in information transfer. These chapters address problems from various perspectives. They provide new insights, also formal models for the characterization of complex systems.

As the editor of this book, hopes that the current selection of researches provides a good overview of the research activities. The results should also boast future research activities within the new actions, meetings and conferences.

I would like to acknowledge Prof. Datuk Dr. Kamarudin Hussin, the Vice-Chancellor of University Malaysia Perlis, for his support and encouragement during the preparation of this book. Also, I would like to thank Prof. Dato’ Dr. Zul Azhar Zahid Jamal, Deputy Vice-Chancellor for Academic and Internationalization; Prof. Dr. Abdul Hamid Adom, Deputy Vice-Chancellor for Research and Innovation; Prof. Dr. Uda Hashim, Director of Institute of Nano Electronic Engineering for their reinforcement and propping for preparing this book. I appreciate the amount of work that goes into writing chapters, the authors are heavily burdened with other demands on their time. Finally, I present my special greetings to the publisher (Scientific & Academic Publishing, USA) for giving us the opportunity to publish and distribute this book.

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Chapter 1

Physical Properties of Bismuth Oxide Nano and Microstructures for Optoelectronic Applications

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Abstract In the present work, nano and micro structures of bismuth oxide thin films are prepared by reactive Q-switching pulsed laser deposition was studied using 9 nsec and 1.06 \textmu m of Nd-YAG laser as an ablating tool for Bi target under the O\textsubscript{2} environment on silicon and glass substrates. Optimum conditions based on laser fluence, oxygen back ground pressure and substrate temperatures were selected for device preparation.

Keywords Bi\textsubscript{2}O\textsubscript{3}, nanostructures, Nd-YAG laser, Characterization, Analysis

1. Introduction

In the last century when 'microstructure' was revealed, it was recognized that refined microstructure often provides attractive properties such as increasing strength and toughness in structural materials. Even more it has been found that these bulk properties may dramatically change when this microstructure is
nanscale [1]. In addition, thus materials with low dimension such as micro and nano structure have been prepared by various methods [2]. Materials at nanoscale (nanomaterial) have attracted more and more interests due to their unique physical and chemical properties which are greatly different from those bulk materials and sensitively depending on their sizes and morphology and the way the atoms organized [3, 4]. Two principle factors caused the properties of nanomaterial to differ significantly from bulk material, firstly it is increasing in the surface area relative to size of material, and secondly the quantum size effect [5]. It has been shown that at low dimension of this material and other similar materials, low Fermi energy and small electron/hole effective mass can show anomalous transport properties because of quantum size effect which arises due to quantization of the normal (to film plane) components of electron momentum of the consequences of this quantization [6].

1. The nonzero point energies of electrons and the holes which lead to a decrease in the overlap between the valence and conduction bands or the separation of the bands depending on films thicknesses.

2. The step-wise variation of the density of state function with thickness.

Manufacturing can reach the nanoscale in two basic approaches, either from the top down by 'machining' to ever-small dimensions or from the bottom up exploiting the ability of molecules and biological systems to "self-assemble" tiny structure [5]. Not only reduction in number of atoms influence the changes depending on size, but also the alter in dimensionality change of dimension may be reduced in three directions, making quantum dot zero dimensional (0-D) material, while reduces in just two directions making quantum wire (1-D), the material reduces in just one direction, making thin film (2-D) material [4]. Bismuth and bismuth oxide nanostructures are one of nanomaterials that has attracted interests, especially for fabricated electronic spin function devises, gas sensor, transparent electronics and surface acoustic wave devise [3, 4]. Many workers have investigated nanostructured oxide physical properties such as CuO, SnO₂, TiO₂, ZnO and Bi₂O₃ due to its special features, which made it applicable to this application [7].
2. Experimental Procedure

2.1. X-Ray Diffraction (XRD) Pattern

In order to explain the structural properties, the nature and the crystal growth of films prepared at different conditions, X-ray diffraction (XRD) measurement was carried out done according to the ASTM (American Society of Testing Materials) cards, using Philips pw 1050 X-ray diffractometer of 1.54 Å from Cu-kα. The grain size ($D_g$) of the crystalline material; which plays the important role in the material properties, can be estimated easily from the XRD by means of Full Width at Half Maximum (FWHM) method that is often calculated by Scherrer relation [8].

$$D_g = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $K = 0.94$, $\lambda$ is the wave length of incident X-ray radiation, $\beta$ is the intrinsic full width at Half Maximum of the peak, and $\theta$ is the Bragg’s diffraction angle of the respective XRD peak, which will elucidate the nature of the prepared SnO$_2$ films [9].

2.2. Optical Properties Measurements

A double-beam UIR-210A spectrophotometer from Shimadzu was used in order to record the optical transmission and absorption spectra of the prepared films at different preparation conditions within the wavelength range (300-900 nm). All films were deposited on quartz substrate. The optical band gap was estimated graphically by applying the Tauc model; the band gap of the prepared material with sharp fall off can be deduced from a plot of the squared absorption coefficient ($\alpha h\nu$)$^2$ versus photon energy ($h\nu$) by extrapolating the straight line of the plot to intersect the energy axis. Since the transmission is defined as $I/I_0$ and for normal incidence, the reflectivity tends to be small and could be neglected, the value of $\alpha$ is obtained from the equation $I = (1 - R_r)2 I_0 \exp(-\alpha t)$. In the direct transition semiconductors (present case), the absorption coefficient and optical energy band gap ($E_g$) are related by [10]: 
\[ \alpha \nu = (h \nu - E_g)^{1/2} \]  \hspace{1cm} (2)

where \( h \) is Planck constant and \( \nu \) is the frequency of the incident photon.

**2.3. Electrical Properties**

The measurements involve resistivity and Seeback coefficient.

**2.3.1. Thin Film Resistivity**

The electrical resistance of the prepared films was determined as a function of the substrates temperature after depositing ohmic contacts on the film side as shown in Fig. 1. A furnace was used to raise the temperature of the sample and Keithley electrometer was utilized to measure the electrical resistance (R).

![Figure 1](image)

**Figure 1.** Ohmic contact and preparation of sample for measurement of electrical resistance

The value of (R) is given for rectangular shape films by:

\[ R = \rho \left( \frac{\ell}{bt} \right) \]  \hspace{1cm} (3)

where \( \rho \) is the electrical resistivity of the sample and \( l, b \) and \( t \) are the length, width and thickness of the sample, respectively. The conductivity was found by taking the inverse value of electrical resistivity.
2.3.2. Figure of Merit

To judge the performance transparent – conducting of films, figure of merit needs to be estimated as found from,

\[ F.M = \frac{\alpha}{\sigma} \]

where \( \alpha \) is absorption coefficient and \( \sigma \) is the film conductivity.

2.3.3. Seeback Coefficient

The thermoelectric power of films prepared at different substrate temperature was measured using the experimental set-up shown in Fig. 2. The difference in temperatures between the outside terminals of the film results in electromotive force (EMF) measured on electrometer in terms of voltage Seeback coefficient (S) is given by:

\[ S = \frac{\Delta V}{\Delta T} \]

![Figure 2. The setup of Seeback coefficient measurement](image)

2.4. Characterization of n-Bi\(_2\)O\(_3\)/p-Si Heterojunction

Next step of fabricating the device; electrical, photovoltaic and detector parameters were investigated to learn about more about these devices.

2.4.1. Current-voltage (I-V) Characteristics in the Dark

A Kiethley-616 electrometer was used to measure the current flow in a solar
cell; manufactured from a structure produced in dark condition with voltage 0-4 V in forward biasing and (0-6) V in reverse biasing. This characterization was adopted to determine the ideality factor (n) and the potential barrier height (ΦB) as follows [11]:

\[ n = \frac{q}{kT} \frac{\Delta V}{\ln \frac{J}{J_s}} \]  

\[ \Phi_B = \frac{kT}{q} \ln \left[ A^* T^2 / J_s \right] \]  

where \( kT/q \) is the activation energy and \( J_s \) is the saturation current density.

2.4.2. Capacitance-voltage (C-V) Measurements

C-V characteristics of the heterojunction were measured under a reverse bias voltage 0.1-1.2 V. The cross point \((1/C^2=0)\) of the \((1/C^2-V)\) curve represents the built-in potential of the heterojunction, the charge-carrier density \( (N_d) \) and width of the depletion layer for both devices are calculated by [12]:

\[ N_d = \frac{2}{q \varepsilon_s} \left[ 1 / d \left( 1 / C^2 \right) / dV \right] \]  

\[ w = \sqrt{\frac{2 \varepsilon_s V_{bi}}{q N_d}} \]  

2.4.3. Carrier Lifetime

When a semiconductor is illuminated with photons of sufficient energy, its conductivity increases due to the generated additional carriers, (resistivity will decrease). The photoconductive property of the semiconductors can be used to determine the excess minority carriers lifetime. The semiconductor sample is chosen to be a bar-shaped with a length of L and cross-section of A. RS is the sample resistance, RL is the load resistance, VA is dc voltage, \( \tau \) is the excess minority carriers life time, and VL is the load or output voltage. RS, and therefore I and VL are time dependent parameters [13].
2.4.4. Photovoltaic Measurements

2.4.4.1. Short-circuit Current ($I_{SC}$)

The short-circuit current ($I_{SC}$) represents amount of the current that can flow through the device as a function of the incident optical power. It was measured using the same Keithley-616 electrometer.

