Catalysis Today 266 (2016) 144–152

Contents lists available at ScienceDirect

Catalysis Today

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

Sputtered bismuth oxide thin films as a potential photocatalytic material

J.C. Medina[a,b], M. Bizarro[a], C.L. Gomez[a,b], O. Depablos-Rivera[a,b], R. Mirabal-Rojas[a,b], B.M. Monroy[a], A. Fonseca-Garcia[a,b], J. Perez-Alvarez[a], S.E. Rodil[a,*]

[a] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A. P. 70-360, Coyoacán C.P. 04510, D.F., Mexico
[b] Posgrado en Ciencia e Ingeniería de Materiales, Universidad Nacional Autónoma de México, Mexico

ARTICLE INFO

Article history:
Received 9 April 2015
Received in revised form 26 August 2015
Accepted 20 October 2015
Available online 23 December 2015

Keywords:
Bismuth oxide
Sputtering
Photocatalysis
Methyl orange

ABSTRACT

Bismuth oxide (Bi_2O_3) thin films were deposited using a magnetron sputtering system under different conditions of power (radio frequency) and substrate temperature. The film structural characterization was done using X-ray diffraction, where it was demonstrated that films presenting different crystalline phases were obtained; cubic delta-Bi_2O_3 and a mixture of α- and β-Bi_2O_3 in different proportions. Three of these films were selected to compare their photocatalytic activity by measuring the percentage of photodiscoloration of 1×10^{-6} M of methyl orange (MO, $C_{14}H_4N_3SO_3Na$) using UV light; moreover, the effect of the pH of the solution on the photodiscoloration was also investigated. The results indicated that the films were only active under acidic pH and that the cubic delta phase was the most efficient. The optical properties were also evaluated by ellipsometric spectroscopy and the results were compared to the optical transmittance spectroscopy. In order to gain understanding about the effect of the pH and the structure, the point of zero charge and the photoluminescence of the three samples were also obtained. Furthermore, the photocatalytic activity of the sample presenting the best results was evaluated using higher concentration of the MO dye, but also using indigo carmine dye and both UV and blue lights.

1. Introduction

Semiconductor driven photocatalysis has shown great potential for water treatment as a low-cost and environmental friendly process. Some critical issues have been already identified for real large-scale applications, which includes reactor design, catalysts recovery in the case of slurry systems and most important, optimization of the semiconductor–catalytic material to function efficiently under visible light. Attaining high photo-efficiency under solar spectrum is a rather difficult task based on TiO_2 materials and so there is a great motivation to investigate other semiconductors. Moreover, to achieve regional sustainability for the photocatalytic processes, the use of natural resources is an important issue to consider. In this work, we evaluated Bi_2O_3 thin films as a semiconductor for photocatalytic water treatment. The selection of a bismuth-based semiconductor was done considering the reported photocatalytic properties of Bi_2O_3 nanoparticles [1–7] under visible light irradiation and the fact that bismuth is a natural resource for Mexico (2nd worldwide producer). Different research papers have shown a relative good efficiency for the photocatalytic degradation of different organic compounds using Bi_2O_3 nanostructures or other Bi-based bimetallic oxides [1–7]. In those papers, the efficiency is associated to the larger optical absorption of the bismuth-based semiconductors in the visible range compared to TiO_2. However, Bi_2O_3 is a polymorphic oxide presenting about 5 different crystalline phases, each one with different optical band gaps (values between 2.2 and 3.9 have been reported [5,8–11]) and not all the phases have been evaluated for photocatalysis. As powders, there are two thermodynamically stable phases; the monoclinic alpha (α) phase is stable at atmospheric conditions and the cubic delta (δ) phase occurs between 730 and 825 °C. Nonetheless, when the material is synthesized as a thin film, the cubic-δ phase can be preserved at ambient conditions [12–15]. The δ-phase has a defective fluorite-structure where the bismuth atoms are arranged in a fcc structure and the oxygen atoms are situated in the tetrahedral sites, occupying only 75% of these sites. These empty sites give the δ-phase an exceptionally high ionic conductivity. During cooling from the high temperature phase, metastable phases have been achieved; beta (β), gamma (γ), and omega (ω) [16]. The published papers

* Corresponding author.
E-mail address: srodil@unam.mx (S.E. Rodil).

http://dx.doi.org/10.1016/j.cattod.2015.10.025
0920-5861/

concerning the photocatalytic activity of bismuth oxide powdered materials refer to α-Bi_2O_3 or the metastable β-Bi_2O_3 phase, showing that at the nanoscale the photocatalytic activity is substantially enhanced [3,5,17–21]. Most of those papers described the photocatalytic response of Bi_2O_3 powders and nanostructures but very few worked with films [22–24]. However, there is an advantage of using thin films instead of powders since the water treatment can be achieved without the complex and expensive filtering process. The production of Bi_2O_3 thin films started around 1999, when Switzer et al. [12] demonstrated the production of the δ-Bi_2O_3 phase using electrodeposition. Since then, other research groups have produced Bi_2O_3 thin films using a variety of deposition methods, so different phases and optical properties have been obtained [13–15]. Sirota et al. [22] produced Bi_2O_3 thin films by sputtering presenting a peculiar disordered nanowire structure which lead to high surface active areas. The photocatalytic activity of those films was evaluated by measuring the discoloration of Rhodamine 6G dye solutions (5×10^{-6} M). They observed a fast decrease in the dye concentration during the first hour of UV–vis illumination, but after 4 h not total discoloration was achieved for any of the films. More recently, Guo et al. [24] reported the photocatalytic discoloration of Rhodamine B (10 mg/L, 2×10^{-5} M) solutions using Bi_2O_3 films deposited by an electrophoretic method. However, the film structure was not well-defined and despite of using high dye concentrations, not information about the mineralization process was provided. Reaction rates about 0.02 min^{-1} were obtained for both UV and visible light experiments. In a parallel work, we have produced β-Bi_2O_3 thin films by spray pyrolysis [25], and the photocatalytic activity of those films was demonstrated by measuring the discoloration of both methyl orange (1×10^{-5} M) and acid blue 113 (1×10^{-5} M and 1×10^{-6} M) dyes under visible, UV and solar light. Moreover, in that paper, degradation of the dyes by the β-Bi_2O_3 films was also confirmed using high performance liquid chromatography (HPLC) and total organic carbon (TOC) measurements.

