

Fabrication and Characteristics Study of n-Bi₂O₃/n-Si Heterojunction

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Abstract—This work presents the fabrication and characteristics of Bi₂O₃/Si heterojunction prepared by rapid thermal oxidation technique without any post-deposition annealing condition. The bismuth trioxide film was deposited onto monocrystalline Si and glass substrates by rapid thermal oxidation of bismuth film with aid of halogen lamp at 500 °C/ 45 s in static air. The structural, optical and electrical properties of Bi₂O₃ film were investigated and compared with other published results. The structural investigation showed that the grown films are polycrystalline and multiphase (α -Bi₂O₃ and β -Bi₂O₃). Optical properties revealed that these films having direct optical band gap of 2.55 eV at 300 K with high transparency in visible and NIR regions. Dark and illuminated I-V, C-V, and spectral responsivity of Bi₂O₃/Si heterojunction were investigated and discussed.

Index Terms—Bismuth oxide, thin film, rapid thermal oxidation, silicon, heterojunction, optoelectronic

I. INTRODUCTION

Bismuth trioxide (Bi₂O₃) thin films have attracted the interest of many researches due to the values of some their characteristics parameters e.g., energy gap, refractive index, photoconductivity, transparency and mechanical strength [1-5]. These films are suitable for many applications such anti-reflecting coating, sensors, fuel cells, optoelectronic devices, as well a parent substance for some high-T_C superconductors [6-8].

Bi₂O₃ films were prepared by different methods; spray pyrolysis [9], anodic oxidation [10], flash evaporation [2], thermal oxidation of bismuth film using furnace [11], and pulsed laser deposition [12].

The literature concerning the photovoltaic properties of Bi₂O₃ is poor. The semiconductor oxide/Si heterojunctions are promising and interested optoelectronic devices due to their advantages and properties. Up to our knowledge no data have been reported on fabrication and characterization of Bi₂O₃/Si heterojunction.

In the present paper, the properties of Bi₂O₃ films prepared by rapid thermal oxidation of bismuth film have been measured and discussed. The main characteristic of Bi₂O₃/Si heterojunctions device were investigated and analyzed.

II. EXPERIMENT

Monocrystalline CZ n-type silicon wafer with electrical resistivity of 1-3 Ω .cm and orientation of (111) was used as substrate. These substrates are dipped in diluted HF acid for 20 s and then in DI water rinse. These substrates were cut into pieces with area of 64 mm². High purity of bismuth film was deposited on silicon substrate using thermal resistive technique under pressure of 10⁻⁷ torr. Bi₂O₃ film was obtained with aid of rapid thermal oxidation system with halogen lamp as oxidation source. The experimental set-up is presented elsewhere [13]. The oxidation condition used to form Bi₂O₃ film was 500°C/35s with heating and cooling rates of 15 °C/s. Ohmic contacts are made on both Bi₂O₃ film and Si substrate by depositing of Ag and Al thick films through certain mask using thermal evaporation system followed by rapid thermal annealing at 300 C/s . Fig. 1 shows the cross-sectional view of Bi₂O₃/Si heterojunction.

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The x-ray diffraction (XRD) spectrum of Bi₂O₃ film grown on glass substrate was investigated by x-ray diffractometer of Cu K α as a target ($\lambda = 0.15417$ nm).

The D.C dark electrical resistivity of Bi₂O₃ as function of temperature was measured using Keithley digital electrometer. Thermoelectric property of the film was estimated. Double-beam spectrophotometer (Shimadzu) was used to measure the transmission and absorption spectra of Bi₂O₃ thin film deposited on glass substrate in spectral range (400 – 900 nm). I-V under dark and white light illumination conditions (50 mW/cm²) and C-V characteristics of Bi₂O₃/Si heterojunction were examined using a potential sweeper and LCZ meter (200 kHz) respectively. Photoresponse measurement in the spectral range of 400 to 950 nm was achieved after making power calibration.

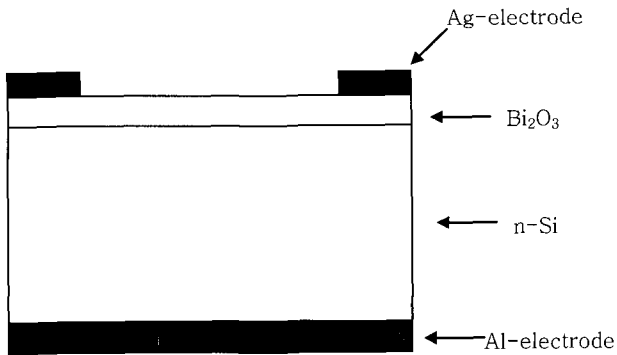


Fig. 1. Cross-sectional view of Bi₂O₃/Si heterojunction.

