PHYSICAL PROPERTIES OF δ–Bi$_2$O$_3$ THIN FILMS

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Polycrystalline thin films of δ–Bi$_2$O$_3$ were prepared by oxidising bismuth films of thickness (120–350 nm) in air at 473 K for 10 hours. X–ray diffraction analysis showed that the films are polycrystalline and correspond to cubic δ–phase of Bi$_2$O$_3$. The electrical and optical properties of δ–Bi$_2$O$_3$ were studied. The effect of the film thickness on these properties was also investigated. From the electrical conductivity measurements at various temperatures (100–473 K), the coexistence of band and multiphonon–assisted hopping conduction between well–localized states has been observed. It was found also that the activation energy ΔE increases and the density of localized states at the Fermi level g_r decreases with increasing thickness of the film. The analysis of the absorption coefficient data revealed the existence of an indirect transition. It was found that the calculated value of the optical energy gap E_g^{opt} increases with increasing thickness of the film.

1. Introduction

Bi$_2$O$_3$ films have been used in many applications as electro–chemical cells [1], humidity sensor [2], optical coating [3], Schottky barrier solar cells [4], and in metal/insulator/semiconductor capacitors [5]. Bi$_2$O$_3$ crystallizes in several forms:

two of them, α and δ, are stable and two, β and γ are metastable [6,7]. Besides these forms, orthorhombic [8] and nonstoichiometric tetragonal [9] forms of Bi_2O_3 were observed in thin films. Thin films of Bi_2O_3 can be obtained by different methods, thermal evaporation of Bi_2O_3 [10], activated reactive evaporation [11] and sputtering in an atmosphere of oxygen. Another method of obtaining Bi_2O_3 films is the thermal oxidation of bismuth films in air [12]. The films obtained using this method are a mixture of the various phases of Bi_2O_3. Recently, methods have been developed to obtain single–phase δ–Bi_2O_3 [13], tetragonal Bi_2O_3 [14] and α–Bi_2O_3, β–Bi_2O_3, γ–Bi_2O_3 [15]. The application and the quality of the devices with Bi_2O_3 depend on the transport and optical properties. Several investigators have been devoted to crystalline Bi_2O_3 [16] and Bi_2O_3 films prepared by different methods [3,10,13,14], and the available data are somewhat contradictive. No extensive study has been published on the transport properties of δ–Bi_2O_3 films [13]. There is no information about the optical properties of δ–Bi_2O_3 films. The object of the present work was to study the electrical and optical properties of δ–Bi_2O_3 films prepared by thermal oxidation of bismuth films in air.

2. Experimental

δ–Bi_2O_3 films were obtained by vacuum evaporation (at 133×10^{-6} Pa) of bismuth (purity 99.999) onto ultrasonically cleaned glass and quartz substrat using Leybold Univex 300 coating unit. The bismuth films were heated in air at 473 K for 10 hours. To ensure complete oxidation of bismuth into δ–Bi_2O_3, the films were investigated by an X–ray diffraction (Philips P. W. 1373). Chemical composition of the films was defined by using atomic absorption GBC 980 and Perkin Elmer (model 1100).

Films of thickness about 100–350 nm were used in the study. On further increasing the film thickness to about 375 nm, it was found that some traces of metallic bismuth remain in the films. The film thickness was determined using the multiple beam interference technique.

The electrical conductivity measurements were carried out by the conventional four–probe method in a temperature range of 100 to 473 K, using the high impedance electrometer (Keithley, type 616) for measuring the current and the voltage. The measurements were done under vacuum (at 133×10^{-3} Pa).

The transmission T and the reflection R at normal incidence for δ–Bi_2O_3 films were recorded using a UV.VIS.NIR. spectrophotometer type 3100 (Schimedzu).

