Tr. J. of Physics
22 (1998) , 825 – 830.
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Characterization of Spray Deposited Bismuth Oxide Thin Films from Non-Aqueous Medium

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Received 03.06.1997

Abstract

Bismuth oxide thin films have been prepared on amorphous glass substrates from non-aqueous medium using spray pyrolysis method. Characterization of the films was carried out with XRD, optical absorption, dark resistivity and thermoelectric power (TEP) measurements. These studies reveal that films as deposited are polycrystalline; having an optical band gap of 2.6 eV; electrical resistivity is of the order of 10^6 ohm-cm; and electron carrier concentration and mobility are of the order of 3.8×10^{19}cm^3 and 1.5×10^{-4}cm^2 V^{-1}s^{-1}, respectively.

Keywords: bismuth oxide, thin films, spray pyrolysis, electrical properties, optical properties

1. Introduction

Oxide semiconductors, though are not suitable for photoelectrochemical solar cells, they exhibit potential usefulness in photoelectrolysis and photoelectrochemical imaging cells [1-3]. M. Merikos-H. Ukovic [4] has studied Bi_2O_3 thin films prepared by anodic oxidation of bismuth, both with n- and p-type behavior. Dolocon and Ivova [5] obtained these films by flash evaporation technique and have studied the optical absorption in the photon energy range 0.6 to 6.2 eV. Hardee and Bard [6] have reported on Bi_2O_3 thin films and found the band gap to be 2.8 eV. Lokhande and Bhosale [7] have reported on chemically converted spray deposited Bi_2O_3 to Bi_2S_3 thin films.

To see the effect of non-aqueous solvents on crystallinity and other properties of spray kept bismuth oxide thin films, the present study examines films deposited using acetic acid as a non-aqueous solvent and reports their properties.

2. Experimental

2.1. Preparation of Thin Films

Bismuth nitrate $Bi(NO_3)_3$ $5H_2O$ was dissolved in acetic acid glacial 0.05 M solution. The films were prepared by spraying 30 ml 0.05M solution of bismuth nitrate onto preheated amorphous glass substrates. The substrate temperature was maintained at 300°C during the deposition. The spray rate was kept at about 10 cc per minute. The modified spray unit described in [8] was used to move the spray nozzle to and fro over the substrates with frequency of 0.29 Hz.

2.2. Characterization

The thickness of the prepared film was measured by gravimetric method, by considering the density of bismuth oxide.

The structural characterization of bismuth oxide as a thin film carried out by analyzing the X-ray diffraction pattern obtained via a Philips X-ray diffractometer model PW-1710 with Cu-K_α radiation.

Optical absorption studies were carried out using UV-VIS-NIR spectrophotometer (Hitachi model 330, Japan) in the wavelength range 350-850 nm.

To study the electrical characterization of the films, dark resistivity measurements were carried out using two point d.c. probe method in the temperature range 300-500K. Silver paste was used to provide ohmic contact with the film.

The thermoelectric power (TEP) of the film was studied by measuring thermoelectric voltage developed across the film at various temperatures.

3. Results and Discussion

In spray pyrolysis method, the starting material is required to be in solution form which, when sprayed onto the preheated substrate, results in the formation of a thin film on the substrate. When the droplets of spray solution reach the hot substrate, due to the pyrolytic decomposition character of the solution, a well adhered, pin-hole free, uniform yellowish colored film of bismuth oxide is formed on the substrate. The film thickness was around 0.20 μm.

The structural identification of bismuth oxide film was carried out using an X-ray diffractometer in the range $10° \leq 2\theta \leq 70°$ and is shown in Fig. 1. It was found that the films are polycrystalline in nature. The 'd' values of the XRD reflection shown in Fig. 1. are estimated and compaired with the standard 'd' values taken from the ASTM diffraction data (Card No: 27-50 and 27-51) for Bi_2S_3 and $BiO_{2.33}$, respectively. The observed and standard 'd' values along with their relative intensities are listed in Table 1. The careful observation of this table shows that the deposited material consists of mixed phase β-Bi_2O_3 and $BiO_{2.33}$. The maximum intensity peak of Bi_2O_3 is observed corresponding to diffraction angle 28.03°. Other peaks of $BiO_{2.33}$ materials are present.

Table 1. Comparison of observed and standard (ASTM) 'd' values for as deposited Bismuth Oxide thin films.