III. RESULTS AND DISCUSSION

1. Bi₂O₃ Film Properties

Fig. 2 shows X-ray diffraction (XRD) spectrum of Bi₂O₃ thin film, it is clear that the film is polycrystalline in nature and multiphase. The film exhibits mixture of α -Bi₂O₃ (monoclinic) and β -Bi₂O₃ (tetragonal structure). No diffracted peaks concerning Bi and nonstoichiometric phases are noticed in XRD spectrum. The d-values of grown film are very close to ASTM diffraction data of Bi₂O₃. The maximum intensity peak belong α - Bi₂O₃ phase is observed corresponding to diffraction angle of $2\theta = 27.1^\circ$ and second peak ($2\theta = 28.1^\circ$) which belongs to β - Bi₂O₃ phase. These results are in good agreement with published results. This is given an indication that

the condition used in this study is optimal. The published results [5] established that the preparation method and condition strongly affect the crystalline and granular structure of Bi₂O₃ films.

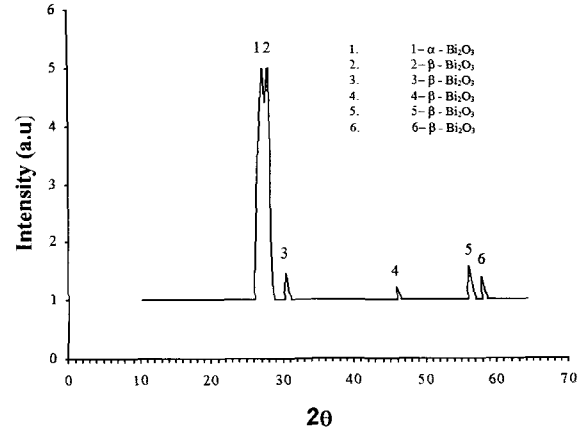


Fig. 2. XRD pattern of grown Bi₂O₃ film.

Fig. 3 displays the transmittance of Bi₂O₃ films in the spectral range (400 – 900) nm. It is obvious that the film give a good transparency with yellowish color characteristics in the visible and NIR regions ($T_{ave.} > 75\%$).

The film shows good uniformity and transparency. On the other hand, the adhesive characteristics of Bi₂O₃ with glass and Si substrates are very good. The optical energy gap of Bi₂O₃ at 300 K was obtained from direct optical transitions (α^2 - $h\nu$ plot) (Fig. 4) and found to be 2.55 eV. This value is very closed to the value of published results [7, 11]. One can notice that this value is very close to the band gap of CdS and CdO, which are promising materials for solar cells and optoelectronic devices.

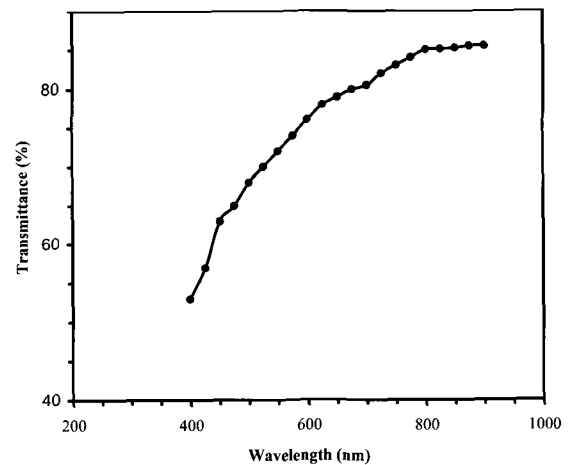


Fig. 3. Transmittance spectrum of Bi₂O₃ film.