3. Results and discussion

3.1. Structural properties of $\delta-Bi_2O_3$ films

Figure 1 shows X–ray diffraction patterns of δ–Bi_2O_3 films of different thickness (120–375 nm). Analysis of these data showed that the films obtained on glass and

of thickness 120–350 nm were polycrystalline and corresponded to cubic δ–phase of Bi_2O_3 ($a = 5.66 \times 10^{-10}$ m). This is in a good agreement with the results published by Gattow and Schrader [17]. The δ–Bi_2O_3 phase has the fluorite structure with two formula units and with two vacancies per unit cell. The prefered orientation of the vacancies is in the $< 111 >$ direction [18]. It was also found that the crystallinity of the films increases as the film thickness increases.
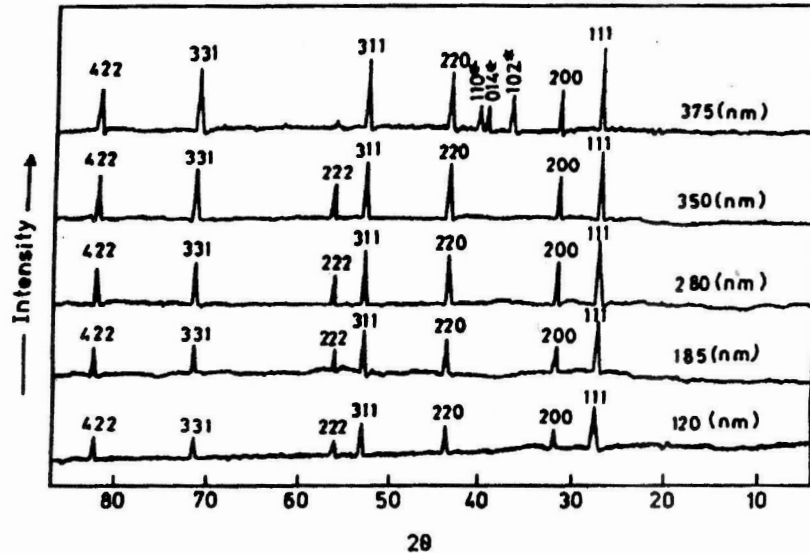

Fig. 1. X–ray diffraction patterns of δ–Bi_2O_3 thin films of different thickness. Lines due to metallic Bi are indicated with asterisks.

3.2. Electrical properties of $\delta-Bi_2O_3$ films

The temperature dependence of electrical conductivity of δ–Bi_2O_3 thin films of different thickness (120–350 nm) in the range of temperature of 100–473 K is shown in Fig. 2. The conductivity of all films increases with increasing temperature. It was observed also that the plot of log σ against $1/T$ cannot be approximated by a single activation energy over a vide range of temperatures. We suggest that the plot shows that two types of conduction channels contribute to the conductivity. The linearity of log σ against $1/T$ in the high temperature region ($T > 300$ K) indicates that the conductivity exhibits activated behaviour, in accordance with the relation:

$$\sigma(T) = \sigma_0 \exp(-\Delta E/kT). \tag{1}$$

The values of the conductivity activation energy, ΔE, were calculated and are shown in Table 1. It is evident that ΔE increases and σ decreases with increasing the film thickness.

TABLE 1.
Parameters obtained from dc conductivity and optical data for δ–Bi$_2$O$_3$ films.

Thickness (nm)	ΔE (eV)	$\sigma_0 \times 10^{-6}$ (Ω^{-1}cm^{-1})	$T_0 \times 10^{-5}$ (K)	$g_f \times 10^{18}$ (eVcm)$^{-1}$	$R \times 10^{-6}$ (cm)	W (eV)	E_g^{opt} (eV)
120	0.604	19.981	2.562	8.511	0.092	0.036	2.38
185	0.631	17.78	3.18	6.71	0.977	0.038	2.51
280	0.722	7.413	4.74	0.596	2.121	0.042	2.65
350	0.831	6.025	6.831	0.382	2.391	0.046	2.79