2.4.4.2. Open-circuit Voltage ($V_{oc}$)

The open-circuit voltage ($V_{oc}$) represents the voltage drop across the device as a function of incident optical power. The incident optical power was varied using a halogen lamp with variable applied voltage.

2.4.4.3. Current-voltage Characteristics under Illumination

The manufactured solar cell was illuminated by varying light power from halogen lamp and the current was measured in reverse bias with a voltage range of 0.1-6 V. The results explained that this device can be operated as a solar cell.

2.4.4.4. Spectral Responsivity ($R_\lambda$)

The measurements of the spectral responsivity were performed using double-beam UIR-210A spectrophotometer operating within the range 200-1000 nm of wavelengths while the current measurements were performed using 8010 DMM Fluke digital multimeter. The spectral responsivity was determined using [14]:

$$R_\lambda = \frac{I_{ph}}{P_i}$$

(11)

where $I_{ph}$ is the measured photocurrent and $P_i$ is the incident optical power.

2.4.4.5. Specific Detectivity ($D^*_\lambda$)
The specific detectivity was determined using the following:

\[ D^*_\lambda = \frac{R_\lambda}{I_n} \sqrt{A\Delta f} \]  

(12)

where \( \Delta f \) is the noise-band width and \( I_n \) is the noise current given by \[ 15 \]

\[ I_n = \sqrt{2qI_d} \]  

(13)

where \( I_d \) is the dark current.

2.4.4.6. Quantum Efficiency (\( \eta \))

The value of quantum efficiency was estimated using the following \[ 16 \]

\[ \eta = 1.24 \frac{R_\lambda}{\lambda} \]  

(14)

2.4.4.7. Rise Time Measurement

The rise time of the device was measured using LED with wavelength of 840 nm and an average power of 0.5 watt. Function generator had been used at \( V=9.8 \) V, \( F=2598 \) Hz to obtain pulses. The output signal is achieved by a storage scope of 8300 D < s type (programmable digital scope) of 100 MHz bandwidth.

2.4.4.8. Response Time

Depending on the result of the rise time, the response time of the detector was calculated as follows \[ 17 \]

\[ \text{Response time} = \frac{\text{Rise time}}{2.2} \]  

(15)

3. Literature Review and Current Results

3.1. Structural Properties

Bismuth oxide is one of the most important polymorphous material which found to have four main polymorphic forms, namely \( \alpha-\text{Bi}_2\text{O}_3 \), \( \beta-\text{Bi}_2\text{O}_3 \), \( \gamma-\text{Bi}_2\text{O}_3 \)
and \( \delta\text{-Bi}_2\text{O}_3 \) [18, 19], while others mention the fifth phase namely \( \omega\text{-Bi}_2\text{O}_3 \) [20, 21] and recently characterized \( \varepsilon\text{-Bi}_2\text{O}_3 \) [22], and two non-stoichiometric phases are \( \text{Bi}_2\text{O}_{2.33}, \text{Bi}_2\text{O}_{2.75} \) [20]. Each polymorph possesses distinct crystalline structure occurs at different preparation conditions, make it important to know and study each phase [22]. Let us start with high temperature cubic phase or face center cubic, namely \( \delta\text{-Bi}_2\text{O}_3 \) fluorite type [19] which is considered among the most effective oxide ion conductors, but it is stable only between 1003 K and bismuth melting point 824°C. The second phase is the low temperature phase, namely monoclinic \( \alpha\text{-Bi}_2\text{O}_3 \) stable phase [22, 23] is a p-type semiconductor with energy gap at 300 K is equal to 2.85 eV where the conductivity of \( \text{Bi}_2\text{O}_3 \) may be dropped by over three orders of magnitude at temperature less than 1002 K when the material transforms to the monoclinic \( \alpha\text{-Bi}_2\text{O}_3 \) [23]. \( \beta\text{-Bi}_2\text{O}_3 \) phase is namely tetragonal with band gap equals to 2.58 eV [17], the transition to this phase from high temperature–phase occurs upon cooling at approximately 923 K. \( \gamma\text{-Bi}_2\text{O}_3 \) is metastable phase, namely body center cubic which obtains from transition on cooling of \( \delta\text{-Bi}_2\text{O}_3 \) or from the melt to 912 K and can persist down to room temperature [24]. \( \varepsilon\text{-Bi}_2\text{O}_3 \) is the novel polymorph, namely orthorhombic and finally a metastable triclinic polymorph called \( \omega\text{-Bi}_2\text{O}_3 \) phase occurs at 1073K on a (BeO) substrate [22]. Transformation between phases may occur during cooling and heating of the sample as shown in Fig. 3.

![Figure 3](image)

**Figure 3.** Transformation temperatures for \( \alpha, \delta, \gamma, \beta, \omega \) and \( \varepsilon\text{-Bi}_2\text{O}_3 \) [22]
It was found that structural properties of Bi$_2$O$_3$ thin film was investigated by many workers greatly affected by oxygen pressure pumped to the vacuum champer to oxides Bi atom that ablated by laser pulse (in pulse laser deposition system) from the bismuth target to form Bi$_2$O$_3$ thin film. Figure 4 shows that all films deposited at glass substrates, having a β-Bi$_2$O$_3$ phase with main different peaks reflecting from (201) and (402) plans at different oxygen pressure [25].

It could be recognized that Bi$_2$O$_3$ films with lowest oxygen pressure including some small diffraction peaks of β- Bi$_2$O$_3$ from (220), (222), (400) and (421) plans while film at higher pressure including small quantity of δ-Bi$_2$O$_3$ except for β-Bi$_2$O$_3$ and the respective diffraction peak from (111) plans [25]. XRD pattern for films evaporated thermally and oxidized at different oxygen flow ratio. Results show that at 2.5 % PO$_2$ ratio mixture of β-Bi$_2$O$_3$ and pure Bi phases could be found when PO$_2$ increases to 5%. The unoxidized pure Bi and δ- Bi$_2$O$_3$ disappear. PO$_2$ gradually increases in ratio up to 100% exhibits same diffraction peaks but with lower intensity [26]. The changes in diffraction peaks of Bi$_2$O$_3$ films at different oxygen flow ratio are shown in the following Fig. 5.
The effect of substrates temperatures on Bi₂O₃ thin films prepared by pulse laser deposition shown in Fig. 6. The XRD pattern at two different temperatures 75 °C and at 350 °C gave a single δ-Bi₂O₃ and β-Bi₂O₃ phases respectively, while mixed phases were observed at substrates temperatures of 200 °C and 500 °C. Whereas β-Bi₂O₃ is the main phase for films at substrate temperature of 500 °C. The diffraction peak of δ-Bi₂O₃ and β-Bi₂O₃ for films at all substrates temperatures are reflected from (111), (222), (201), and (402) plane respectively [25].

**Figure 5.** XRD of as-deposited thin films at substrate temperature of 200 °C and with different oxygen flow ratios [26]

**Figure 6.** XRD patterns of Bi₂O₃ films prepared by pulsed laser deposition at different substrate temperatures [25]
The XRD analysis of bismuth oxide films thermally evaporated on glass substrates and oxidized at different oxidation temperatures ranging from 423 K to 573 K found in Fig. 7. The result shows a mixed phases of monoclinic $\alpha$-Bi$_2$O$_3$ and tetragonal $\beta$-Bi$_2$O$_3$ at oxidation temperatures of 423 K, 473 K and 523 K, although some increases or decreases in these phases have been seen during the change in the oxidation temperature $T_{O2}$ of about 423 K, the monoclinic peak $\alpha$-Bi$_2$O$_3$ was dominated over all other peaks of tetragonal $\beta$-Bi$_2$O$_3$ while at $T_{O2}$ of 523 K, the intensity of monoclinic $\alpha$-Bi$_2$O$_3$ peak decreased as compared with that of tetragonal $\beta$-Bi$_2$O$_3$ and a single phase of $\alpha$-Bi$_2$O$_3$ has been observed at $T_{O2}$ of 573 K since sufficient time and energy has been provided for Bi atom to react with O$_2$ to form a stable phase. However, the overall intensities of diffraction peaks have been increased with increasing of oxidation temperature [27].

Figure 7. The XRD patterns of Bi$_2$O$_3$ thin films on glass substrate, oxidized at different temperatures: (a) 423 K, (b) 473 K, (c) 523 K and (d) 573 K [27]

On the other hand, XRD result of bismuth films prepared at different substrates temperatures (200-100 °C) using pulse laser deposition on glass substrate shows reflection belonging to different crystal plans (110), (112), (12i)
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and (221) [28], as is explained in Fig. 8. Relative intensities similar to those of bulk bismuth metal, indicating that the films are polycrystalline with random orientations.