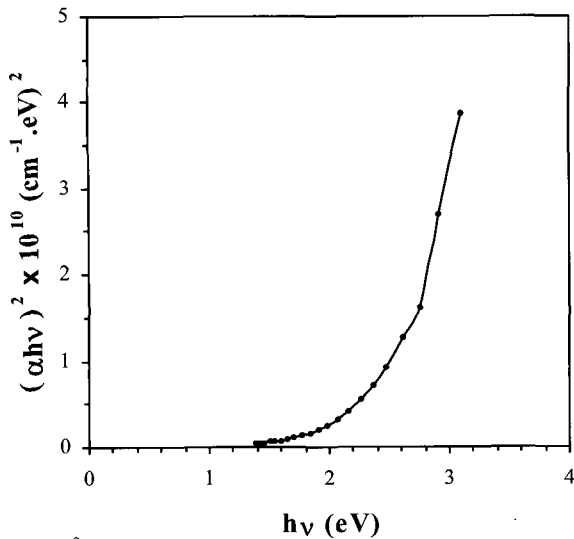


Fig. 4. α^2 versus photon energy plot.

Thermoelectric power (TEP) properties of Bi_2O_3 film was carried out and show that the Bi_2O_3 film is n-type material possible reasons for this are donors formation by oxygen vacancies and interstitial Bi atoms. The variation of electrical resistance of the film is function of temperature reciprocal is revealed in Fig. 5. This curve confirms the semiconducting behavior of Bi_2O_3 film. The activation energy of film was 1.25 eV which is in good agreement with that of film prepared by thermal oxidation of bismuth in oven [14]. On the other hand, the activation energy was lower than of optical energy gap of film. The electrical resistivity and electron mobility of Bi_2O_3 were measured and found to be $8 \times 10^3 \Omega \cdot \text{cm}$ and

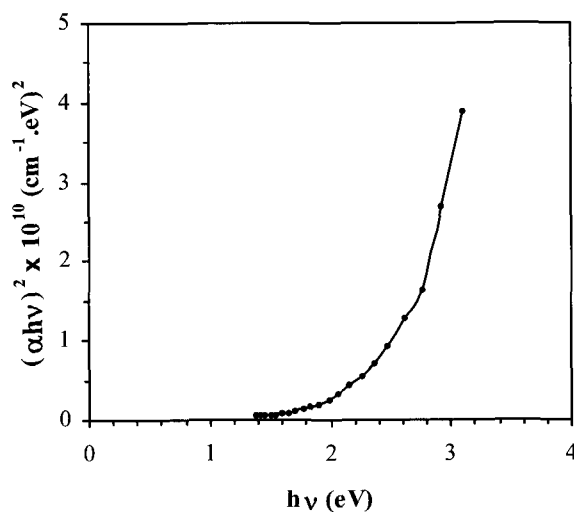


Fig. 5. Variation of films resistance with T^{-1} .

close to those of sprayed and thermally oxidized Bi_2O_3 $61 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}$ respectively. These results are close to those of sprayed and thermally oxidized Bi_2O_3 films obtained by others [7,15]. The high resistivity of the film might be explained by the presence of the crystallites with lower size.

2. Characteristics of n- Bi_2O_3 /n-Si Heterojunction

Fig. 6 shows dark and illuminated I-V characteristics of $\text{Bi}_2\text{O}_3/\text{Si}$ isotype heterojunction in forward and reverse directions. It is obvious that the junction has relatively good diode rectification characteristics about 300 at 2 V. No breakdown has been noticed at voltages > 4 V and the dark current of diode was less than 100nA. It is also clear that recombination current dominated at low bias voltages while the domination of diffusion current starts at voltages > 1 V. The ideality factor was found to be around 4.8, this high value suggest that the recombination in this device occurs primarily in the junction depletion region and / or at the junction interface [16]. Furthermore, the large lattice mismatch between Bi_2O_3 and Si could affect diode ideality factor. The effect of series resistance, which arises from the high resistivity of Bi_2O_3 film is displayed at high bias voltage. The illuminated I-V characteristics of the heterojunction are shown in Fig. 6. This Fig. reveals the good sensitivity of $\text{Bi}_2\text{O}_3/\text{Si}$ heterojunction for white light.

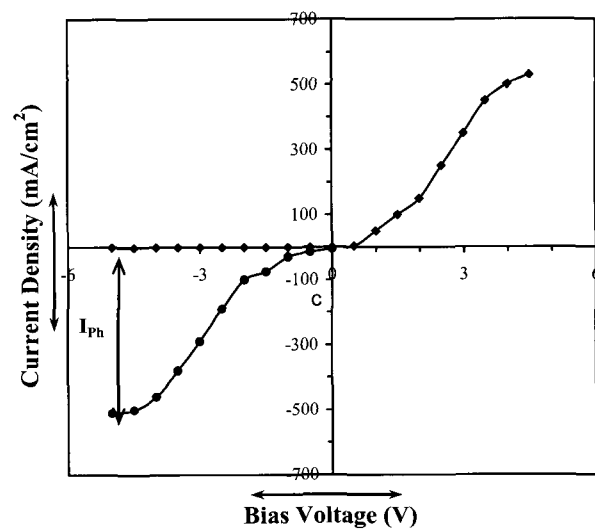


Fig. 6. Dark and illuminated I-V characteristics of $\text{Bi}_2\text{O}_3/\text{Si}$ heterojunction.

