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ZnO thin films deposited by RF magnetron sputtering: Effects of the annealing and atmosphere conditions on the photocatalytic hydrogen production

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ABSTRACT

This work studied the effect of different annealing conditions of ZnO thin films grown by RF magnetron sputtering and their application as photocatalysts for hydrogen production without any sacrificial agent or co-catalyst. ZnO films were annealed in air, nitrogen, and argon atmospheres to study the effect of their physical properties in the photocatalytic activity. ZnO films showed high crystallinity and optical transparence of around 75–90% after annealing. Changes in composition and optical properties of the ZnO films were studied by x-ray photoelectron spectroscopy (XPS) and ellipsometry spectroscopy (SE), and results were correlated with the photocatalytic performance in hydrogen production. The highest photocatalytic hydrogen production was obtained with the ZnO thin film annealed in an air atmosphere with a result of 76 μmol.

Introduction

Currently, the generation of clean and renewable energy from sustainable energy sources such as sunlight is a fundamental topic to avoid the emission of greenhouse gases to the atmosphere. The hydrogen generation from water splitting by photocatalysis processes has become very important because it is an alternative energy vector to replace fossil fuels. In order to produce this energy vector, several semiconductors materials have been proposed. In particular, TiO_2 powder is the most used material as a photocatalyst, mainly in dye degradation. However, there is also literature where TiO_2 is used for hydrogen production in powder form or as photoanode in photo-electrochemical water splitting [1–4]. Additionally, the use of tantalates, titanates, and niobates as highly active photocatalysts have been reported; even though their band gaps are too large to absorb visible light, their crystal structure influences positively on the photocatalytic activity in a water-splitting activity reaction [5–8]. Alternative

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photocatalyst based in heterostructures containing TiO_2, ZnO, CuO, and CdS have also been used to enhance their photocatalytic efficiency in hydrogen evolution reaction [9–11]. In general, the H_2 generation via photocatalysis involves the use of a powder semiconductor to carry out the oxidation-reduction process of the water molecule. However, one of the main disadvantages of using semiconductor particles in suspension is their separation and recovery of the liquid phase. In addition, suspensions are associated with a low quantum yield as a consequence of a high recombination speed of the hole-electron pair [12]. However, the use of thin film as a photocatalyst has numerous advantages such as rapid electron transport and homogeneous exposure of the photocatalyst, and it is possible to deposit the photocatalyst over different substrates, efficient absorption of solar energy, and high surface area. ZnO thin films modified by nonmetal and metal elements have been widely studied primarily for dyes degradation [13–18] and for H_2 generation. For instance, ZnO thin films deposited by chemical vapor deposition doped with Ag can produce until 0.5 μmol cm^{-2} h^{-1}, while the use of Na_2S and Na_2SO_3 as sacrificial agents in ZnO films doped with CeO_2 helps to improve the H_2 production of the films. The photoelectrochemical H_2 production has been reported as well for ZnO thin films impregnated with Cu–In–Zn–S with a yield of 0.7 μmol cm^{-2} h^{-1} [19–21]. Some authors have reported the use of different atmospheres to perform heat treatment to ZnO thin films after deposition, with the purpose of modifying his optical or electrical properties, modifying the surface, and increasing the conductivity of ZnO thin films [22–24]. ZnO crystal structure gives rise to polar symmetry along the (002) plane in the hexagonal axis which is a key factor in crystal growth and defect generation, which include oxygen vacancies and zinc interstitial [25]. So, one way to improve ZnO properties in a thin film is to employ different thermal treatments under specific atmospheres, for example, when the thermal treatment is carried out in oxygen poor atmospheres, such as Ar, Nitrogen, etc., which helps to avoid the defects as oxygen vacancies and Zn interstitial [26]. The novelty of this paper is to determinate how concentration of defects, as oxygen vacancies and interstitial zinc, affect the photocatalytic efficiency in ZnO, especially when ZnO is deposited as a thin film.

In this work, we propose the use of the ZnO thin films obtained by RF magnetron sputtering as a photocatalyst in H_2 generation from water splitting. Where, the absence of oxygen inside the sputtering chamber during deposition, contributes to the presence of defects, as oxygen deficiencies and interstitial zinc. So, the ZnO films were annealed in different atmospheres (air, nitrogen, argon) in order to assessing the structural, optical, and surface properties with respect to its photocatalytic activity in the hydrogen production without using sacrifice agents or co-catalysts.

Experimental

Growth of ZnO thin films by RF-Sputtering

ZnO thin films were deposited by RF magnetron sputtering over glass substrates using a ZnO target (99.999% Pure, 2.00″ diameter × 0.250″ thick; Kurt J. Lesker). Glass substrates were ultrasonically cleaned in acetone, isopropyl alcohol, and deionized water and then dried with air. The vacuum pressure of the chamber was lowered to 8.6×10^{-6} Torr using a turbomolecular pump before introducing argon gas. Working pressure was fixed at 1.6×10^{-2} mTorr with an argon flow rate of 15 sccm. Substrates were heated at 300 °C and deposited at a constant power of 80 W for 2 h; distance between the target and substrate was 8.5 cm. Before deposition, the target was pre-sputtered for 10 min. After the deposit process, ZnO thin films were annealed in argon, nitrogen, and air atmospheres at 400 °C for 1 h [27,28], in order to evaluate the photocatalytic activity for hydrogen production, usually the choice of this temperature depends on the type of substrate and their melting fusion [29,30].

Characterization

Structural properties were determinate using an X-ray diffractometer PANalytical with a Cu Kα radiation of 1.54 Å in grazing angle. Transmittance measurements were performed using a UV–Vis NIR spectrophotometer (Cary 5000). Spectroscopic ellipsometry measurements were collected using a Horiba, Jobin Yvon UVISEL HR 320 ellipsometer at an incident angle of 70°. The morphology of the samples was analyzed by scanning electron microscopy (SEM), using a FEI Nova NanoSEM 200 microscope with an accelerating voltage of 30 kV. The chemical states and elemental composition were determined by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific, Escalab 250Xi, equipped with an Al Kα monochromatic x-ray source ($h\upsilon$ = 1486.7 eV) with a line width of 0.20 eV in an analysis chamber at a bass pressure of $<4.3 \times 10^{-10}$ mbar.

Photocatalytic activity

Photocatalytic activity of ZnO thin films (15 cm^2) were evaluated using a cylindrical Pyrex batch reactor of 200 mL at room temperature. Thin films were fixed inside the reactor and then filled with nitrogen to remove the oxygen in the medium. Once the oxygen was removed from the reactor, thin films were irradiated using an UV Pen Ray Lamp of 254 nm of irradiance of 4400 μW cm^{-2}. Photocatalytic hydrogen production was measured every 30 min using a gas chromatograph Thermo Scientific trace GC Ultra with a thermal conductivity detector (TCD).

Results

Structural properties

XRD patterns of ZnO thin films deposited, annealed at 400 °C in air, nitrogen, and argon atmospheres, are shown in Fig. 1. All thin films are polycrystalline and peaks correspond to ZnO Wurtzite phase according to the JCPDS card 01-089-1397. ZnO thin films deposited have poor crystallinity compared to those heat treated. When thin films were annealed in different atmospheres the crystallinity improved, with the thin film annealed in argon atmosphere being the one that exhibited

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