At low temperatures ($T < 250$ K), the angular slope of all curves in Fig. 2 continuously decreases with decreasing temperature, i.e., the dependence of log σ on T^{-1} is nonlinear and exhibits a non–activated behaviour. The observed non–activated temperature dependence of the dc conductivity at low temperatures is, at least in part, a manifestation of multiphonon nature of acoustic phonon–assisted hopping between well–localized states near the Fermi level [19]. The localized states necessary for such a conduction process are a consequence of imperfections associated with the polycrystalline films. Such a jumping was found to follow the following relation [20]:

$$\sigma = \frac{\sigma_0'}{\sqrt{T}} \exp\left(-T_0/T\right)^{1/4}. \tag{2}$$

T_0 is a measure of the degree of disorder and is related to the density of localized states at the Fermi level g_f by the relation:

$$T_0 = \frac{16\alpha_0^3}{kg_f} \tag{3}$$

where α_0^{-1} is a localization radius.

The factor σ_0' is given by:

$$\sigma_0' = 3e^2\nu_{ph}\sqrt{\frac{g_f}{8\pi\alpha_0 k}} \tag{4}$$

where $\nu_{ph} = 10^{13}$ Hz is the phonon frequency.

The length of jumping R and the jumping energy W are given by the expressions:

$$R = \left(\frac{9}{8\pi\alpha_0 Tkg_f}\right)^{1/4} \tag{5}$$

$$W = \frac{3}{4\pi R^3 g_f}. \tag{6}$$

The plot of log $\sigma T^{1/2}$ against $T^{-1/4}$ was found to be linear (see inset of Fig. 2). From Fig. 2, the values of σ_0' and T_0 can be calculated.

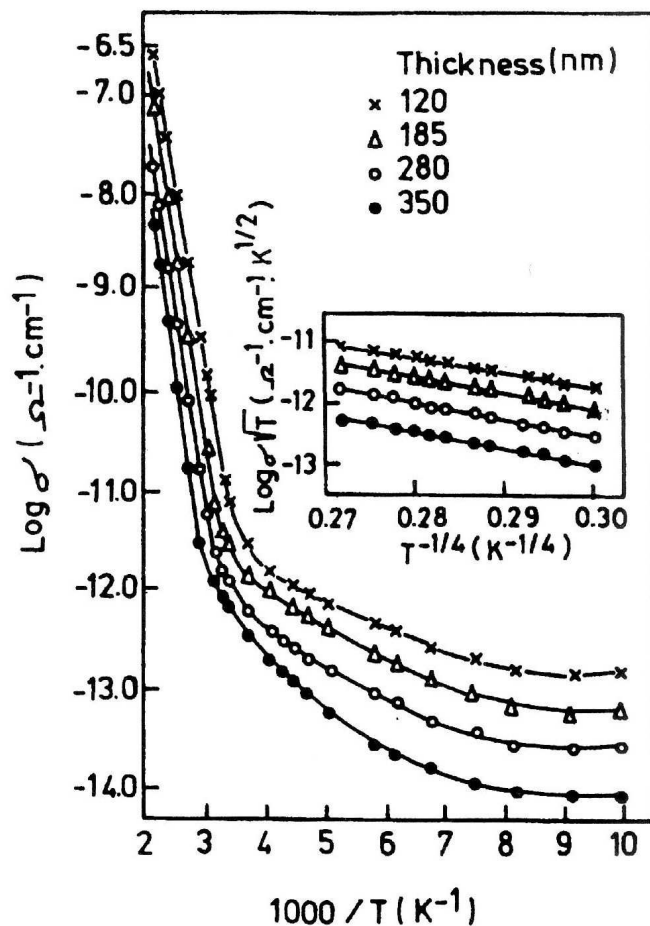*Fig. 2. Temperature dependence of dc conductivity for δ–Bi_2O_3 thin films of different thickness. The inset shows the plot of $\log \sigma T^{1/2}$ vs. $T^{-1/4}$.*

The calculated values of σ_0', T_0, g_f, R and W for films of different thickness (120–350 nm) are given in Table 1.