![Figure 8. XRD analysis of Bi films at 200 °C and 100 °C substrate temperature [28]](image)

For films deposit at lower substrate range 93 °C to 75°C reflection from (111), (222), (333) planes start to grow as shown in Fig. 9.

![Figure 9. XRD of Bi films at 93 °C and 75 °C substrate temperature [28]](image)

At 30 °C, only peak (111) exists in the θ-2θ XRD patterns, so films could be either highly preferred at (111) orientation or single crystalline. Figure 10 shows this prefered (111) orientation at range 50 °C to -30 °C substrates temperatures. At 40 °C, no obvious peaks are seen, where the structure could be amorphous or Nano crystalline [28] as shown in Fig. 11.
3.1.1. Current XRD Results

XRD is an important experimental technique used to identify the crystal structure of solid, lattice orientation of single crystal and preferred orientations of polycrystalline, so it is considered as an effective tool for determining the actual position of atoms in crystal. Bi$_2$O$_3$ has five main crystalline phases and non-stoichiometric phases, and since each phase possesses different crystal structure, it is important to study the effect of different preparation conditions on the crystalline structure, to determine which phase or phases may exist at each preparation conditions then select the condition that gave us best structure with phases of semiconductor properties for the fabrication of a heterojunction detector. The effect of laser flounce on the structural properties of Bi$_2$O$_3$ films is shown in Fig. 12. The XRD patterns of the prepared film at 1.8 J/cm$^2$ shows an amorphous structure with a peak related to bismuth metal at 20=26° reflected from (003) plane. This indicates that the incomplete oxidation of bismuth metal during film growth. Besides, the existence of non-stoichiometric Bi$_2$O$_{2.33}$ phase at 20=29.6° which reflected from (107) plane is seen, also a very weak peak diffracted from monoclinic phase $\alpha$- Bi$_2$O$_3$ at 20 = 32°, 27° from (20-2), (121) plane, respectively is obvious with no sign for tetragonal phase $\beta$ with monoclinic phase at this laser flounce.

The same peak still appear at higher laser flounce 3.8 J/cm$^2$ as shown in Fig. 12 (b) at 20° = 26°, 29.7°, 27°. Beside the presence of another small peak related
to \(\beta\)-Bi\(_2\)O\(_3\) at \(2\theta=28^o\) reflected from (201) plane, we could recognize the non-stoichiometric phase of Bi\(_2\)O\(_{2.33}\) to be more intense at this laser flounce. The existence of Bi\(_2\)O\(_{2.33}\) at both laser fluencies may be attributed to the uncompleted oxidation process in the prepared films. Similar result was reported previously [14].

Increasing laser energy up to 5.8 J/cm\(^2\), the XRD pattern in Fig. 12 (c) gives peaks that are related to \(2\theta=27^o\), \(28^o\), \(33^o\) reflected from (121), (201), (220) planes. These peaks are related to \(\alpha\)-Bi\(_2\)O\(_3\) and \(\beta\)-Bi\(_2\)O\(_3\), respectively.

Bismuth metal appeared at \(2\theta=26.7^o\) and \(31.3^o\) which are reflected from (003) and (012) planes, respectively. The grow in peak intensity may indicate gradual improve in the film crystallization as compared with previous films with obvious peak of \(\beta\)-Bi\(_2\)O\(_3\), \(\alpha\)-Bi\(_2\)O\(_3\) bismuth oxide phases. Although bismuth peak still appeared and grew further more than the previous at lower laser flounce that means we still not reach the best laser flounce and total transformation to Bi\(_2\)O\(_3\) oxide film.

The XRD pattern for film prepared at 7.8 J/cm\(^2\) laser fluence is shown in Fig. 12 (d). The disappearance of Bi metal from the film structure mean the formation of Bi\(_2\)O\(_3\) only, although a non-stoichiometric phase Bi\(_2\)O\(_{2.33}\) appeared at \(2\theta=21.5^o\), \(29^o\) reflected from (008), (107) plane, respectively. An increase in the \(\alpha\)-Bi\(_2\)O\(_3\) at \(2\theta=27.2^o\) is due to reflection from (121) plane peak intensity that is so clear with appearance of \(\delta\)-Bi\(_2\)O\(_3\) at \(2\theta=27^o\) oriented at (111) plane and two other peak assign to \(\beta\)-Bi\(_2\)O\(_3\) phase at \(2\theta=28^o\) and \(30.5^o\) reflected from (201), (123) plans, respectively. At this laser flounce 7.8 J/cm\(^2\) both monocline and tetragonal phase exist with no presence to any peak related to Bi metal so this laser flounce is consider the best laser flounce for the structure required. Further increase of laser flounce up to 9.8 J/cm\(^2\) diffraction peak appears at \(2\theta=26^o\) is recognized as a result of reflection from (003) plane belongs to Bi metal. This is attributed to the fact that high laser flounce ablate large species from the target as particulates. A small peak for monoclinic phase at \(2\theta=27^o\) reflected from (121) plane, diffraction peaks at \(2\theta = 30.4^o\), \(34^o\) and \(46^o\) are corresponding to \(\beta\)-Bi\(_2\)O\(_3\) which are due to the reflection from (123), (220) and (222) planes, respectively. Film structure at this laser fluencies is shown in Fig. 12 (e).
a) 1.8 J/cm²
1: Bi metal(003)
2: α-Bi₂O₃ (121)
3: Bi₂O₃,₃₃ (107)
4: α-Bi₂O₃ (20-2)

b) 3.8 J/cm²
1: Bi metal(003)
2: α-Bi₂O₃ (121)
3: β-Bi₂O₃ (201)
4: B₂O₂,₃₃ (107)
c) 5.8 J/cm²
1: Bi metal (003)
2: α-Bi₂O₃ (121)
3: β-Bi₂O₃ (201)
4: Bi metal (012)
5: β-Bi₂O₃ (220)
6: Bi₂O₃·33 (008)

d) 7.8 J/cm²
1: Bi₂O₂.₃₃ (008)
2: α-Bi₂O₃ (121)
3: β-Bi₂O₃ (111)
4: β-Bi₂O₃ (201)
5: Bi₂O₂.₃₃ (107)
6: β-Bi₂O₃ (123)
Effect of oxygen pressure on the prepared films' structure at optimum laser flounce 7.8 J/cm² and 423 K substrate temperature is shown in Fig. 13. Films prepared at 50 mbar oxygen pressure. Figure 13 (a) shows monoclinic phase at 2θ = 27.4° orientated at (121) plane with tetragonal phase at 2θ = 28° reflected from (201). Bi₂O₂.₃₃ phase appears at 2θ = 29° is reflected from (107) plane and films prepared at this oxygen pressure shows poor crystalline structure. Diffraction pattern at higher oxygen pressure of 100 mbar shows the domination of α-Bi₂O₃ phase which appear at 2θ = 27.2° reflected from (121) plane with the presence of other peaks appear at δ-Bi₂O₃ at 2θ = 27° oriented at (111) plane and two other peak assign to β-Bi₂O₃ phase at 2θ = 28° and 30.5° reflected from (201), (123) planes, respectively. We could also notice non-stoichiometric phase of Bi₂O₂.₃₃ appeared at 2θ = 21.5° and 29° reflected from (008), (107) plane respectively as shown in Fig. 16 (b). At 150 mbar of
Fig. 13 (c) gives an evidence of peak at $\theta = 27.4^\circ$ orientated at (121) corresponding to monoclinic phase with $\beta$-phase at $\theta = 28^\circ$, $30.4^\circ$ and $34^\circ$ reflected from (201), (123), (220) planes, while $\text{Bi}_2\text{O}_2.33$ at $\theta = 29^\circ$ is reflected from (107) plane. Oxygen pressure condition of 200 mbar is shown in Fig. 13 (d) which demonstrates a better crystallization of $\text{Bi}_2\text{O}_3$ film structure for $\alpha$ and $\beta$ phases with higher intensity for bismuth oxide phases at $\theta = 27.5^\circ$ and $28^\circ$ reflected from (121) and (201) planes, respectively. The same film shows the formation of two peaks for tetragonal phase at $\theta = 31.4^\circ$ and $46^\circ$ reflected from (002), (222) plane respectively along with $\text{Bi}_2\text{O}_2.33$ at $\theta = 29^\circ$ orientated at (107) plane. At 250 mbar oxygen pressure of Fig. 13 (e), we could recognize the presence of $\alpha$-$\text{Bi}_2\text{O}_3$ at $\theta = 27.5^\circ$ orinated at (121) plane with an additional peak related to $\beta$-$\text{Bi}_2\text{O}_3$ at $\theta = 28^\circ$, $30^\circ$ and $34^\circ$ reflected from (201), (123) and (220) planes, respectively. Also the non-stoichiometric $\text{Bi}_2\text{O}_2.33$ at $\theta = 29^\circ$ orientated at (107) plane still appears. Although the excepted crystallization is shown for a film deposited at this oxygen pressure but the overall intensity of the oxide peak for tetragonal and monoclinic phase is lower due to the fact that the increase of oxygen pressure which improves the stoichiometry of the films associated with incorporation of oxygen at oxygen vacancies however a further increase in oxygen pressure above the optimum value or equilibrium value might worsen the stoichiometry of films introducing interstitial oxygen vacancies. Similar result is reported in te literature [20]. The XRD pattern analysis at 300 mbar shows monoclinic phase at $\theta = 27.5^\circ$ and $32^\circ$ orinated at (121) and (20-2) planes, respectively and tetragonal phase at $\theta = 30.5^\circ$ reflected from (123) plane. It appears continuous but higher than that in 250 mbar. Other peaks appear in 300 mbar corresponding to $\theta = 28.5^\circ$ and $46^\circ$ reflected from (201) and (222) planes, respectively for tetragonal bismuth oxide structure are shown in Fig. 13 (f). In the last three oxygen pressure condition, we could notice the optimum oxygen pressures condition at 200 mbar.
Figure: X-ray diffraction patterns of Bismuth Oxide nano and microstructures.

