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ON THE PHOTOCONDUCTIVITY OF Bi_2O_3 IN THIN FILMS*

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The spectral characteristics of photoconductivity for Bi_2O_3 thin films were investigated. The films were prepared by thermal oxidation in air of Bi evaporated films. As revealed by X-ray diffraction and polarizing microscopy studies, polycrystalline and multiphasic films were obtained. From the photoconductivity spectral curves, the bandgap energy values were determined, by using the Moss criterion. The influence of oxidation (preparation) conditions on the E_g values is discussed. The photoconductivity of Al-Bi_2O_3-Al, Cu-Bi_2O_3-Cu and Al-Bi_2O_3-In_2O_3 structures is also investigated.

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1. Introduction

An increasing interest, was paid to Bi_2O_3 (bismuth trioxide) thin films both theoretically and experimentally due to an important number of applications [1-4].

This oxidic compound is characterised by significant values of refractive index, polarizability of Bi^{3+} cation [5], and a remarkable photosensitivity. Also, its energy gap is close to that of CdS, which is considered a outstanding candidate for solar cells [6].

Five polymorphs of Bi_2O_3, known as α-, β-, γ-, δ- and ω- Bi_2O_3 [7, 8] were reported. The low-temperature α phase and the high-temperature δ phase are stable; the other three polymorphs are high-temperature metastable phases [7, 8]. Each one is characterised by completely distinct structure and physical properties [8-10].

Owing to its interesting characteristics, Bi_2O_3 is used in microelectronics, sensor technology, optical coatings, as well as a parent substance for transparent ceramic glasses [11-13].

The study of photoconduction of Bi_2O_3 in thin films has been reported by few authors, to our knowledge [14, 15].

In the present paper, the spectral characteristics of the photoconductive response of Bi_2O_3 thin films at room temperature are investigated. The influence of the oxidation conditions on these properties was examined. Some correlations between the photoconductivity characteristics and film structure were also established.

2. Experimental

The investigated Bi_2O_3 films have been obtained by thermal oxidation, in air, of Bi (purity 99.999 %) evaporated films, in a vacuum system of UVN-61P type (pressure ~ 10^{-5} Torr). Glass substrates maintained at 325 K, during Bi films deposition, have been used.

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The experimental arrangement used for the oxidation of Bi films, which is in detail described in [16], permits a strong control of the characteristic parameters of this thermal process: heating/cooling rates, annealing time and temperature [16].

There are three technological runs used for oxidation of Bi films: (1) a slow or rapid heating from room temperature, with a rate of about 2 K/min, respective 10 K/min; (2) annealing for a certain time (10÷120 min) at a determined temperature (in the range 518÷795 K); (3) a slow or quick cooling to room temperature, with a temperature rate of about 3-4 K/min and over 10 K/min, respectively.

By modifying the values of the above mentioned parameters, various preparation conditions were created, which resulted in films with different structures and phase compositions.

The film thickness was measured by a MII-4 type microscope (interferometrical method). It ranged between 0.07 and 3.00 μm.

The film structure was investigated by X-ray diffraction analysis, using a DRON-2 diffractometer, and by appealing to ICDD database resources [17]. Studies of optical polarizing mycroscopy were performed by means of a MIN-8 type microscope.

The experimental setup for the investigation of photoconductivity characteristics is described in [16]. All photoconductivity measurements have been carried out at room temperature, (293 K), using unpolarized light and d.c. voltage.

3. Results and discussion

As revealed from structure investigations, polycrystalline and multiphasic films have been obtained.

The phase composition is conditionned by the characteristics of preparation, especially heat treatment. Thus, slow heatings, associated or not to long durations (of the order of hours), results in predominance of low-temperature α-Bi_2O_3 phase, with a gap E_g of about 2.90 eV [16, 18].

On the other hand, rapid oxidations, characterised by high heating rates seem to favorise the formation of the dominant BiO phase, with $E_g > 3$ eV [16].

Besides, depending on the oxidation conditions, the presence of stoichiometric β-Bi_2O_3 and of two nonstoichiometric phases, $Bi_2O_{2.33}$ and $Bi_2O_{2.75}$, as well of BiO and unoxidized Bi has been established [16].

A detailed analysis of the influence of oxidation conditions on films structure is given in [16].

In the present paper, the obtained results concerning spectral dependences of photoconductivity response of Bi_2O_3 thin films are presented.

Fig. 1 shows the photoconductivity spectra for the typical sample CH.1.