Observed	Standard	Observed	Standard	Material	(h k l)
4.367	4.388	9	4	$BiO_{2.33}$	108
3.181	3.190	112	100	β-Bi_2O_3	100
3.045	3.054	40	100	$BiO_{2.33}$	100
2.929	2.925	35	32	$BiO_{2.33}$	012
2.728	2.722	80	92	$BiO_{2.33}$	110
2.511	2.508	8	14	$BiO_{2.33}$	014
1.957	1.950	1	24	$BiO_{2.33}$	018
1.649	1.665	13	22	$BiO_{2.33}$	019

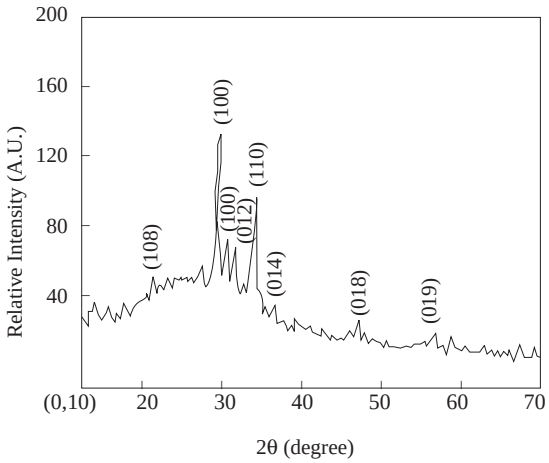

Figure 1. X-ray diffraction pattern of Bismuth oxide thin films deposited on glass substrates.

The optical density (αt) of the film was recorded in the wavelength range 350 to 850 nm. Figure 2 shows the variation of relative absorbance αt with wavelength λ for bismuth oxide thin films. Absorption coefficient is of the order of $10^4 \mathrm{cm}^{-1}$.

In order to confirm the nature of the film's optical transition as direct allowed or direct forbidden, the optical data was analyzed using the classical relation [9]

$$\alpha = \alpha_0 \frac{(h\nu - Eg)^n}{h\nu}, \tag{1}$$

where α_0 is a constant depending upon the type of the transition that prevails. Specifically, for an allowed, direct allowed transition n is 1/2. Figure 3 shows the variation of $(\alpha h\nu)^2$ versus $h\nu$, which is a straight line, indicating that direct transition is the dominant transition involved. The energy gap is obtained by extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ plot to $\alpha = 0$. The band gap energy is found to be 2.6 eV, and is slightly less than value reported earlier [6,7].

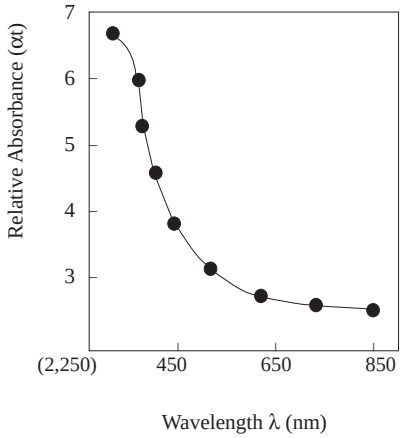

Figure 2. The variation of relative absorbance (αt) with wavelength λ.

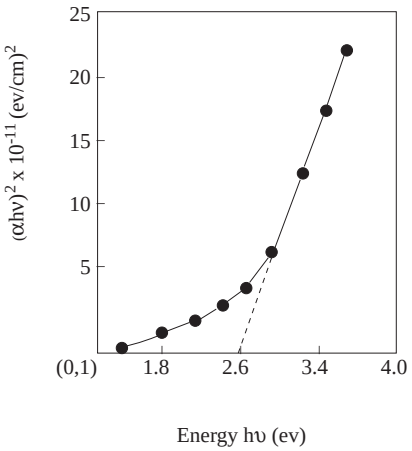

Figure 3. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for bismuth oxide thin films.

The two point d.c. probe method of dark resistivi measurement shows that the prepared films have dark resistivi of the order of 10^5 to 10^6ohm-cm. The high resistivity of the film may be due to grain boundary, discontinuity and thickness of the film. The variation of $\log(\rho)$ with 1/T depicted in Figure 4 indicates the semiconducting nature of the film. The thermal activation energies Ea are calculated by using the relation

$$\rho = \rho_0 \exp(Ea/KT), \tag{2}$$

where ρ_0 is the pre-exponential factor, K is the Boltzman constant and T is absolute temperature. The value of activation energy is estimated to be 0.58 eV and represents the average energy of the carriers with respect to the fermi energy of the carriers, if the carrier concentration can only move at the bottom or top of the well defined band.

The thermoelectric power (TEP), which is defined as the ratio of thermally generated voltage to the temperature difference across the semiconductor, gives information about the type of carriers in the semiconductor. The variation of TEP with temperature is studied for the bismuth oxide thin films and is shown in Fig. 5. It is found that the polarity of thermoelectric voltage for the film is in favour of an n-type semiconductor. 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.