(c) 150 mbar
1: $\alpha$-Bi$_2$O$_3$ (121)
2: $\beta$-Bi$_2$O$_3$ (201)
3: Bi$_2$O$_2$ (107)
4: $\beta$-Bi$_2$O$_3$ (123)
5: $\beta$-Bi$_2$O$_3$ (220)

(d) 200 mbar
1: $\alpha$-Bi$_2$O$_3$ (121)
2: $\beta$-Bi$_2$O$_3$ (201)
3: Bi$_2$O$_2$ (107)
4: $\beta$-Bi$_2$O$_3$ (002)
5: $\beta$-Bi$_2$O$_3$ (222)
Figure 13. XRD for films prepared at different oxygen pressure (a) 50 mbar, (b) 100 mbar 4.5(c) 150mbar, (d) 200 mbar, (e) 250 mbar and (f) 300 mbar
The Effect of substrate temperatures on X-ray results was investigated. The substrates temperatures significantly influence the type of crystalline structure at optimum laser flounce 7.8 J/cm\(^2\) and constant oxygen pressure 200 mbar. XRD results at \(\Delta T_{\text{sub}}\) are shown in Fig. 14. At 323 K, the existent of single strong peak of \(\alpha\)-Bi\(_2\)O\(_3\) at \(2\theta=27.5^\circ\) oriented at (121) plane and a peak of \(\beta\)-Bi\(_2\)O\(_3\) at \(2\theta=28^\circ, 30.1^\circ\) reflected from (201), (123) plane could be recognize respectively. Additionally, there is a peak assigned to non-stoichiometric phase at \(2\theta=21.6^\circ\) and \(35^\circ\) reflected from (008), (013) plane respectively as shown in Fig. 14 (a). Diffraction peak at substrate temperature of 373 K is shown in Fig. 14 (b). In addition to the main peak of \(\alpha\)-Bi\(_2\)O\(_3\) appear at \(2\theta=25.8^\circ, 27.5^\circ\) oriented at (301), (121) plane respectively and \(\beta\)-Bi\(_2\)O\(_3\) at \(2\theta=28^\circ\) reflected from (201) another peak shown in the film diffracted from \(2\theta=46.7^\circ\) orientated from (222) for \(\beta\)-Bi\(_2\)O\(_3\). The XRD results of the prepared film at 423 K have peak of \(\alpha\)-Bi\(_2\)O\(_3\) at \(2\theta=27.5^\circ\) reflected from (121) plane, in addition to a peak of \(\beta\)-Bi\(_2\)O\(_3\) at \(2\theta=31.8^\circ, 28^\circ\) and \(46^\circ\) reflected from (201), (222) and (002) plane, respectively. Bi\(_2\)O\(_{2.33}\) at \(2\theta=29^\circ\) orientated at (107) plane appeared. An increase in peak intensity over the previous substrate temperature was notice. The great enhancement of the peak indicates the good improvement in the crystalline structure with domination of the monoclinic phase as depicted in Fig. 14 (c). An interesting change in the structure of films prepared at higher temperature 473K–723 K is shown in Fig. 14 (d-g). At 473 K, Fig. 14 (d), the XRD pattern exhibits a degradation of \(\alpha\)-Bi\(_2\)O\(_3\) at \(2\theta=27.5^\circ\) reflected from (121) plane dominated at \(2\theta=27.5^\circ\) reflected from (201) plane of \(\beta\)-Bi\(_2\)O\(_3\) along with strongest minor peak assigned to \(\beta\)-Bi\(_2\)O\(_3\) at \(2\theta=25.8^\circ, 46^\circ\) and \(56^\circ\) reflected from (301), (222) and (624) plane, respectively. The XRD pattern of 523 K shows further domination of tetragonal phase \(2\theta=28^\circ\) at (201) plane over monoclinic phase \(2\theta=27.5^\circ\) reflected from (121) plane associated with another peak for \(\beta\)-Bi\(_2\)O\(_3\) at \(2\theta=46.6^\circ\) reflected from (222) plane and a new peak for \(\beta\)-Bi\(_2\)O\(_3\) \(2\theta=30^\circ\) diffracted from (123) plane as shown in Fig. 14 (e) at 623 K. Figure 14 (f) of the X-RD pattern of Bi\(_2\)O\(_3\) shows the almost diminished monoclinic phase at \(2\theta=27.5^\circ\). Bi metal appeared in the film structure at
$2\theta=31.5^\circ$ reflected from (012) plane and that we attributed to the substrates temperature along with high laser flounce which results because of sublimation of Bi metal ablated from the target surface and deposited on the substrate surface. Peaks related to $\beta$-$\text{Bi}_2\text{O}_3$ at $2\theta=25.9^\circ$, 28°, 33°, 46° and 55.9° reflected from (301), (201), (220), (402) and (421) plane, respectively. XRD pattern at 723 K shows peaks related to $\beta$-$\text{Bi}_2\text{O}_3$ at $2\theta=28^\circ$, 30° and 33.2° reflected from (201), (123) and (220) respectively along with appearance of bismuth metal in the film structure at $2\theta=32^\circ$ reflected from (200) plane. All peaks related to the tetragonal phase made this phase the dominated phase and this result coincides with UV visible properties of the same films show an energy gap value of to 2.6 eV which is the known value for the tetragonal phase [29]. XRD spectrum of the film prepared at 723 K as shown in Fig. 14 (g).
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(b) $373 \text{ K}^0$

1: $\alpha$-Bi$_2$O$_3$ (301)
2: $\alpha$-Bi$_2$O$_3$ (121)
3: $\beta$-Bi$_2$O$_3$ (201)
4: $\beta$-Bi$_2$O$_3$ (222)

(c) $423 \text{ K}^0$

1: $\alpha$-Bi$_2$O$_3$ (121)
2: $\beta$-Bi$_2$O$_3$ (201)
3: Bi$_2$O$_3.33$ (107)
4: $\beta$-Bi$_2$O$_3$ (002)
5: $\beta$-Bi$_2$O$_3$ (222)
3.2. Surface Morphology

Effect of the oxygen pressure on the surface morphology of Bi$_2$O$_3$ thin films on glass substrates prepared by PLD shows, that grain size of the films decreases obviously with an increase in oxygen pressure, while the root mean square (RMS) roughness of Bi$_2$O$_3$ films steeply decreases with oxygen pressure up to a specific value and then no obvious different has been observed at higher pressure. Thus, may be due to the increase in, the oxygen pressure lead to decrease in size and kinetic energy of the formed nuclei [25]. The AFM image in the following Fig. 15 shows the effect of oxygen pressure on bismuth oxide thin films prepared by pulse laser deposition.

Similar results have shown [26] about the effect of different oxygen pressure of Bi$_2$O$_3$ films deposited on silicon (100) substrate, the sputtered Bi$_2$O$_3$ films prepared at oxygen pressure range of about (5%, 10%, 20% and 80%) have uniform and dense substrate with grain size decrease as the oxygen pressure increases from 5% to about 20%, then at 80% the gain size limited and did not grow further with increased oxygen pressure. The following Fig. 16 shows
SEM image of Bi$_2$O$_3$ at different oxygen pressure.

Figure 15. AFM images of Bi$_2$O$_3$ films prepared by PLD at different oxygen pressures and substrate temperature of 350 °C, (a) 0.15 Pa, (b) 1.5 Pa, (c) 11 Pa, (d) 45 Pa [25]
Figure 16. SEM of $\delta$-Bi$_2$O$_3$ films deposited at substrate temperature of 200°C and with different oxygen flow ratios: (a) 5%, (b) 10%, (c) 20% and (d) 80% [26]

Figure 17. AFM of Bi$_2$O$_3$ films prepared by PLD under different substrate temperatures at oxygen pressure of 11 Pa: (a) 75 °C; (b) 200 °C; (c) 350 °C and (d) 500 °C [25]
The effect of substrate temperature on the morphology of Bi$_2$O$_3$ thin films prepared by PLD shows the grain size increase with increased substrate temperature while the surface roughness of the films is not obviously different [25]. Figure 17 shows the AFM image for films at different substrate temperature.