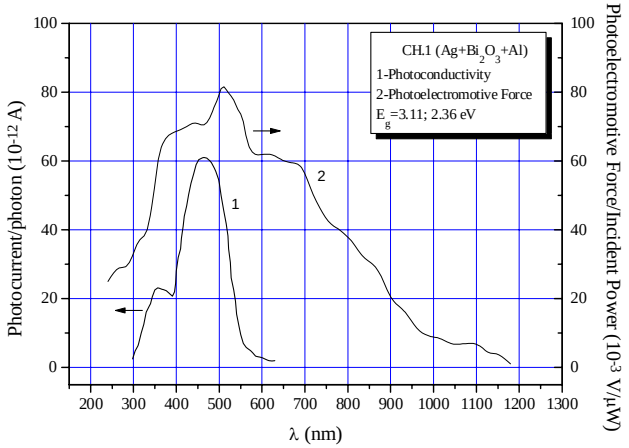


Fig. 1. Spectral dependence of the photoconductivity and photoelectromotive force for sample CH.1 (d = 0.79 μm; preparation conditions - quick heating, 30 min annealing at 245 ^oC, rapid cooling). Planar configuration.

As shown by the curve 1, the studied sample is characterized by a mixture of two principal phases. From this curve, the values of energy gap of both phases were determined, by using the Moss criterion [19]. The first indicated value, of 3.11 eV, probably corresponds to BiO, which forms mainly in the case of higher rates of heating, while the smaller value, of 2.36 eV, is likely to belong to a nonstoichiometric phase-$Bi_2O_{2.75}$ [18].

As for curve 2, which evidences a large spectral domain of photoelectromotive force variation, the main maximum, positionned at 2.46 eV, corresponds to band to band transitions, distorted by the electrodes; the secondary maximums (at 1.99, 1.80, 1.44 and 1.22 eV) give the positions of impurity levels into the bandgap relative to upper limit of valence band.

Our experiments show evidence for the major influence of thermal oxidation process (heat treatment) on the energy gap of the samples. In this way, strongly different preparation conditions (regarding the heating rate and duration) lead to distinct values of energy gap. This feature is illustrated in Fig. 2, which presents comparatively the photoconductivity response for two typical samples, CH.2 and CH.3. As determined by the mentioned Moss crriterion, the greater value of E_g, in the case of sample CH.2, corresponds to the higher rate of heating, which favorises the preponderance of BiO, with an energy gap >3 eV [16]. In the same time, the lower value of E_g (sample CH.3) is conditionned by the slow oxidation, which results in predominance of α-Bi_2O_3, with an energy gap of about 2.90 eV [16, 18].

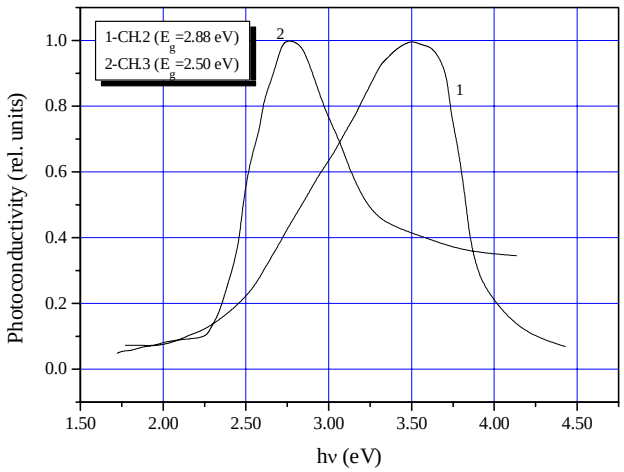


Fig. 2. Photoconductivity spectra for two typical samples: CH.2 (d=2.70 μm; rapid heating, 20 min annealing at 390 ^oC, rapid cooling) and CH.3 (d=0.81 μm; slow heating, 2 h annealing at 300 ^oC, slow cooling). Planar configuration.

The spectral characteristics of photoconductivity (e.g. photoelectromotive force) in sandwich structures of Al-Bi_2O_3-Al, Cu-Bi_2O_3-Cu, and Al-Bi_2O_3-In_2O_3 type are also investigated. The thermal oxidation of Bi was performed with rapid heating and cooling runs.

The polarity of photoelectromotive force generated under illumination with an A-type source of light of about 100 lx, was always positive at the semiconductor (e.g. Bi_2O_3), irrespective of contact nature.

In Fig. 3, the spectral dependences of photoelectromotive force for symmetrical structures of Al-Bi_2O_3-Al and Cu-Bi_2O_3-Cu type are presented.

In the case of curve 1.1, the band from 590 nm is due to the fundamental absorption of phase with the smallest value of E_g. One evidences, in the same time, two impurity bands: first is positioned at 1.71 eV, and the second is doubled: 1.55 and 1.47 eV.