It is known that the conductive disordering structures can have both the tails of the energy bands and a non–zero density of states in the energy gap. The obtained data given in Table 1 show that g_f decreases, and T and W increase with increasing the thickness of δ–Bi_2O_3 film. This means that the degree of disorder and defects present in the structure decreases with increasing thickness of the film.

3.3. *Optical properties of* $\delta-\mathrm{Bi_2O_3}$ *films*

Optical properties of the δ–$\mathrm{Bi_2O_3}$ films near the absorption edge are characterized by spectral dependence of absorption coefficient, α. They were evaluated from the relation [21]:

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \tag{7}$$

where T, R are the transmission and reflection coefficients at normal incident and d is the thickness of the film.
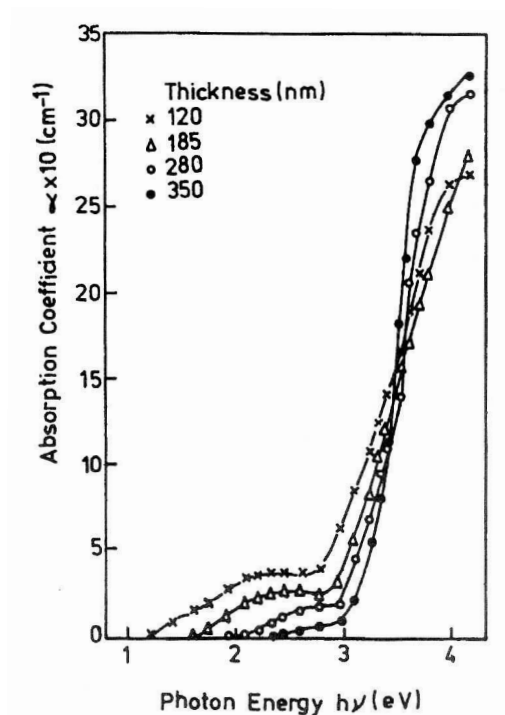

Fig. 3. *Spectral dependence of absorption coefficient,* α, *for* δ–$\mathrm{Bi_2O_3}$ *films of different thickness.*

The functional dependence of α, on photon energy, $h\nu$, for δ–$\mathrm{Bi_2O_3}$ films of different thickness (120, 185, 280 and 350 nm) is shown in Fig. 3. It was found that the optical absorption coefficient, α, for all films can be expressed by the exponential relation,

$$\alpha = \frac{A}{h\nu}(h\nu - E_g^{\mathrm{opt}})^2 \tag{8}$$

where $h\nu$ is the energy of incident photons, E_g^{opt} is the optical energy gap and A is a constant.

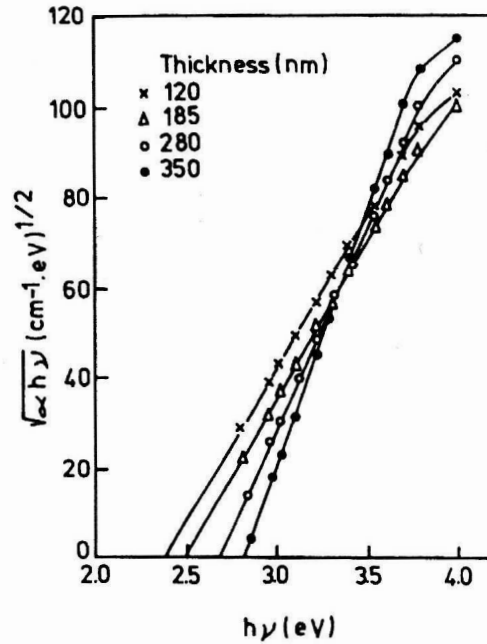This indicates that the absorption is due to an indirect transition.

Fig. 4. $(\alpha h\nu)^{1/2}$ as a function of photon energy $(h\nu)$ for δ–Bi_2O_3 films of different thickness.