### 3.2.1. Current Surface Morphology Study

Effect of laser energy on the nature of the films surface was investigated by Atomic Force Microscopy (AFM) to find the grain size and films roughness. Figure 18 shows the AFM image for films prepared at different laser fluence, we notice an increase in grain size with increasing in laser fluence from 101 nm, 129.67 nm to 131.6 nm corresponds to increasing laser fluence from 5.8 J/cm$^2$, 7.8 J/cm$^2$ and 9.8 J/cm$^2$, respectively. Since increasing the laser fluence means increases the kinetic energy of the particles being ejected from the target. Effect of oxygen pressure ambient on the grain size and root meant square. We could recognize that all films show a uniform dense surface, result also exhibit decrease in grain size with increasing oxygen pressure.

This is attributed to the collisions rate and of reactions leading to Bi$_2$O$_3$ formation, between the ejected Bi species and the oxygen atom which increase with increasing oxygen pressure. Size and kinetic energy of the formed nuclei decrease with increasing oxygen pressure thus larger nuclei with grain size of 97.5 nm and high kinetic energy is formed at 100 mbar, then the kinetic energy decrease and grain size further decrease to about 75.42 nm and 65.12 nm with increasing oxygen pressure further to 200 mbar and 300 mbar, the AFM result of Bi$_2$O$_3$ at different oxygen pressure is shown in Fig. 19. Similar result were reported [25], while the root mean square did not show an obvious change in its value at higher oxygen pressure similar result was observed [25].
Figure 18. AFM result for films prepared at different laser fluences (a) 5.8 J/cm² (b) 7.8 J/cm² (c) 9.8 J/cm²
Substrate temperature is one of the most important factors that greatly affected the nature of films growth. From the AFM result of Fig. 20. It could be recognized that grain size of films increase from 75.91 nm to about 120.36 nm with increasing substrate temperature from 423 K to 523 K, this related to the
fact that at higher substrate temperatures, the impinging flux on the surface acquires higher energy and hence a large mobility, as a result, the diffusion distance of the adatom on the surface increases and the collision process initiates the nucleation for more adatoms joining to form larger grains, then grain size decreased to about 90 nm with increasing substrate temperature up to about 623 K, this was due to the fact that at higher substrate temperature the larger particle size will reflect. It also obviously those films show dense surfaces with pyramid like shape reflect from a well uniform surface. At higher substrate temperature this uniform structure start to deform, while the root mean square RMS increase with increasing grain size due to the fact that when larger grain is grown the more compact the films will be the RMS is increase from 2.06 nm to 2.22 nm and 4.68 nm with increasing substrate temperature from 423 K to 532 K and 632 K, respectively. After chose 7.8 J/cm² laser fluence and 200 mbar oxygen pressure as best condition and determined 523 K as best substrate temperature from figure of merit a surface image was taken by Scan Electron microscopy (SEM). The SEM produces topological images of surfaces at very high magnification and it is even possible to observe the fine structure of the film surface such as nano and microstructures. The aim of this investigation is to obtain information about the surface morphology and geometry of structures that show very homogeneous and constructed of small micro particles of about 117 nm diameter and we could recognize that each particles consisting from other nanoparticles in what called nanocluster take the shape of cauliflower as in the figure below, also showing no cracks which in close agree to the AFM grain size result. SEM image for optimum condition is shown in the Fig. 21.
Figure 20. AFM result for films deposited at (a) 423 K, (b) 523 K, (c) 623 K

Figure 21. SEM image for Bi$_2$O$_3$ at optimum condition of laser fluence 7.8J/cm$^2$, oxygen pressure of 200 mbar and substrate temperature 523 K
3.3. Optical Properties

Optical properties is one of the important characteristic which enable us determined several important features of bismuth oxide thin films such as energy gap value of $\text{Bi}_2\text{O}_3$ which enables us to establish which phase is dominating on films structure. Due to the fact that certain phase has known energy gap value, such as $\alpha$-, $\beta$-$\text{Bi}_2\text{O}_3$ have energy gap value of about $2.3\text{eV}$ and $2.58$ or $2.6\text{ eV}$ [29, 30].

Optical transmittance (T%) reaches to about 75% in the visible and near infrared region for $\text{Bi}_2\text{O}_3$ films prepared by PLD method was found by researcher [25], where effect of oxygen pressure could be shown in Fig. 22. The absorption edge is taking as differential curves ($dT/d\lambda$) versus $\lambda$ of transmission spectra showing two peaks for films at different oxygen pressure which indicated the existence of two absorption edges.

![Figure 22](image)

**Figure 22.** Optical transmission spectra for $\text{Bi}_2\text{O}_3$ films prepared by pulsed laser deposition at different oxygen pressures. The insert shows the plot of $dT/dk$ versus $\lambda$ [25]

$\delta$-$\text{Bi}_2\text{O}_3$ thin films prepared by radio frequency (RF) reactive sputtering grown on Si (100) slices and quartz glass have been achieved at various oxygen flow ratio of about 5%, 10%, and 20%. High oxygen of about 20% flow results
in a low refractive index (n) and extinction coefficient (K), which may occur, due to the close relation of refractive index to the density of material. It is being lower refractive index at low density. Two factors affect the density of thin film:

- The excess oxygen in the vacuum chamber might be absorbed in the films during sputtering due to the low reaction rate between Bi and O ions.
- The higher the oxygen particle pressure, the lower the energy of the arriving species of Bi and O₂ ions on the substrate. The lower the mobility of the condensed particles the surface mobility favors the three dimensional (3-D) island growth leading to the growth of large number of small crystallites; while the high surface mobility favors the two–dimensional (2-D) manner leading to the formation of large grain size, and thus the dense packing structure was formed at low oxygen flow ratio and the loose structure was formed at high oxygen flow ratio [31]. This decreases in refractive index and extinction coefficient with increasing of oxygen pressure as shown in Fig. 23.

Figure 23. Shows the change of refractive index and extinction coefficient with different oxygen flow ratio [31]

Low absorbance of Bi₂O₃ films, which thermally evaporated at different oxidation temperature, have reported [27] as shown in Fig. 24.

The optical transmission spectra of bismuth oxide/bismuth films prepared by thermal evaporation onto glass substrates maintained at different temperatures
(300 K, 373 K). Subsequently, their thermal oxidation in air was performed for 1 and 2 hours, respectively. This method of preparation of Bi₂O₃ films reveals that these films have a good transparency in spectral range λ (300-1000 nm). The transmission spectra changed only slightly with increasing thermal oxidation time and showed a weak dependence upon the temperature Ts [32]. Figure 25 shows the transmission for both films at two oxidation stages.

**Figure 24.** The absorption with wavelength, of Bi₂O₃ thin films oxidized at (a) 423 K, (b) 473 K, (c) 523 K and (d) 573 K [27]

**Figure 25.** Optical transmission spectra for Bismuth oxide/Bismuth structures deposited onto glass maintained at Ts=300 K (left) and Ts=373 K (right), respectively, for the two oxidation stages [32]
Effect of oxygen pressure on the estimated band gap value for Bi$_2$O$_3$ thin films prepared using PLD method could be shown in Fig. 26. The energy gap results show the existence of two-energy gap due to the existence of two absorption peaks. Results show energy gap value in the range of Bi$_2$O$_3$ energy gap value [25] as shown in Fig. 26.

![Figure 26.](image)

The band gap value for Bi$_2$O$_3$ thin films thermally evaporated at different oxidation temperatures range between 423 to 573 K. Variation of band gap with oxidizing temperature of bismuth oxide films is evidence. It is seen that initially as oxidizing temperature has increased from 423 to 523 K. The band gap was increased from 2.40 to 2.55 eV. Lastly, at oxidizing temperature 573 K, the band gap was increased remarkably. It was not mention the energy gap value at 473 K, but it is clear from Fig. 27, this energy gap value shows irregular behavior with increase over the oxidation temperature 523 K [27]. This increase in band gap with oxidation temperature is shown in Fig. 27.

The band gap value for thermally evaporation bismuth films onto glass substrates prepared and maintained at different temperatures. Subsequently, their thermal oxidation in air was performed for 1 and 2 hours, respectively. Results for films corresponding to substrate temperature of 300 K show a slight
increases from 3.23 to 3.55 eV when passing from 1st stage to the 2nd stage of oxidation, while films deposited at substrate temperature of about 373 K, band gap did not change at all when passing from the 1st to the 2nd oxidation stage as still $E_g$ of 3.897 eV [32]. These two results of the $E_g$ for both oxidation stages are shown in Fig. 28.