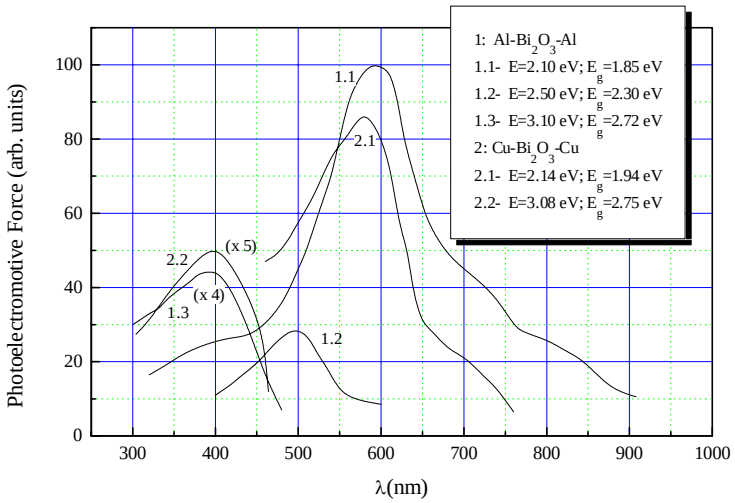


Fig. 3. Spectral curves of photoelectromotive force for Al-Bi_2O_3-Al (d = 2.00 μm) and Cu-Bi_2O_3-Cu (d = 2.15 μm) structures. The oxidation temperature is 783 K; annealing time: 1.1-10 min; 1.2 - 20 min; 1.3 - 30 min; 2.1 - 10 min, and 2.2 - 25 min. E - position of the main maximum. (× n)-signal amplification by n times.

By increasing the oxidation time from 10 min to 20 min, and further to 30 min, the fundamental band displaces from 2.10 eV to 2.50 eV and 3.10 eV, respectively. As one can clearly see from the last figure, the values of energy gap, as determined by the Moss criterion, show an important increase as a result of advancing of oxidation process, as its duration becomes larger. This feature is commented in detail in [6, 16]. In the same time, a substantial decrease of the photoconductivity and the disappearance of impurity bands, as a result of increasing oxidation durations, are registered.

In the case of Cu-Bi_2O_3-Cu structures, one can note a marked photoconduction in the visible domain. Its behaviour with respect to the increase of oxidation duration has similar characteristics to that of previous observed structure based diminuishing of photoconductivity, displacement of spectral curves to the high energies domain, and atenuation/disappearance of impurity bands. Taking into account that the impurity bands are seen to vanish at a prolonged oxidation of both structures, one can consider that they belong to unoxidized Bi atoms.

Fig. 4 presents the spectral curves of photoconduction for a sandwich structure of Al-Bi_2O_3-In_2O_3 type. The principal maximum, positionned at 2.23 eV in the case of curve 1, depends on the heat treatment: by increasing its duration, the fundamental band shifts to the UV domain, with a speed of 0.04 eV/min.

As one can see from the last figure, the spectral curve 1 (the smallest duration of oxidation) contains 6 characteristic maximums, which diminish or amplify afterwards, depending on the amount of respective phase.

Generally, the behaviour of of photoconductivity response is analogous to that of previous case (Fig. 3). Besides, one can observe a characteristic feature regarding dynamics of samples phase composition: a continuous modification of phase composition is recorded, together with the increase of the oxidation duration up to 30 min, after that one reach a stable phase structure (the maximums of curves 3 and 4 are practically overlapped).

The maximum situated at about 730 nm is common to all investigated structures and may be considered as of impurity nature; it is probably due to an excess of unoxidized Bi atoms in the studied films.

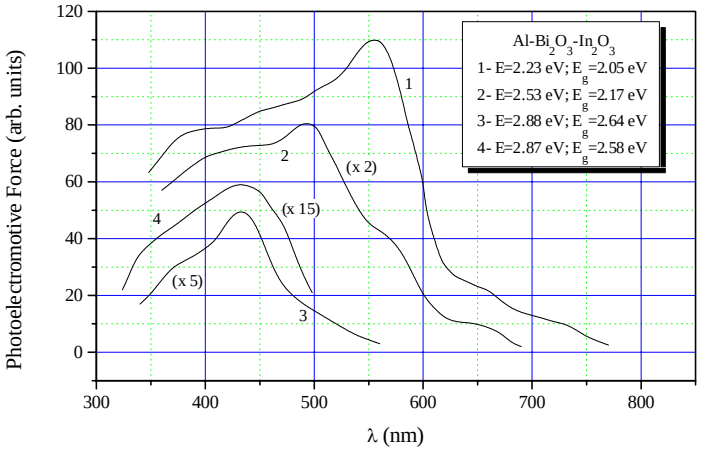


Fig. 4. Spectral dependences of photoelectromotive force for Al-Bi_2O_3-In_2O_3 (d = 2.25 μm) structures. The oxidation temperature is 793 K; annealing time: 1 - 15 min; 2 - 20 min; 3 - 30 min; 4 - 35 min. E – position of principal maximum. (× n) - signal amplification by n times.

Our investigations suggest a possible utilisation of Bi_2O_3 thin films as photoelectronic sensors (vidicon films [18], image convertors etc.) in the spectral domain by the UV-VIS limit. These devices require photosensitive materials with low dark conductivity and small dielectric constant, conditions that our Bi_2O_3 films fully satisfy.

4. Conclusions

The photoconductivity response of Bi_2O_3 thin films strongly depends on the oxidation conditions during preparation. The values of the energy gap, E_g, for films prepared in various conditions, have been determined by using the Moss criterion. The characteristics parameters of the preparation process, especially the heating rate and duration, exert a decisive influence on the structural phases in the films, which, in turn, determine the photoconductive behaviour of the investigated samples.

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