Fig. 4 shows the spectral dependence of α, in the form of $(\alpha h\nu)^{1/2}$ against $h\nu$. The relations are found to be identical in character and indicate tailing of the absorption coefficient towards low photon energies. These tails may be due to the broadening of the impurity band which extends into the forbidden gap. The values af the optical band gap were determined for δ–Bi_2O_3 films of different thickness and tabulated in Table 1. It is clear from this figure that the energy gap increases from 2.38 eV to 2.79 eV with increasing thickness of the films from 120 nm to 350 nm. The presence of defects in the films which in turn produce localized states in the band structure, is responsible for the low value of the energy gap in the case of film thickness of 120 nm. By increasing the thickness of the film, greater depositions build up a more homogeneous films and reduce the number of defects and disorder. The diminution of disorder and defects in the structural bonding decrease the density of localized states in the band structure and consequently increase the optical energy gap E_g^{opt}.

The refractive index (n) of δ–Bi_2O_3 films of different thickness was determined from reflection and transmission measurements. Fig. 5 shows the variation in the

refractive index with photon energy. It is clear that the general behaviour of the curves is the same for all films.
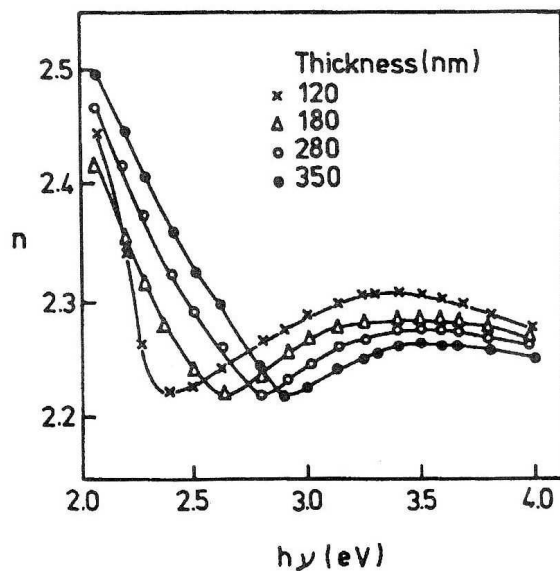

Fig. 5. Dispersion curves of refractive index (n) for δ–Bi$_2$O$_3$ films of different thickness.

4. Conclusions

The electrical and optical properties of δ–Bi$_2$O$_3$ films were studied. The obtained results allow to make a conclusion about a nonzero density of states near the Fermi level in δ–Bi$_2$O$_3$ films where the jumping conductivity is realized at low temperatures. The analysis of the absorption coefficient data revealed the existence of an indirect transition and the calculated value of the optical energy gap increases with increasing thickness of the film.

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FIZIKALNA SVOJSTVA δ–Bi$_2$O$_3$ TANKIH FILMOVA

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Polikristalični tanki filmovi δ–Bi$_2$O$_3$ pripravljeni su oksidacijom tankih slojeva bizmuta debljine 120–135 nm u zraku pri 473 K, tijekom 10 sati. Analiza difraktiranog rendgentskog zračenja pokazuje da su filmovi polikristalični i da korespondiraju kubičnoj δ-fazi Bi$_2$O$_3$. Proučavana su električna i optička svojstva δ–Bi$_2$O$_3$ u ovisnosti o debljini filmova. Mjerenjem električne vodljivosti na različitim temperaturama (100–473 K) opažena je koegzistencija vodljivosti vrpce i višefononsko asistiranih preskoka između lokaliziranih stanja. Nađeno je da se povećanjem debljine povećava aktivacijska energija a smanjuje gustoća lokaliziranih stanja na Fermijevom nivou. Analiza optičkih podatka ukazuje na postojanje indirektnih prijelaza. Nađeno je da se izračunate vrijednosti optičkog energijskog procijepa povećavaju s povećanjem debljine filma.