Fig. 7 reveals the reciprocal of square capacitance versus reverse bias voltage. The linearity characteristic of this plot confirms that the junction is abrupt type [17]. The built-in potential of heterojunction was calculated from C^{-2} -V plot and was found around 1 V.

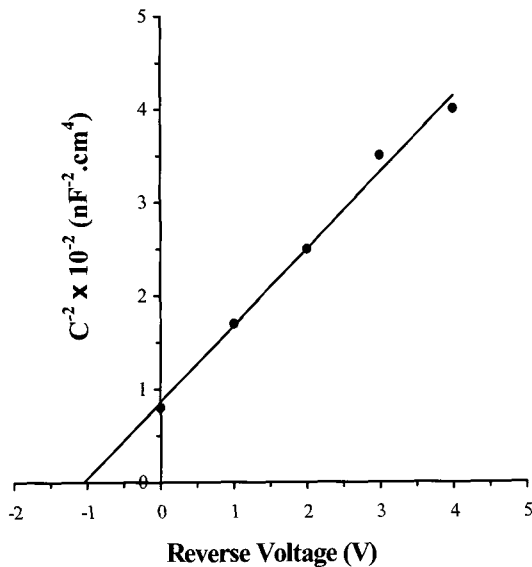


Fig. 7. C^{-2} vs bias voltage

Fig. 8 represents the spectral responsivity curve of Bi₂O₃/Si heterojunction photodetector biased at 2 V. The spectral response shows the window effect between 0.55 and 0.95 μ m. These wavelengths correspond to the band edges of Bi₂O₃ and Si respectively. The response is not flat over this spectral range and displays significant minima around 700 nm, this is can be ascribed to the effect of traps defects.

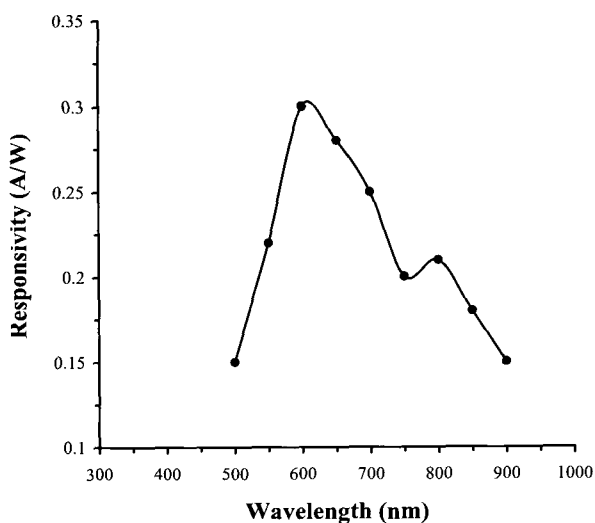


Fig. 8. Spectral responsivity of Bi₂O₃/Si heterojunction.

The maximum responsivity was around 600 nm. This result can be attributed to the fundamental absorption of Bi₂O₃ material. The responsivity at visible region is high and encouraged (visible-enhanced photodetector). The peak response of Bi₂O₃ is very close to that for CdO/Si [18, 19] and CdS/Si [20] but with lower value. This can be attributed to the high resistivity of Bi₂O₃ and the large value of mismatch lattice constant between Bi₂O₃ and Si. Furthermore, the preparation method of bismuth oxide on Si is strongly affect the responsivity value and profile.

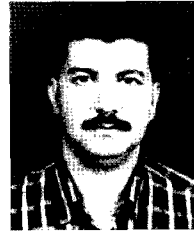
IV. CONCLUSIONS

The structural, optical, and electrical properties of undoped polycrystalline Bi₂O₃ thin film prepared by rapid thermal oxidation technique and their application to Bi₂O₃/c-Si heterojunction photodetector were examined. The encouraged optoelectronic properties of this heterojunction suggest that it candidate to be visible-enhanced photodetectors. The method of fabricating Bi₂O₃ layer by rapid thermal oxidation is relatively new and it is hoped it can be improved either by doping or annealing.

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