From the previous references, it can be observed that Bi_2O_3 thin films present interesting properties to function as visible light photocatalysts and their performance depend on both the synthesis method and the crystallographic phase. The contribution from the present paper is to evaluate the potential of sputtered deposited Bi_2O_3 thin films presenting different crystallographic phases to induce discoloration of methyl orange solutions as a screening test for the photocatalytic activity. The results are analyzed in terms of the film-optical properties and the photoluminescence spectra.

2. Experimental details

2.1. Film deposition

Bismuth oxide thin films were produced by magnetron sputtering from an α-Bi_2O_3 (99.9% purity) target. The base pressure was 6.7×10^{-4} Pa and the deposition pressure was fixed at 2.7 Pa using an 80:20 Ar:O_2 gas relation. Previous experiments indicated that the film structure and optical properties were highly dependent on both the radiofrequency (RF) power and the substrate temperature [26]. Therefore, in this paper, three different deposition conditions were selected to investigate the photocatalytic response; the details are shown in Table 1. Sample M150 consists of a pure δ-Bi_2O_3 phase, while samples M200 and M250 are a mixture of the monoclinic α and the tetragonal β phases, in different proportions. Pieces of corning glass (2.5 cm × 1.25 cm) and Si (1 0 0) were used for fabricating the Bi_2O_3 films, adjusting the deposition time to obtain similar thicknesses (450 nm).

2.2. Films characterization

The crystal structure of the films was investigated using a Rigaku-Ultima IV X-ray diffractometer (CuK_α 1.5406 Å, 40 kV, 44 mA and angle step of 0.02°) in the Bragg–Brentano configuration. The diffraction patterns were analyzed using the PDXL2 software to identify the phases, determine the grain size (Halder–Wagner method) and the relative percentage of each phase in the case of phase-mixtures (Relative Intensity Ratio, RIR method) [26]. The optical properties were studied by spectroscopic ellipsometry (Horiba–Jobin Yvon phase modulated system) from 1.5 to 5 eV at an incidence angle of 70° since the samples deposited on Si were used. The optical properties of the films were obtained using a three-layer model: substrate/film/roughness. The optical properties of the film were parameterized using the Tauc–Lorentz model [27] (valid since the grain size was relatively small) and the roughness layer was modeled using a Bruggeman effective medium (50% voids + 50% film) model. The estimated absorption coefficient (α) was compared to the optical transmittance of the films deposited on glass. The transmittance was measured using an UV–vis spectrophotometer Unicam UV 300 model. The film thickness was measured using a Veeco profilometer model Dektak 150. Meanwhile the chemical composition was determined by X-ray photoelectron spectroscopy (XPS) using a VG Microtech Multilab ESCA 2000 with a CLAM MCD detector, the radiation was Al K_α ($h\nu$ = 1453.6 eV) and for pass energy 50 and 20 eV were used for the acquisition of the low- and high-resolution spectra, respectively.

2.3. Photocatalytic discoloration experiments

The photocatalytic activity of the Bi_2O_3 films was evaluated by measuring the evolution of the absorbance spectrum of 1×10^{-6} M aqueous solution of methyl orange dye as a function of the irradiation time. The concentration used was chosen considering that the amount of catalyst was very small; the Bi_2O_3 mass in the 3.125 cm^2 of sample reached only 0.6 mg. Two samples were added for each experiment leading to 1.2 mg; the grams of catalyst per mole of pollutant are comparable to other works [5,28,29]. Three different values of pHs were used: pH = 3.5, 6.5 and 11. The original pH solution was 6.5, so in order to modify the pH, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were adequately used. For the discoloration tests, each film was immersed in 10 mL of the dye solution and exposed to UV light (9 W lamp with main emission centered in 368 nm; 26 W/m^2). It is worth to mention that at this research stage, where the objective was to select the Bi_2O_3 coating with the best photocatalytic response, we chose UV light as the illumination probe to minimize the misleading effect of the self-sensitization mechanism [30]. During the self-sensitization mechanism, the visible light is absorbed by the dye molecule and the excited dye can inject electrons to the conduction band of the semiconductor, creating active species on the semiconductor surface that induce the degradation of the dye molecule. The sensitization effect is reduced under illumination by UV light due to the smaller absorption cross section of the dye at wavelengths <400 nm.

The UV–vis measurements (Perkin Elmer Lambda 35 spectrophotometer) were carried out up to 180 min every 30 min interval. The discoloration percentage of the films was calculated using the following equation:

$$\%\ \text{Discoloration} = \left(1 - \frac{A}{A_o}\right) \times 100 \quad (1)$$

where A_0 and A are the absorbance maxima of the dye solution before and after the irradiation time, respectively.

The rate of reaction of the samples was obtained using the Langmuir–Hinshelwood model by plotting $\ln(A_0/A)$ versus the