Thin Solid Films 578 (2015) 103–112

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Opto-electronic properties of bismuth oxide films presenting different crystallographic phases

Celia L. Gomez [a,b], Osmary Depablos-Rivera [a,b,*], Phaedra Silva-Bermudez [a,c], Stephen Muhl [a], Andreas Zeinert [d], Michael Lejeune [d], Stephane Charvet [d], Pierre Barroy [d], Enrique Camps [e], Sandra E. Rodil [a]

[a] Instituto de Investigaciones en Materiales, UNAM, Circuito Exterior s/n CU, México D.F. 04510, Mexico
[b] Posgrado en Ciencia e Ingeniería de Materiales, UNAM, Unidad de Posgrado, Edificio C, Piso 1, Zona Cultural de CU, México, D.F. 04510, Mexico
[c] Instituto Nacional de Rehabilitación, Calz. México Xochimilco No. 289 Col. Arenal de Guadalupe, C.P.14389, Ciudad de México, D.F., Mexico
[d] Laboratoire de Physique de la Matière Condensée, Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens Cedex 1, France
[e] Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca S/N, kilómetro 36.5. La Marquesa, Municipio de Ocoyoacac, CP 52750, Estado de México, Mexico

ARTICLE INFO

Article history:
Received 18 September 2014
Received in revised form 14 January 2015
Accepted 6 February 2015
Available online 15 February 2015

Keywords:
Bismuth oxide
Thin film
Sputtering
Opto-electronic properties

ABSTRACT

The optical, electrical and structural properties of bismuth oxide thin films deposited by radio frequency reactive magnetron sputtering were studied. The Bi_2O_3 thin films were grown on Si and glass substrates under different power and substrate temperatures in an oxygen-enriched plasma leading to films with different crystalline phase as evidenced by X-ray diffraction and Raman spectroscopy. The optical properties of the films were measured using ellipsometric spectroscopy and optical transmission spectra. In order to parameterize the optical dispersion functions (n, k) of the films, the Tauc–Lorentz dispersion model was used. The optical bandgap was then assessed by different methods and the results are compared to the thermal variations of the electrical resistivity of the films. It was found that the refractive index, extinction coefficient and optical gap strongly depend on the deposition conditions and the crystalline phase; the fluorite defect cubic δ-Bi_2O_3 phase showed the lowest optical gap and lower resistivity.

1. Introduction

Bismuth oxide (Bi_2O_3) is an interesting ceramic material, for which optical gaps between 1.7 and 3.6 eV have been reported depending on the crystallographic phase. Most of the synthesis has been done using solid-state reactions although more recently different nanostructures, including thin films, have been also reported. Bismuth oxide thin films have been proposed as candidate for a wide range of applications, such as gas sensors, optical coating [1], catalysis [2], electrochromic and photocatalysis [3–7]. Nevertheless, their real use is less extensive, as for these nanostructures one major issue is to obtain a single stable phase needed for technological applications. As a bulk material at least six polymorphs have been identified for the Bi_2O_3 composition. The stable phases are: α (monoclinic) from room temperature (RT) to 730 °C, and δ (face centered cubic) above 730 °C up to melting temperature. Two intermediate metastable polymorphs appear during cooling down from the δ-phase: β (tetragonal) and γ (body centered cubic); the transformation into these phases occurs around 650 and 640 °C, respectively, and it depends on the purity and texture of the samples. Other metastable phases have been obtained under special conditions: ω (triclinic) [8] and ε (orthorhombic) [9].

All these phases present different physical properties, although not all of them have been deeply studied. Among them, the δ-Bi_2O_3 phase draws much attention since this material presents the highest ionic conductivity [10,11], even though this property is rapidly lost when the temperature is decreased and the microstructure changes to some of the low-temperature phases.

The synthesis of bismuth oxide as thin films is of great interest for some of the above-mentioned applications. The earliest work reports the initial stages of the formation of a continuous anodic layer of bismuth oxide on a solid bismuth electrode, in the pH range 5–14 [12,13], finding that the film thickness was limited to a few nanometers. However, in those papers not much information about the film structure was given. By 1999, Switzer et al. [14] showed that it was possible to grow epitaxially δ-Bi_2O_3 thin films on Au substrates by electrodeposition. Such work was followed by Bohannan et al. [15] and Helfen et al. [16], who used electrochemical deposition to show that the δ-stabilization was also possible on other substrates and possibly driven by the nanocrystalline size and strain.

