Thin Solid Films 594 (2015) 192–196

Contents lists available at ScienceDirect

Thin Solid Films

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

Formation of bismuth oxide nanostructures by reactive plasma assisted thermal evaporation

Aleksandras Iljinas *, Liutauras Marcinauskas

Department of Physics, Kaunas University of Technology, Studentų 50, LT-51368 Kaunas, Lithuania

ARTICLE INFO

Article history:
Received 30 January 2015
Received in revised form 10 October 2015
Accepted 13 October 2015
Available online 22 October 2015

Keywords:
Bismuth oxide
δ-Bi_2O_3
Nanostructures
Optical properties
Reactive plasma-assisted thermal evaporation

ABSTRACT

Bismuth oxide films and nanostructures were deposited using reactive plasma assisted thermal evaporation. The growth temperature varied in the range of 30–500 °C in order to obtain the single phase Bi_2O_3. The as-deposited Bi_2O_3 structures were characterized for their structural, surface morphological and optical properties using X-ray diffraction (XRD), scanning electron microscopy, and optical absorption measurements, respectively. The XRD analyses demonstrated the formation of Bi_2O_3 films amorphous phases at deposition temperatures below 200 °C. Meanwhile the crystalline phase's (β-Bi_2O_3 with δ-Bi_2O_3 or δ-Bi_2O_3) bismuth oxide nanostructures were formed at higher grown temperatures. The nanostructures were approximately 100–500 nm of length with the diameter of 50–100 nm. The optical band gap of Bi_2O_3 films and nanostructures varied in the range of 2.75–3.05 eV.

1. Introduction

Bismuth oxide (Bi_2O_3) films and nanostructures are very attractive due to unique physical, properties such as: high refractive index, high oxygen conductivity, wide band gap, dielectric permittivity, photoconductivity, and photoluminescence [1–9]. These remarkable properties allow Bi_2O_3 films use as optical coatings, capacitors, catalyst, gas sensors, photovoltaic cells, etc. [4–9]. Nowadays, there are various techniques for the formation of Bi_2O_3 films and nanostructures, such as: electrochemical deposition [10], magnetron sputtering [1,4,11,12], thermal oxidation [2], pulse laser deposition [3], sol–gel [6], electrospinning [13], etc. Reactive plasma assisted thermal evaporation technique allows producing high volume manufacture of uniform, dense, and high adhesive films. The deposition process is easily controlled and high deposition rates are achieved. This technique allows directly deposit the Bi_2O_3 films and eliminates the additional oxidation procedure [14].

Bismuth oxide has five main polymorphic phases: α-, β-, γ-, δ-, and ε-Bi_2O_3. The optical band gap values of the bismuth oxide vary from 1.7 eV to 3.6 eV, depending on the crystal structure [1–3,7,11]. The variation of the process parameters and the formation methods allow producing Bi_2O_3 films or nanostructures with the desirable crystalline phase. As a result, the Bi_2O_3 films will have different electrical, optical, catalytic or mechanical properties [2–5,11,13]. B. Sirota et al. [1] have shown that β-Bi_2O_3 nanowires may be grown using magnetron sputtering deposition at 350 °C temperature. M.G. Hale et al. [15] obtained Bi_2O_3 nanowires by simultaneous templating and electrochemical adhesion techniques. X. Liu [10] prepared 3D Bi_2O_3 flower-like structures and indicated that the ramp rate and reaction temperature influence nanostructure dimensions (shape and form). The produced nanostructures normally consist of mixed phases or mainly of β phase [9,10,16,17]. Meanwhile, the formation of pure Bi_2O_3 nanostructures without the catalyst is very limited. The phase composition of Bi_2O_3 films or nanostructures is very sensitive to the formation temperature and method of preparation [16–18]. H.T. Fan [11] found that the substrate temperatures have great effect on the phase components of the thin Bi_2O_3 films. The variation of the annealing temperatures influenced on the crystallite size, optical band gap, and surface porosity. Other authors [6–8] also indicated that the variation of temperature (usually during the oxidation process) leads to the phase transition in Bi_2O_3 structures.

There are no researches concerning the formation of Bi_2O_3 films or nanostructures by reactive plasma assisted thermal evaporation. Nowadays the influence of the process parameters, especially substrate temperature and oxygen ion bombardment on the Bi_2O_3 films crystallite phase, growth rate, surface morphology, band gap value etc. is still unknown.

In this work, the influence of the substrate temperature on the growth, phase composition and optical properties of Bi_2O_3 structures prepared by reactive plasma assisted thermal evaporation were investigated.

2. Experiment

The Bi_2O_3 thin films were deposited onto soda lime glass substrates by reactive plasma assisted thermal evaporation in O_2 gas environment (pressure of 4 Pa) from the molybdenum evaporation boat. Metallic Bi pieces (Kurt J. Lesker Company (of 99.999% purity)) of 0.2 mg mass

* Corresponding author.
E-mail address: aleksandras.iljinas@ktu.lt (A. Iljinas).

http://dx.doi.org/10.1016/j.tsf.2015.10.031
0040-6090/

Table 1
The deposition parameters and their values.

Deposition parameters	Values
Initial pressure, Pa	$5 \cdot 10^{-3}$
Partial pressure of active O_2 gas, Pa	4
Distance between the boat and the substrate, cm	10
Evaporation rate, nm/min	86
Discharge voltage, V	390
Discharge current, A	0.625
Substrate temperature, °C	30, 200, 400, 500

were thermally melted in the molybdenum evaporation boat and used as the evaporated material. The formation of the films was done at 30 °C, 200 °C, 400 °C, and 500 °C temperature substrates. Before deposition, the glass substrates were cleaned ultrasonically using acetone for 20 min with de-ionized water and dried in nitrogen flow. The deposition conditions of the films are summarized in Table 1. The O_2 plasma was generated between the resistively heated molybdenum boat shield and the substrate holder. The distance between boat shield and substrate was 10 cm. The substrate holder was heated and negatively biased during deposition; the bias voltage was 400 V.