**Figure 27.** $(\alpha h\nu)^2$ ver. $(h\nu)$ for Bi$_2$O$_3$ films at different oxidation temperature (a) 423 K, (b) 473 K, (c) 523 K, (d) 573 K [27]

**Figure 28.** Energy gap value for films at two stages and two substrates temperature [32]
3.3.1. Current Optical Results

The influence of different preparation conditions on the optical properties of Bi$_2$O$_3$ thin films grown on glass substrates are studied deeply. Prepared films were examined using a spectrophotometer to find the transmission spectra for each film in the UV-visible and NIR spectrum. The transmission spectra of the prepared films at different laser fluence, oxygen pressure of 100 mbar and substrate temperature of 423 K are shown in Fig. 29 (a), where a decrease in transmission spectra with increasing laser fluence from 1.8 J/cm$^2$ to 9.8 J/cm$^2$ is recognized. This may be due to the fact that at higher laser energy, the films thickness increase.

The converged transmission at 5.8 J/cm$^2$ and 3.8 J/cm$^2$ laser fluence may be attributed to the uncompleted oxidation of the Bi metal. Also, the fundamental absorption edge shows a positive shift in the wavelength (red shift) with increasing grain size, which indicates a shift in the optical band gap to lower energy value and this results are agree with the estimated energy gap value, which decrease from 2.9 eV at 5.8 J/cm$^2$ to 2.4 eV at 7.8 J/cm$^2$ then to 1.2 eV at 9.8 J/cm$^2$ as shown in Fig. 29 (b), where other worker report similar results [30]. It could be recognize that the tendency of the band gap value to move away from the typical value of Bi$_2$O$_3$ thin films which related to the presence and predominating of unoxidized Bi atoms in the depositing material and the high defect present in the film prepared at this laser fluence and this another reasen prove that best laser flunce is 7.8 J/cm$^2$.

Optical transmission of films prepared at different oxygen pressures ($\Delta$PO$_2$) shows an increasing in films transparency, when (PO$_2$) increase from 50 mbar-300mbar. This may due to decrease in films thickness which subsequently leading to increase in films transparency as shown in Fig. 30 (a). Energy gap value show an increase from 2.31 eV for 100 mbar and 2.58 eV with increasing oxygen pressure up to 200 mbar and 2.6 eV for further increase to 300 mbar as shown in Fig. 30 (b). This increase in energy gap value leads to blue shift in the band gap to shorter wavelength which is a phenomena that notice for Bi$_2$O$_3$ films in similar worker [26, 31]. This shift in energy gap may due to decrease in grain size with increasing O$_2$ pressure, such effect is related
to the quantum confinement effect. Other factors, such as the reduction in the number of defects disorder in Bi$_2$O$_3$ thin film and the increase in stoichiometric composition, might also lead to the increase in the optical band gap. Similar result is reported elsewhere [26].

Figure 29. Transmittance spectra for Bi$_2$O$_3$ films, (b) the energy gap value, at different laser fluence and oxygen pressure of about 100 mbar and substrate temperature 423 K
Effect of substrate temperature on the transmission spectra of the prepared films at constant laser flounce 7.8 J/cm$^2$ and 200 mbar oxygen pressure could recognize in Fig. 31. All the obtained results show a good transparency with a slight decrease at the first three substrate temperature 323 K, 423 K and 523 K, which may be related to the fact of increasing films thickness and surface roughness at these temperature. The optical transmission reached to about high value at higher substrate temperatures of 623 K and 723 K. This behavior of the
transmission at higher substrate temperature may be caused by the decreasing of optical scattering due to densification of film crystallites [16]. The estimated energy gap for the films prepared at 423 K, 523 K and 623 K substrate temperature as shown in Fig. 31 (b), it could be recognize that energy gap values have comparable result which related to the total transformation of the ablated metal to it oxide, where Bi₂O₃ semiconducting films appear at its monoclinic phase at 423 K substrate temperature. Farther increase in the substrate temperature up to 523 K and 623 K could be recognized the phase transformation from monoclinic to tetragonal, resulting in an energy gap value familiar for this phase. Similar results obtained by others [17, 29].

Figure 31. (a) Transmittance spectra (b) optical energy gaps at different substrate temperature and laser fluence 7.8 J/cm² and oxygen pressure 200 mbar
3.4. Electrical Properties

Normal semiconductor behavior (decrease in resistivity with temperature) has been observed for Bi$_2$O$_3$ prepared from vacuum evaporated Bi film by thermal oxidation in air at different temperature [27]. Figure 32 shows the variation in dark resistivity (log $\rho$) with temperature (1000/T).

![Figure 32](image)

**Figure 32.** The dark resistivity (log $\rho$) with temperature (1000/T, 1/K) of Bi$_2$O$_3$ thin films oxidized at: (a) 423 K, (b) 473 K, (c) 523 K and (d) 573 K [27]

![Figure 33](image)

**Figure 33.** Real part of permittivity for Bi$_2$O$_3$ at different thickness and oxidation temperature, imaginary part at different thickness and oxidation temperature [33]
The effect of oxidation temperature and thickness of $\text{Bi}_2\text{O}_3$ films of dielectric constant was studied using thermal oxidation for preparing Bi films, then oxidized them at different temperatures where it has shown that at decrease of oxidation temperatures, the dielectric constant showed low value. Figure 33 shows the real part and imaginary part of the permittivity ($\varepsilon$) for two thicknesses and three different oxidation temperatures, while the impedance did not vary with oxidation temperature and showed an inductive nature [33].

The current–voltage behavior of $\text{Bi}_2\text{O}_3$ thin films were prepared using dry oxidation method [10] shows that all prepared films at different oxidation temperatures show ohmic behavior as recognized in Fig. 34.

**Figure 34.** $I$-$V$ characteristics of $\text{Bi}_2\text{O}_3$ thin film [10]
3.4.1. Preparation Techniques of Bi$_2$O$_3$

The bismuth oxide thin films have been prepared by different methods, since physical properties of bismuth oxide polymorphous strongly depends on the preparation technology and preparation conditions [34]. Thus, it is important to determine which method and conditions produce the desired phase structure. Bi$_2$O$_{2.33}$ phase using spray pyrolysis method from nono aqueous medium is prepared [29], while other worker reported the preparation of monoclinic Bi$_2$O$_3$ films by anodization of electrochemically deposited Bi films and by chemical bath deposition method. Pulse laser deposition technique is one of these methods [25, 35], although only few workers reported the preparation and characterization of bismuth oxide properties, bismuth oxide is focused for optoelectronic device. Figure 35 shows schematic sketch of cross section layer with arrows, representing the incoming and scattered light.

**Figure 35.** Schematic sketch of the cross section of the multilayer light-trapping structure based on Bi$_2$O$_3$ Nano-islands [36]

**Figure 36.** (a) I-V curves at 300 K and 77 K denoted as A and B respectively (b) expand scale to show leakage region [37]
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The light tapping efficiency result shows tapping efficiency in long wavelength region of 800 nm–1100 nm with less than 10% when Si (1.2 μm) thick. Structure with low cost, exhibiting high efficiency for solar cell [36]. The I-V curves at 300 K and 77 K of the ZnO-Bi$_2$O$_3$ junction where Bi$_2$O$_3$ terminal was taken as voltage reference, ZnO will be biased against Bi$_2$O$_3$ either positive or negative as shown in Fig. 37.

3.4.2. Heterojunction Using Bismuth Oxide

In general, heterojunction known as an intimate contact between two semiconductors materials are different in their electrical properties which includes (energy gap $E_g$, electron affinity ($\chi$), work function ($\Phi$) and permittivity ($\varepsilon$), thus heterojunction could be divided in two types:

(a) Abrupt heterojunction as the band diagram is shown in Fig. 37 (a).
(b) Graded heterojunction as the band diagram is shown in Fig. 37 (b).

![Figure 37. Heterojunction type (a) abrupt (b) graded](image)

A typical energy band profile of two isolated pieces of p- and n- type semiconductors and an equilibrium energy band profile of an abrupt p-n heterojunction formed by bringing them into intimate contact are shown in Fig. 
38. It is clear that the electron affinity of the wide–band gap material $\chi_p$ is less than that of narrow–band gap material $\chi_n$. The difference between the two conduction band energies is denoted by $\Delta E_c$ and the difference between the two valances band energies is denoted by $\Delta E_v$ according to;

$$\Delta E_c = \chi_n - \chi_p$$  \hspace{1cm} (16)

$$\Delta E_v = (E_{gp} - E_{gn}) - (\chi_n - \chi_p)$$  \hspace{1cm} (17)

and

$$\Delta E_c + \Delta E_v = E_{gp} - E_{gn} = \Delta E_g$$  \hspace{1cm} (18)

where $E_{gp}$ and $E_{gn}$ are the energy gaps of the wide band gap and narrow-band gap material, respectively.

In general, ideal heterojunction in thermal equilibrium and according to Fermi levels in the two materials to be aligned, electrons from the narrow–gap n-region and holes from the wide-gap p-region must flow across the junction. As in the case of homojunction, this flows of charge creates a space charge region in the vicinity of the metallurgical junction. The space charge width into the n-type region is denoted by $X_1$ and the space charge width into the p-type region is denoted by $X_2$ [38].

