Materials Science in Semiconductor Processing 37 (2015) 105–111

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Photoluminescent and photocatalytic properties of bismuth doped strontium aluminates blended with titanium dioxide

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ARTICLE INFO

Available online 27 February 2015

Keywords:
Photocatalyst
Photoluminescence
Bismuth
Strontium
Aluminates
Phosphorescent

ABSTRACT

Bismuth co-doped long persistent phosphor (LPP) powders were obtained by a combustion synthesis technique followed by a post-annealing under carbon atmosphere. Bismuth content was varied from 1.0 to 15.0 mol%. X-ray diffraction analysis revealed that the powders show mainly a mixture of three phases: the $SrAl_2O_4$, the $SrAl_{14}O_{25}$ and the $Sr_2Al_6O_{11}$ crystalline phases. Photocatalyst composites were obtained by wet mixing of TiO_2 anatase and LPP powders followed by annealing in air at 450 °C. Photoluminescence measured spectra under 380 nm excitation show a tunable emission from green (510 nm) to greenish-blue (463 nm) in which peak wavelength localization is related to the Bi content. Photoluminescence intensity decreases as Bi content increases. Degradation of methylene blue solutions, irradiated by UV light (254 nm), was monitored by the decrease of its 650 nm absorption peak in regular periods. The best photocatalytic activity is observed when in the composite blend a 2.0 mol% of Bi content was used, and complete methylene degradation is reached after 210 min. These photocatalyst composite powders are potential candidates to clean-up wastewater applications, and might be potential candidates for photocatalytic hydrogen generation in aqueous solutions.

1. Introduction

Long persistent phosphors (LPP) are widely used in several applications such as emergency signaling, textile printing and decoration due to their afterglow and brightness properties in darkness [1,2]. LPP commonly are excited with ultraviolet (UV) and/or visible light, they absorb energy, and gradually emit light for long periods of time when the source of excitation is removed. The most popular LPP are the strontium aluminates such as $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} which emit green light and greenish-blue light, at 510 nm and 490 nm, respectively [3,4]. These materials emit at different wavelengths because the crystalline field at the different strontium aluminate phases affect distinctly the 4d-5f Eu^{2+} ion allowed transitions.

Recently, the co-doping of strontium aluminates with different ions such as Li^{3+}, Cr^{3+}, Sm^{3+} and Nd^{3+} has been used in order to enhance their luminescent properties [5–9]. Besides, there are few reports where bismuth (Bi) has been used as a co-dopant in Eu, Dy doped strontium aluminates, and in such cases it has been used as flux [10]. Lately, the $TiO_2/SrAl_4O_2:Eu^{2+}$, Dy^{3+} composite has been proposed as a photocatalyst because it can create free carriers (electron or holes). These free-carriers promote the photocatalysis at the surface of the photocatalyst composite under UV irradiation. The $TiO_2/SrAl_4O_2:Eu^{2+}$, Dy^{3+} composite has been successfully used for the photocatalytic oxidation of gaseous benzene [11]. Also, other report shows an enhanced photocatalytic activity

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http://dx.doi.org/10.1016/j.mssp.2015.02.032
1369-8001/

of Ag_3PO_4 when it is blended with the $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} phosphor [12]. There the composite is used to degrade the rhodamine B in water solutions under UV irradiation and without irradiation. To our knowledge Bi co-doping has not been explored in $TiO_2/SrAl_4O_2:Eu^{2+}$, Dy^{3+} composites to study Bismuth content effect on photocatalytic activity.

In this work, strontium aluminate samples doped with Eu, Dy and co-doped with different Bi molar concentrations (x=0.0–15.0%) are synthesized by a simple combustion method followed by a post-annealing process under reductive carbon atmosphere. In addition, selected Bi co-doped (x=0.0%, 1.0%, 2.0%, 5.0% and 15.0%) samples were blended with TiO_2 (anatase) in order to obtain and enhanced photocatalyst composite. The effect of the Bi co-doping on the luminescent properties of the strontium aluminates, as well as the photocatalytic activity of the $TiO_2/SrAl_4O_2:Eu^{2+}$, Dy^{3+},Bi composites were studied.