The surface morphology of the samples was analyzed using scanning electron microscopy (SEM) (RAITH-e-LiNE, Raith GmbH). The SEM images were performed at the voltage of 10 kV and distance of 5.6 mm and 10.6 mm, respectively. The elemental compositions of the deposited Bi_2O_3 structures were measured by energy dispersive spectrometry (EDS) (Bruker AXS from GmbH). Measurements were performed from 1.05 mm^2 surface area using 10 kV at 5 different points and average values were calculated. The crystallographic structure of thin films was investigated by X-ray diffraction (XRD) (Bruker D8 Advance) using monochromatic Cu K_α radiation with (Bragg-Brentano) geometry. The average size of thin films crystallites were determined from the peak broadening by single line and multiple line analysis. The transmittance and reflectance spectra of the films were measured at a normal incidence with UV–VIS–NIR spectrophotometer (Ocean Optics USB4000). The absorption edge of the transmittance spectra was analyzed using Tauc method and optical band gap E_g was determined.

3. Results and discussions

The substrate temperature has great effect on the surface morphology of the Bi_2O_3 films. SEM images of the bismuth oxide surface structures deposited at different temperatures are shown in Fig. 1. It can be seen that films grown at the lowest temperature (30 °C) has uniform and quite dense structure, the grain size varies in the range of 100–200 nm (Fig. 1a). The grain size decreased down to 20–30 nm, the spaces between grain boundaries disappeared, and density increased, as the substrate temperature increased to 200 °C (Fig. 1b and c). The thickness of bismuth oxide films prepared at 30 °C and 200 °C temperatures was ~600 nm and ~570 nm, respectively. The formation of the nanostructures on the surface was observed when the deposition was done under higher temperatures (400 °C and 500 °C). The surface was covered by non-regular branched-like shape 3D nanostructures at 400 °C temperature. The length of Bi_2O_3 nanostructures was in range of 100–500 nm and the diameter was 50–100 nm (Fig. 1d and e). A large number of nanowires per unit area on the substrate were observed when the highest temperature was used. The diameter of nanowires was in the range of 50–100 nm, while the length varied from 100 nm

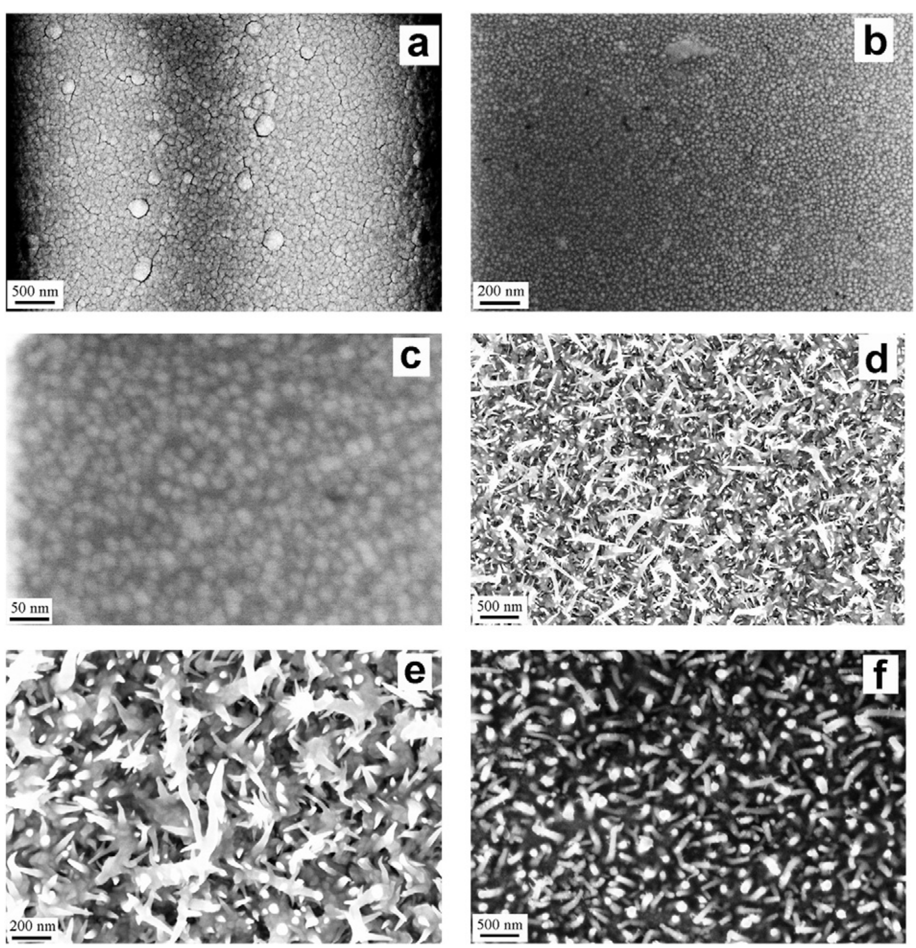

Fig. 1. SEM images of Bi_2O_3 films and nanostructures deposited at different substrate temperatures (a) 30 °C, (b–c) 200 °C, (d–e) 400 °C and (f) 500 °C.