Since then, other groups have deposited Bi_2O_3 films using physical and chemical methods; Leontie et al. [17] showed the effect of the temperature on the optical properties of bismuth oxide films produced by thermal oxidation of Bi surfaces; however, no information about

* Corresponding author at: Instituto de Investigaciones en Materiales and Posgrado en Ciencia e Ingeniería de Materiales, Universidad Nacional Autónoma de México, México D.F. 04510, Mexico. Tel.: +52 55 5622 4734; fax: +52 55 5616 1251.
E-mail address: osmarydep@yahoo.com (O. Depablos-Rivera).

http://dx.doi.org/10.1016/j.tsf.2015.02.020
0040-6090/

structure was given. Similarly, Patil et al. [18] produced polycrystalline and multiphase bismuth oxide films by thermal evaporation of Bi thin films using different temperatures and annealing times, however not much detail was given about the structural variations. Fruth et al. [19] tried a wet chemical method (sol–gel) obtaining an oxygen deficient phase. Later on, Weidong et al. [20] showed that monoclinic and tetragonal phases could be obtained by the sol–gel route after annealing above 450 °C. Another chemical method was tried by Gujar et al. [21]; chemical bath that is based on the formation of a solid phase after nucleation and growth from a saturated solution. The structural information showed the co-existence of α, β and the $Bi_2O_{2.33}$ substoichiometric phase. Spray pyrolysis, which is also a chemical-based method, was used by Lokhande and Bhosale [22] and Rico-Fuentes et al. [23]. The latter used bismuth acetate as the source solution and obtained two bismuth oxide phases: β-Bi_2O_3 and the substoichiometry $Bi_2O_{2.33}$; this later was converted into the β-phase after annealing. Soitah et al. [24] studied the optical and electrical properties of bismuth oxide films produced by a Pechini modified route and annealing. The X-ray diffraction (XRD) patterns of their films annealed at different temperatures showed formation of mixed phases of tetragonal β-Bi_2O_3 and $Bi_2O_{2.33}$ along with the presence of tetragonal phase Bi_2SiO_5. Physical deposition methods, such as pulsed laser deposition (PLD) and magnetron sputtering have also been used. Shimanoe et al. [25] compared the electrochromic properties of sputtered (from a Bi_2O_3 target) and thermally oxidized evaporated bismuth films. They found that the electrochromic response was dependent on the annealing temperature, results that were most probably related to the different crystallographic phases, but not many details were given. Leontie et al. [26] ablated Bi_2O_3 sintered pellets and obtained a mixture of nanocrystalline and amorphous bismuth oxide films. The optical properties were studied as a function of the film thickness, but no information about the crystalline phases was presented. The same group reported the deposition of multiphase δ- and β-Bi_2O_3 films by reactive magnetron sputtering at room temperature; the samples were deposited at fixed deposition conditions and the optical properties were analyzed by ellipsometry. Fan et al. [1] also used the reactive sputtering of a Bi target to deposit bismuth oxide films. In that work, it was shown that the preferential phase depended on the substrate temperature and the O_2 partial pressure. They found that a minimum 5% of O_2 was required to form the oxide and that at 100 °C, the films were amorphous, at 200 °C, the delta phase was obtained and further substrate temperature increments lead to a mixture of α and β phases. The most interesting result was to demonstrate that using magnetron sputtering it was also possible to stabilize the δ-Bi_2O_3 phase, which is one of the most interesting phases due to their possible use as an electrolyte for micro solid oxide fuel cells or gas sensors. Such results have been recently confirmed by Popa et al. [27] and Gomez et al. [28].

The present paper can be considered as an extension of Fan et al.'s paper [1] to demonstrate the efficiency of magnetron sputtering in the production of Bi_2O_3 semiconductor thin films, adding the radio frequency (rf) power as a deposition variable parameter. Here, we have studied in more detail the different Bi_2O_3 phases that can be obtained by rf magnetron sputtering using an α-Bi_2O_3 target and by varying both the substrate temperature and the deposition power. The different structures and both optical and electrical properties were carefully studied for each of the deposition conditions.