**Figure 38.** Band diagram for heterojunction, a) before contact, b) after contact
When the junction formed between materials have different properties. Various factors will influence the properties of the grown heteroepitaxial layers. N-Bi$_2$O$_3$/p-Si heterojunction was prepared by rapid thermal oxidation process by some workers [39]. They investigated electrical properties and detector parameters for the device. The cross section view of the device is shown in Fig. 39.

![Figure 39. n-Bi$_2$O$_3$/n-Si heterojunction cross section view [39]](image)

Metal-insulator-semiconductor (MIS) solar cell of GaAs with physical deposited Bi$_2$O$_3$ interfacial layer was investigated [40]. Two methods were used deposited the Bi$_2$O$_3$ layer, thermal evaporation and electron beam with flat and texture surface for both method. Figure 40 shows the illuminated current–voltage curves of cell for flat and textured surface, the cell with Bi$_2$O$_3$ layer show substantial improvement in open circuit voltage over cell made without Bi$_2$O$_3$ layer, cell with textured surfaces yield 30% increase in short–circuit current "light trapping" in textured surface is primarily responsible for this increase while 3% decrease in $V_{o.c}$ for textured surface have been attributed to higher pinhole density. Overall significant increase in conversion efficiency has been obtained for textured surface [40].

Other group has deposited Bi$_2$O$_3$ on GaSe where fresh cleaved surface of p-GaSe plates heated and then Bi$_2$O$_3$ thin film with different thickness in rang of 95-125 nm was deposited by RF magnetron sputtering. Study shows the J-V characteristics for both bias. Figure 41 shows J-V characteristics for this junction [41].
Figure 40. (a) Illuminated current-voltage curves of cells with (1) baseline textured surface (2) electron beam MIS textured surface (3) thermal evaporation MIS textured surface. (b) Illuminated current-voltage curves of cells with (1) baseline flat surface. (2) Electron beam MIS flat surface, (3) thermal evaporation MIS flat surface [40]
3.4.3. Current Electrical Results

The logarithmic conductivity as a function of heating temperature for Bi$_2$O$_3$ thin films is prepared at optimum laser fluence, oxygen pressure and different substrate temperature as given in Fig. 42. It is obvious from result that conductivity of Bi$_2$O$_3$ films increase as temperature increases showing a typical semiconductor behavior due to the fact that at higher temperature the number of generated electron–holes pairs increase and thus conductivity increase.

![Figure 41. Bi$_2$O$_3$/GaSe structure (a) forward bias (b) reverse bias [41]](image_url)

![Figure 42. Conductivity as a function with temperature for films prepared at different substrate temperature](image_url)
Figure 43 shows the resistivity for Bi$_2$O$_3$ films as a function of temperature samples, i.e. decrease in resistivity with temperature. Curve deposited at 323 K substrate temperature shows distorted behavior with temperature, this is because of comparatively more oxide vacancies in Bi$_2$O$_3$ films, heating of the sample during measurement may cause redistribution of oxide vacancies thus sample leap, similar result is shown by other worker [27], the relatively high resistivity may be attributed to the presence of non-stoichiometric phase of Bi$_2$O$_{2.33}$ and Bi$_2$O$_{2.75}$ and the total transformation to tetragonal phase also the presence of other insulating phase.

![Figure 43. The variation in resistivity with temperature](image)

3.4.3.1. Figure of Merit

Figure of merit is a calculated value from measured parameter in order to ranks the performance of transparent conductive oxide thin films. Figure 44 shows the figure of merit for Bi$_2$O$_3$ thin films prepared at optimum laser fluence, oxygen pressure and at different substrate temperature in order to achieve a best approach between two important qualities with which they can be judged absorption coefficient and conductivity. Results show that the value of figure of merit at 323 K substrate temperature has small value then start to increase at
423 K reach its maximum value at 523 K, then decrease at 623 K and 723 K substrate temperature. These results may be attributed to the fact that at 523 K films have lowest conductivity and moderate absorption, since transmission and electrical conductivity are somewhat related to each somehow, at low conductivity low concentration of electron in the film thus film are more transparent [42]. We found that 523 K is best substrate temperature used to prepared our device.

3.4.3.2. Seeback Measurement

The conductivity type of the prepared semiconducting films are introduced by measuring seeback coefficient and Fig. 45 gives the relation between thermoelectric power and the heating temperature for samples prepared at optimum laser fluence and oxygen pressure. Seeback result indicates that the material under study is n-type semiconductor, possible reasons was the donors formation by oxygen vacancies and interstitial Bi atoms. The plot shows that the TEP increases with temperature, which can be attributed to the increase in concentration and mobility of the charge carriers with rise in temperature, similar result of conductivity type is reported by other worker [43, 44].

![Figure 44. Figure of merit for Bi$_2$O$_3$ thin films as a function of substrate temperature](image-url)
3.4.3.3. Optoelectronic Device

In our work, three devices were fabricated by depositing bismuth oxide layer at different thickness on silicon substrate with n-Bi$_2$O$_3$/p-Si structure electrical, photovoltaic properties and device parameter was done.

3.4.3.3.1. I–V Characteristic in Dark

The results of the I-V measurements at forward and reverse bias in dark case for n-Bi$_2$O$_3$/p-Si heterojunction devices prepared at optimum condition and at three different active layer thicknesses are shown in Fig. 46, these characteristics are very important to describe the device performance and all device parameters depending on it. It is obvious that forward biasing current for all device consist of two region, the first region represents recombination current result where majority charge carriers injected from the applied voltage into the junction, which lead to reduction in depletion layer width and decrease in built in potential. This leads to increase in the concentration of the generated charge carrier to higher value, higher than intrinsic carrier concentration as ($n_i$),
i.e. \((n*p>ni^2)\), thus work on junction area will work to reach to the equilibrium state, means exited electron in the conduction band will recombined with hole in the valance band which result in reduction in the \((n*p)\) multiplication and this curren called recombination current which found at low applied voltage, while at high applied voltage The second region at high voltage represented the diffusion region.

Figure 46. I-V characteristics of n-Bi_2O_3/p-Si devices fabricated at different active layer thickness

Under reverse biasing, it is clear that the curve contains two regions: the first is the generate current region where the reverse currents depend on applied voltage where at increasing biasing voltage the depletion region width increase resulting in reduction of the carrier concentration than the equilibrium state means \(n*p<ni^2\) thus the generation current is present at low voltage. In the second region, a significant increase in the reverse bias means high voltage can be recognized. In this case, the current resulted from the diffusion of minority carriers through the junction. The high forward currents at 210 nm thickness compared with other two thicknesses are related to the fact. The result for
ideality factor refer to good rectification properties for these prepared devices. This relatively high value of ideality factor as seen in Table 1, suggest that the recombination in the device occurs primarily in the junction depletion region and/or at the junction interface. Furthermore, the surface state and large lattice mismatch between Bi$_2$O$_3$ and Si could affect diode ideality factor. Similar high value of ideality factor was reported in similar worker [39, 45].

**Table 1.** Result of ideality factor and potential barrier height for n-Bi$_2$O$_3$/p-Si devices

<table>
<thead>
<tr>
<th>Devices active layer thickness (nm)</th>
<th>Ideality factor ($\eta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>2.7</td>
</tr>
<tr>
<td>210</td>
<td>2.8</td>
</tr>
<tr>
<td>240</td>
<td>3.7</td>
</tr>
</tbody>
</table>

3.4.3.3.2. Capacitance–Voltage Characteristics

It is consider one of the most important measurement which enable us in determine several important feature of the heterojunction device such as built-in potential, junction type, depletion layer width and device capacitance. Figure 47 shows the variation in the capacitance with applied reverse voltage for device prepared at different thicknesses reduction in the device capacitance with increasing bias voltage resulted from the expansion of depletion layer with the applied voltage. The depletion layer capacitance refers to the increment in charge per unit area to the incremental charge of the applied voltage. This properly gives an indication of the behavior of the charge transition from the donor to the acceptor region, which was found to be "abrupt" which is confirmed by the relation between $1/C^2$ and reverse bias being a straight line. The slight reduction in junction capacitance at higher active layer thickness is very usual result and related to the increment in the depletion layer which resulted from the reduction of the O$_2$ atom by the silicon substrate formation SiO$_2$ insulating layer but further increase in active layer thickness resulting in capacitance shunting of the junction, However there might be two possible contribution to this capacitance, one from the grain boundary and other from the parasitic capacitance through coupling to the substrate [46].
Figure 47. C-V for n-Bi$_2$O$_3$/p-Si devices fabricated at different active layer thicknesses

Figure 48 shows the variation of reciprocal of square capacitance versus bias voltage ($1/C^2-V$) this plot shows a linear relationship with bias voltage indicates that the junction is an isotype abrupt type heterojunction, the built-in potential can be calculated by extrapolating ($1/C^2-V$) plot to ($1/C^2=0$). The built-in potentials for all device tabulated in Table 2. Where an increase in the built-in potential value could be recognize as the active layer thickness increased from 180 nm to 210 nm, then decreased at 240 nm, and this result is coincident with capacitance result.