The TEP was used to evaluate carrier mobility and carrier concentration using relation

$$TEP = \frac{K}{e}\{A + \ln[2(2\pi m_e KT)^{3/2}]\}, \tag{3}$$

where A is a thermoelectric factor (2 for Bi_2O_3). The other symbols have their usual meanings. After substitution of various constants, Equation (3) simplifies to [10]:

$$\log(n) = (3/2)\log(T) - 0.005TEP + 15.719. \tag{4}$$

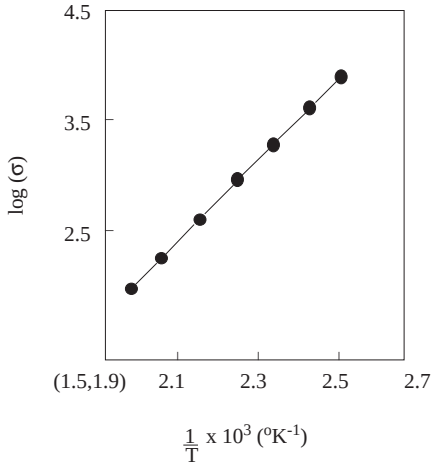

Figure 4. Variation of log(ρ) versus 1/T for bismuth oxide thin films.

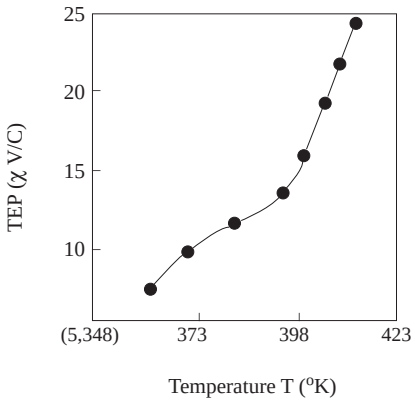

Figure 5. Variation of TEP with temperature for bismuth oxide thin films.

The electron density was calculated by using above relation and is of the order of $3.8 \times 10^{19}\text{cm}^{-3}$ for the sample. Charge carrier mobility μ is determined from the relation

$$\mu = \sigma/ne, \tag{5}$$

where n is electron density and σ is the conductivity.

The variation of log(n) and log(μ) as a function of temperature is shown in Figure 6. It is observed that electron density and mobility increase with temperature. The mobility is estimated to be $1.5 \times 10^{-5}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Here, the mobility is controlled by a combination of optical mode scattering at high temperature, charged impurity scattering at low temperature and a scattering mechanism at intermediate temperatures called piezoelectric scattering, which is found in crystals where acoustic lattice waves cause an electrical polarization in the material.

The intergranular barrier height (ϕ_b) was estimated from the following equation [11]:

$$\mu = \mu_0 \exp(-\phi_b/KT), \tag{6}$$

where all the terms have their usual meanings. The value of ϕ_b obtained from the plot of log(μ) versus 1/T is 0.65 eV.

4. Conclusions

From the results reported here it is concluded that bismuth oxide thin films deposition by the spray pyrolysis method is possible using acetic acid as non-aqueous solvent. As deposited films of Bi_2O_3 and $BO_{2.33}$ are polycrystalline in nature with n-type in conductivity. The electrical conductivity is of the order of 10^{-5} to 10^{-6} ohm^{-1} cm^{-1}. The

optical band gap (direct) is 2.6 eV. The electron carrier concentration and mobility are estimated to be $3.8 \times 10^{19}\text{cm}^{-3}$ and 1.5×10^{-4} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively.

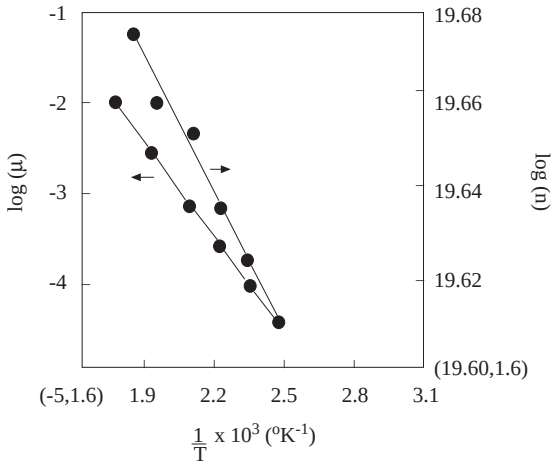

Figure 6. Variation of $\log(n)$ versus $\log(\mu)$ for bismuth oxide thin films.

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