Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Research Bulletin 41 (2006) 1558–1564
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Spray pyrolysed bismuth oxide thin films and their characterization

T.P. Gujar, V.R. Shinde, C.D. Lokhande *

Thin Film Physics Laboratory, Department of Physics, Shivaji University, Kolhapur-416004 (M.S.), India

Received 10 August 2005; received in revised form 10 January 2006; accepted 13 January 2006
Available online 14 February 2006

Abstract

Uniform, adherent and reproducible bismuth oxide thin films have been deposited on glass substrates from aqueous $Bi(NO_3)_3$ solution, using the solution spray technique. Their structural, surface morphological, optical, and electrical properties were investigated by XRD, AFM, optical absorption, electrical resistivity and thermo-emf measurements. The structural analysis from XRD pattern showed the formation of mixed phases of monoclinic Bi_2O_3 (predominant), tetragonal β-Bi_2O_3 and nonstiochiometric $Bi_2O_{2.33}$. The surface morphological studies on atomic force micrographs revealed round grain morphology of bismuth oxide crystallites. The optical studies showed a direct band gap of 2.90 eV for as-prepared bismuth oxide films. The electrical resistivity measurements of bismuth oxide films indicated a semiconducting behavior with the room temperature electrical resistivity of the order of 10^7 Ω cm. From thermo-emf measurements, the electrical conductivity was found to be of n-type.

Keywords: A. Oxides; A. Structural materials; A. Thin films; B. Chemical synthesis; C. Atomic force microscopy

1. Introduction

Metal oxide films have been deposited using several deposition techniques. Among these, spray pyrolysis is a promising technique for the production of metal oxide films. The spray pyrolysis technique is based on spraying the gas and solution (aerosol) and to direct the mixture onto the heated surface of the substrate, where a chemical reaction leaves a desired solid film. This is probably the easiest, low cost, nonvacuum and suitable technique to prepare large area thin films, which has been employed to prepare several types of materials, like: transparent conductive contacts [1], semiconductors [2], luminescent materials [3], sulfides [4], selenides [5,6], oxides [7,8], etc.

Bismuth oxide is one of the important transition metal oxides, which plays a significant role in modern solid-state technology due to its peculiar properties such as band gap, refractive index, dielectric properties etc. Due to the predominance of certain phase, which depends on preparation technology, the electrical conductivity of bismuth oxide may change by five orders of magnitude, while its band gap may change from 2 to 3.96 eV. These properties made it suitable for a large range of applications, such as optical coatings, photovoltaic cells, microwave integrated circuits [9–11], etc. Along with these applications, recently introduced applications of Bi_2O_3 are in fuel cells, oxygen sensors and oxygen pumps [12–14].

A characteristic feature of bismuth oxide consists of its polymorphism: five modifications, known as α-, β-, γ-, δ-, and ω-Bi_2O_3, have been reported in the literature [15–17]. Two of them, the low-temperature α and the

* Corresponding author. Fax: +91 231 2691533.
E-mail addresses: gujar_tp@yahoo.com (T.P. Gujar), l_chandrakant@yahoo.com (C.D. Lokhande).

0025-5408/$ – see front matter
doi:10.1016/j.materresbull.2006.01.024

high-temperature δ phases, are the stable phases. The others are the high-temperature metastable phases [16,17]. Each polymorph possesses distinct crystalline structure and physical properties (electrical, optical, photoelectrical, etc.). For example, at 300 K, the band gap of monoclinic α-Bi_2O_3 is equal to 2.85 eV, while that of tetragonal β phase is 2.58 eV [18]. It is experimentally established that the preparation method and conditions strongly influence the crystalline structure and phase composition of bismuth oxide films [17,19]. In case of thin Bi-oxidized films, depending upon preparation parameters, BiO and two non-stoichiometric phases ($Bi_2O_{2.33}$ and $Bi_2O_{2.75}$) have been also observed [18]. The bismuth oxide thin films have been prepared by different chemical methods. Killedar et al. [20] obtained $Bi_2O_{2.33}$ phase using spray pyrolysis method from nonaqueous medium. Lokhande and Bhosale [21] have reported deposition of Bi_2O_3 thin film using spray pyrolysis, which was further used to convert into Bi_2S_3. Recently, in our previous work we have reported the preparation of monoclinic Bi_2O_3 films by anodization of electrochemically deposited Bi films and by chemical bath deposition method [22,23]. Switzer et al. [14] obtained single crystalline δ-Bi_2O_3 films on gold substrate by electrodeposition. Leontie et al. [24] studied optical properties of Bi_2O_3 thin films obtained by thermal oxidation of bismuth films. Metikos-Hukovic [25] has studied Bi_2O_3 thin films prepared by anodic oxidation of bismuth with n- and p-type behavior.

In the present investigation, polycrystalline bismuth oxide thin films have been obtained using the chemical spray deposition technique from aqueous medium. Structural, surface morphological, optical, and electrical characterizations have been carried out.

2. Experimental

For the careful cleaning of glass substrates, the substrates were initially boiled in chromic acid for 10 min, washed with double distilled water and dipped in labogent detergent and again washed with double distilled water. These substrates were further treated with ultrasonic waves for 15 min, prior to deposition.

For the deposition of bismuth oxide thin films, 0.1 M bismuth nitrate was dissolved in sufficient quantity of concentrated HCl. The pH of solution was adjusted at ∼6 by addition of ethylene diamine tetra acetic acid (EDTA). The solution was sprayed through a glass nozzle onto ultrasonically cleaned hot glass substrates kept at 723 K. The spray rate of 1.70 cc/min was maintained by using air as carrier gas. The temperature was controlled with an electronic temperature controller. Hazardous fumes evolved were expelled out from deposition chamber by an exhaust system attached to spray pyrolysis unit. The nozzle to substrate distance was 28 cm. To study the structural properties of the films, X-ray diffraction analysis was performed on a Philips (PW 3710) diffractometer with chromium target (λ = 2.2896 Å). The surface morphological study of the bismuth oxide films was carried out by atomic force microscopy using a nanoscope AFM apparatus. The optical absorption was measured within the wavelength range 325–900 nm using a systronic spetrophotometer-119. A two-probe method was used for electrical resistivity measurements. Thermo-emf measurements were carried out to determine the type of electrical conductivity of the films.

3. Results and discussion

3.1. Film formation

Aqueous solution of bismuth nitrate, when sprayed over the hot substrates, fine droplets of solution thermally decompose after falling over the hot surface of substrates. This results in the formation of well adherent and uniform bismuth oxide film. The possible chemical reaction that takes place is as follows:

$$2Bi(NO_3)_3 6H_2O + 6HCl \overset{\Delta}{\Rightarrow} Bi_2O_3\downarrow + 6NO_2\uparrow + 3Cl_2\uparrow + 9H_2O\uparrow \quad (1)$$

The formed bismuth oxide thin films were yellowish in color and these films were used for the further characterization.

3.2. Film characterization

3.2.1. X-ray diffraction studies

The structural analysis of bismuth oxide films was carried out on a Philips PW-3710 diffractometer with chromium target by varying diffraction angle 2θ from 20 to 100°. Fig. 1 shows a typical XRD pattern of as-deposited bismuth