2. Experimental details

The bismuth oxide thin films were deposited by rf magnetron sputtering using a pure 4″ α-Bi_2O_3 target (99.99% Plasmaterials). The depositions were done using an Ar:O_2 flow ratio of 80:20. The films were deposited on glass and Si (100) substrates, the substrate–target distance was fixed at 5 cm, the base pressure was below 5.3×10^{-4} Pa and the deposition pressure was fixed at 2.7 Pa. The variables chosen were the rf power and the substrate temperature; the first was changed between 100 and 180 W (every 20 W), meanwhile three substrate temperatures (T_s) were selected: 150, 200 and 250 °C. Three deposition times were used to estimate the deposition rates.

The film thickness was measured by a Dektak profilometer. The structure was characterized using a Rigaku Ultima IV diffractometer using the Cu Kα radiation in the thin film mode (incident parallel beam) but since the signal was good enough even for the thinnest films, the θ–2θ geometry from 20–60° was used (to avoid the strong (100) Si reflection). The chemical composition was studied by X-ray photoelectron spectroscopy (XPS), using a VG Microtech Multilab ESCA 2000 using a CLAM MCD detector. The XPS was operated at 8×10^{-7} Pa using Al Kα radiation $h\nu = 1486.6$ eV with a spatial resolution of 500 μm and 50 and 20 eV pass energy to acquire the survey and high resolution spectra, respectively. The spectra were acquired before and after Ar ion cleaning of the surface in order to assure that only the contaminant carbon signal (C 1s peak set at 285 eV) was removed during the cleaning process and also to detect any shifts in the binding energies due to the insulating character of the films. The high resolution spectra were fitted using the SDPv4.1 software® to obtain the surface elemental chemical compositions. Results are reported as the mean of measurements in two different samples per each deposition condition; the overall associated error was considered as the standard 5% measurement error of the XPS technique. The optical properties of the films were measured by both UV–VIS (ultraviolet–visible) transmittance (samples deposited on glass), using an Unicam model UV300 spectrophotometer, and spectroscopic ellipsometry (samples deposited on Si). A Jobin-Yvon UVISEL phase modulated ellipsometer was used in the 1.5 to 5 eV range, energy step of 0.05 eV and incidence angle of 70°. The optical properties of the films were obtained using the Tauc–Lorentz dispersion model in which the dielectric functions are parameterized using Eq. (1).

$$\epsilon_2(E) = \begin{cases} \sum_n \frac{1}{E} \frac{A_n E_{0n} C_n (E - E_{TL})^2}{\left[(E^2 - E_{0n}^2) + {C_n}^2 E^2\right]}, & E > E_{TL} \\ 0 & E < E_{TL} \end{cases} \quad (1)$$

where $\epsilon = \epsilon_1 + i\epsilon_2$ is the complex dielectric function, ϵ_2 is calculated fitting the ellipsometric variables adjusting the free parameters in Eq. (1), A represents the optical transition element matrix, E_0 is the peak transition energy, C is the broadening term, E is the photon energy and E_{TL} is the bandgap; all parameters are in units of energy. Finally, the real part is calculated using the Kramers–Kronig approximation. The surface roughness was modeled adding a layer composed of 50% voids and 50% film. As discussed later, depending on the predominant phase, single, two or three oscillators ($n = 1$, 2 or 3 in Eq. (1)) were used.

The electrical properties were measured as a function of the temperature (RT to 600 °C) using the samples deposited on glass. Platinum electrodes were deposited by sputtering using a circular configuration and the voltage was scanned from −2 to 2 V using a Keithley electrometer model 6517A. Micro-Raman spectroscopy was used to identify the presence of metallic bismuth and the structural uniformity of the Bi_2O_3 films since each phase has a characteristic Raman spectrum [29–31]. The measurements were done using a Horiba Jobin-Yvon micro-Raman, with a wavelength of 532.07 nm. Finally, scanning electron micrographs of the films surface were obtained using a Field Emission-Scanning Electron Microscope (JEOL7600F FE-SEM) at 0.5 and 2.0 kV.

3. Results

The deposition conditions described above were selected after some screening experiments; the initial trials indicated that it was necessary to add O_2 into the sputtering gas (Ar) in order to form the oxide film; otherwise a bismuth film was obtained although the target was Bi_2O_3. The formation of pure Bi films was more easily identified using the Raman spectra (not shown) than the XRD due to overlapping diffraction peaks between Bi and the different Bi_2O_3 phases. The Raman spectrum