2. Materials and methods

2.1. Bi co-doped strontium aluminates synthesis

Bi, Eu, Dy co-doped strontium aluminates were produced by a combustion synthesis (CS) method followed by a post-annealed treatment at high temperature for 6 h under a reductive carbon atmosphere. For all synthesized samples the Eu and Dy concentration were fixed at 1.0 mol% and 2.0 mol%, respectively; whereas the Bi co-doping molar concentration (x) was varied from 0 to 15.0 mol%. Thus, samples will be referenced only by its Bi content. The synthesis and the reductive treatment were made as follows: all nitrates were obtained from Reacton, Puratronic, and Alfa Aesar. Europium nitrate [$Eu(NO_3)_3 \cdot 6H_2O$], dysprosium nitrate [$Dy(NO_3)_3 \cdot 6H_2O$], aluminum nitrate [$Al(NO_3)_3 \cdot H_2O$], strontium nitrate [$Sr(NO_3)_3 \cdot H_2O$], and bismuth nitrate [$Bi(NO_3)_3 \cdot H_2O$] were dissolved in 15 ml of deionised water for 1 h in order to obtain a transparent blend. All reagents were adjusted to 2:1 M ratio of Sr/Al and a small amount (around 0.17 mol%) of boric acid (H_3BO_3) was added as flux. A proper amount of urea [CON_2H_4] was added to the mixture of nitrates in order to have an oxidation to fuel ratio (O/F) of 1.0; such ratio allows the reaction to reach the maximum combustion heat [13]. Then, the homogeneous blend of the nitrates and the urea was placed into a preheated furnace at 600 °C, and shortly after, the combustion synthesis occurred lasting for ~30 s. As a result of this step Bi, Eu, Dy co-doped strontium aluminate as-synthesized powders were obtained. Later on, the as-synthesized powders were pressed with 2.5 t in order to obtain disk pellets of 2.0 g of mass and 13.0 mm in diameter. Subsequently, the disk pellets were annealed in alumina crucibles under carbon atmosphere at 1150 °C for 6 h. As a result of this step, tunable green (510 nm) to greenish-blue (463 nm) phosphorescent strontium aluminates, depending on Bi content (x=0.0%, 1.0%, 2.0%, 5.0%, 10.0% and 15.0 mol%) were obtained.

2.2. Composite blends of TiO_2 and bismuth co-doped strontium aluminates

The phosphorescent disk pellets were grinded for 1 h in agate mortar and then blended with commercial TiO_2 (anatase) from Sigma-Aldrich by using a standard physical process at 450 °C for 1 h [12]. The physical process was as follows: 1) 0.5 g of TiO_2 and 0.5 g of Bi co-doped strontium aluminates powder were mixed and strongly stirred in 10 ml of ethanol at room temperature for 1 h. Subsequently, the product was then heated at 450 °C for 1 h. Finally, the blended powders obtained were grinded again for 1 h and used as photocatalyst.

2.3. Photocatalysis experiments

In order to evaluate the TiO_2/bismuth strontium aluminate blended powders as photocatalysts, these were used to degrade methylene blue (MB) solutions in water. Water solutions of MB (0.5 mM) with 30 mg of the blended powders, for different bismuth contents (0.0%, 1.0%, 2.0% and 15.0 mol% of Bi), were stirred in darkness to allow the adsorption of the MB molecules on the photocatalyst surface. The volume of the solutions was set at 50 ml for each photocatalysis experiment. A home-made reactor, which is described in detail in previous Ref. [14,15], was used. After the stirring in darkness, the UV lamps (λ=254 nm) were turned ON while keeping the stirring. The quartz beaker with the solution was ~0.10 m in diameter. Subsequently, liquid samples of 0.2 ml were regularly extracted and centrifuged at 5000 rpm. The pH at the beginning of the photoreaction was pH=10 and at the end of the reaction was pH=11. Absorbance spectrum of each liquid sample was regularly measured in the range of 200–800 nm by means of a UV–vis Cary-60 Agilent spectrophotometer.

2.4. Characterization

All the powder samples were characterized by X-ray diffraction (XRD) in a Philips X'pert diffractometer with CuK_α (λ=0.15406 nm) radiation. Morphology of the sample powders was analyzed by scanning electron microscopy (SEM) with a field emission electron JSM-7800F microscope at room temperature using 200 kV of accelerating voltage. Absorbance spectra of Bi- codoped samples and the undoped one sample were measured in the range of 220–800 nm by diffuse reflectance by using an Ocean Optics QE65000 spectrophotometer coupled with two optic fibers of 0.6 μm in diameter and a tungsten lamp. We take spectralon standard as a baseline. Photoluminescence (PL) spectra and long persistence decay curves were collected with a Hitachi FL-4500 spectrofluorometer. The photomultiplier tube was operated at 400 V for all measurements. The phosphorescent decay time curves were taken after 5 min of irradiation by means a 20 W Philips DC-65 compact fluorescent lamp. All measurements were obtained at room temperature.

3. Results and discussions

3.1. Structure and morphology of the Bi co-doped strontium aluminates

Fig. 1b compares the XRD patterns of the Bi co-doped strontium aluminates for the different (x) concentrations. For the low (x) concentrations of Bi [x=0.0%, 1.0% and