Table 2. Presents built-in potentials for n-Bi$_2$O$_3$/p-Si devices fabricated at different thickness Photovoltaic measurements.
These measurements represent important results since they describe the performance and feature of the fabricated devices and it includes the following measurements:

**a) Current-Voltage characteristics under illumination**

The photocurrent as a function of reverse biasing voltage for n-Bi$_2$O$_3$/p-Si photo detectors which prepared at different thicknesses was measured under different illuminating powers as shown in Fig. 49.

The results show that all devices exhibit increase in photocurrent with increasing applied reverse biasing which may attribute to the increasing depletion layer width where more light will absorbed within this area or the area on both side of the depletion layer width, thus the probability of generated carrier that contributed in the photocurrent will increase. Also photo current will increase when the illumination power of the incident light increased. This due to increasing the number of incident photon on the device. This also will result in increasing the generated charge carrier, which diffuse through the depletion layer and on both side of depletion layer to a distance equal to the diffusion length of the charge carrier to a distance depend on the minority charge carrier life time. When the thickness of active layer increased the
photocurrent increased as well due to increased depletion layer width; this means more photon will incident and absorb in the wide depletion layer, which lead subsequently to increase of the generated photocurrent and this result is obvious in Fig. 49 as the active layer increased further up to 240 nm, the a reduction in the photocurrent could be recognize and this may be due to the increased number of deposited layer, thus many defect will formed due to lattice mismatch which will cause a reduction in the generated photocurrent.

Figure 49. I-V under illumination for n-Bi$_2$O$_3$/p-Si devices at active layer thicknesses
b) Carrier Life Time

Carrier life is an important parameter in explaining the optoelectronic properties of the fabricated device prepared at different thicknesses. Figure 50 shows the decay pulse of open circuit voltage for device prepared at different thickness of Bi₂O₃ films on p-Si substrate. The result shows that the pulse may be divided into three regions: the first region is high injection where the injected minority charge carriers concentration is higher than the majority charge carrier concentration. The second region is the intermediate injection where the generated minority charge carriers concentration is higher than the minority charge carriers concentration in equilibrium and less than the majority charge carrier concentration at equilibrium. The third region is the low injection region where the generated minority charge carriers concentration is less than the minority charge carriers concentration in equilibrium. Table 3 presents the carrier lifetime for devices at different thicknesses.

Table 3. Carrier lifetime for n-Bi₂O₃/p-Si devices fabricated at different active layer thickness

<table>
<thead>
<tr>
<th>Devices active layer thickness (nm)</th>
<th>Carrier life time (μsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>193</td>
</tr>
<tr>
<td>210</td>
<td>201.52</td>
</tr>
<tr>
<td>40</td>
<td>113.15</td>
</tr>
</tbody>
</table>

The reduction in carrier life time as a function of active layer thickness could be recognized from the obtained result (which is the product of carrier mobility (μ), the electric field (ε) and the carrier lifetime (τ)). The lifetime of both types of carriers exceeds their transit time; all generated free carriers can be collected by the electrodes as in the first two cases, but if the active layer thickness is longer than drift lengths of electrons and holes, that is to say, the lifetime (τ) of both types of carriers is smaller than the transit time, the carrier will be accumulated in the active layer. In the last active layer thickness, the reduction in carrier life time is due to the increased lattice mismatch and generated defect [47].
Figure 50. Open voltage decay for n-Bi$_2$O$_3$/p-Si devices active layer thickness (a) 180 nm, (b) 210 nm, (c) 240 nm
3.4.3.3.3. Detector Parameters

a) **Spectral responsivity ($R_\lambda$)**

Responsivity is an important factor that one could determine from it the spectral range the detector work through it. Figure 51 shows the spectral responsivity for devices fabricated at different active layer thickness a function of spectral wavelength. Relative spectral response of the fabricated devices at different thickness, performed in the spectral range 200 nm-1280 nm. It is noted that the responsivity curve shows good band-pass behavior (window effect), and it is comprised of four distinct regions, the first region (corresponding UV region in range of 160 nm to 280 nm) shows an increase in responsivity with wavelength, attains the maximum value at wavelength of 200 nm. The lower responsivity at the shorter wavelength region may be due to the absorption of the light near the surface (shallow absorption depth), which has large amount of surface recombination of the photo generated carriers, the second region of the plot shows a decrease in responsivity with a minimum value at) wavelength of 440 nm, this could be attributed to a high degree of carrier recombination at the interface, the third region shows an increase in the responsivity passing through the maximum value at wavelength of 880 nm corresponding to light absorption at transition region on silicon side. The fourth region shows that responsivity decreases reaching the absorption edge of the silicon 1.1 eV. The smaller responsivity at longer wavelength this attributed to the carriers generated deep in the bulk of the silicon. At different thickness of the active layer thickness from 180 nm to 210 nm the spectral responsivity show an increased in responsivity with increased thickness which may be attributed to the reduction of the resistance in series with increasing the thickness, further increased in active layer thickness resulted in decreased in responsivity of the device fabricated at 240 nm active layer thickness.

The specific detectivity consider one of the most important parameter that should be calculated in order to determine the efficiency of the fabricated device. We calculated the detectivity by the relationship mention in chapter three. Detectivity for device fabricated at different active layer thickness shown in Fig. 52. The calculated value of detectivity with dark current value of 63, 89
and 102 nA for the three devices respectively. The results show variation in specific detectivity with increase active layer thickness.

**Figure 51.** Responsivity for n-Bi$_2$O$_3$/p-Si device fabricated at different active layer thickness Detectivity D$_\lambda$

**Figure 52.** Detectivity for n-Bi$_2$O$_3$/p-Si devices fabricated at different active layer thickness

**b) Quantum efficiency**

Figure 53 represents the relationship between the wavelength of the incident light and spectral responsivety $R_\lambda$ of the device, and because the quantum
efficiency (Q.E) function of the responsivity. Therefore, the result is related to the spectral responsivity.

Figure 53. Quantum efficiency for n-Bi$_2$O$_3$/?-Si devices at different active layer thickness

c) Rise and response time

The idea of the rise time depending on the developing of internal voltage with the depletion region, which is used to separate the electron-hole pairs resulting from the absorption of the light energy on the device surface. This mechanism take a specific time depended on the device characteristic. Figure 54 shows the rise time pulses obtain from experiment and Table 4 shows the calculated value for rise and response time for devices prepared at different no. of pulses and tile angle.

Table 4. Rise and response time for n-Bi$_2$O$_3$/?-Si devices

<table>
<thead>
<tr>
<th>Devices active layer thickness (nm)</th>
<th>Rise time (μsec)</th>
<th>Response time (μsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>173</td>
<td>78.6</td>
</tr>
<tr>
<td>210</td>
<td>75</td>
<td>34</td>
</tr>
<tr>
<td>240</td>
<td>120</td>
<td>54.5</td>
</tr>
</tbody>
</table>
Rise time pulses for devices fabricated at different active layer thickness (a) 180 nm, (b) 210 nm, (c) 240 nm

Figure 54. Rise time pulses for devices fabricated at different active layer thickness (a) 180 nm, (b) 210 nm, (c) 240 nm

Rise and response time results tabulated in table (4.4), result show decrease in rise time with increasing active layer thickness from 180 nm to 210 nm then increased again at 240 nm, lowest rise time achieve at 210 nm (i.e., the faster detector) may attributed to low lattice mismatch at this thickness, while devise fabricated at 240 nm active layer thickness show increased in response time this may due to negative effect for the formation of a considerably thick SiO layer an oscillatory rise and response time result achieve elsewhere [48, 49].
4. Conclusions

1. This work gives trends to the formation of high purity Bi\textsubscript{2}O\textsubscript{3} oxide from their high purity metal by reactive pulse laser deposition at optimum laser fluence (7.8 J/cm\textsuperscript{2}), oxygen pressure (200 mbar), while optimum substrate temperature is 523 K that could be used to prepare highly oriented Bi\textsubscript{2}O\textsubscript{3}.

2. XRD pattern for Bi\textsubscript{2}O\textsubscript{3} at laser fluence (7.8 J/cm\textsuperscript{2}), oxygen pressure (200 mbar) and substrate temperature (523 K) exhibit the domination of tetragonal phase (201) over monoclinic phase (121).

3. The optical properties result shows that Bi\textsubscript{2}O\textsubscript{3} band gap is 2.6 eV at optimum conditions with cut off wavelength around 476 nm.

4. The AFM and SEM image at the optimum preparation condition give an average grain size of about ~120 nm.

5. The Electric and photovoltaic characteristics of n-Bi\textsubscript{2}O\textsubscript{3}/p-Si heterojunction device are strongly dependent on the active layer thickness, while the C-V measurements revealed that the anisotype junction is abrupt type.

6. Detector parameters revealed that the device fabricated with active layer thickness of 210 nm is the best among the three devices, with spectral responsivity, detectivity, quantum efficiency and rise time of about 0.23 A/W, 1.6 \times 10^{11} \text{W}^{-1}\text{cm.Hz}^{1/2}, 28.54 and 75 µsec, respectively.

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