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Chemical state analysis, optical band gap, and photocatalytic decolorization of cobalt-doped ZnO nanospherical thin films by DC/RF sputtering technique

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ABSTRACT

We have used direct current radio frequency (DC/RF) sputtering to deposit cobalt- incorporated zinc oxide (Co:ZnO) thin films on glass substrate. The x-ray diffraction (XRD) was applied for structural observation while topography was examined by atomic force microscopy (AFM). The optical studies were carried out by UV–vis absorption spectroscopy. The elemental composition was performed via x-ray photoelectron spectroscopy (XPS). The chemical state studies were also investigated. The shifting of XRD pattern towards higher diffraction angle confirmed successful incorporation. The optical observation showed "d–d" electron transition during the thin film deposition. The photocatalytic response was carried through the degradation of methylene blue (MB). The improved photocatalytic behavior of Co:ZnO thin films were attributed to the high binding energy component (HBEC) of oxygen vacancies. We have also proposed the tentative mechanism of cobalt incorporation into ZnO through XPS finding. We also checked the stability of deposited thin films. Co:ZnO thin films are new attractive candidates for degradation of waste dyes.

1. Introduction

The Photocatalysis is among the best contender for the degradation of the environmental pollutant under visible and natural solar energy [1]. So, it is the need of era to develop the efficient materials with enhanced photocatalytic activities.

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Table 1
Experimental conditions for pure and Co:ZnO nano-spherical thin films.

No	Deposition parameters	Values
1	Base pressure	9×10^{-6} Torr
2	Operating pressure	5×10^{-3} Torr
3	Deposition time	600 s
4	Substrate temperature	25 °C
5	RF power for ZnO	200 W
6	DC power for Co target	0, 30, 40 and 50 W
7	Film thickness	100, 107, 112 and 120 nm
8	Target/substrate distance	14 cm
9	Argon partial pressure	20 SCCM

The electron and hole pair is created when the metal oxide photocatalysis absorbs the light from an external source. The generated pair of electron and hole creates the energy at the surface which results in photo-degradation process [2].

ZnO has attractive natural properties for living organisms and environmental friendly [3]. During the last few years, it has received great attention to solve the environmental pollutants issues because of its low cost and nontoxic nature [4,5]. However; the negative aspect of the photocatalytic efficiency is the fast reunion of electrons and holes [6,7]. It is possible to enhance the photocatalytic response of the ZnO by the doping of transition metal which helps to restrain the electron and holes recombination [8]. The transition metals like nickel, iron and manganese are in practice to improve the photo-degradation process of ZnO [9–11].

Hammad et al. [12] have successfully shown the change in structural characteristics of ZnO by Co doping. Lu et al. [6] have proved the enhanced photo-degradation process of ZnO by Co doping because of reticent the recombination of electron holes pairs. Xiao et al. [13] showed the photocatalytic activity ZnO by the creation of oxygen defects through Co doping which results in the enhancement of photocatalytic efficiency.

The present research deals with the successful incorporation of Co into ZnO by DC/RF. The incorporated thin films have improved photocatalytic behavior under the visible light as linked to the pure one. We have also described the enhancement of photocatalytic response through x-ray photoelectron chemical state investigation. Furthermore, complete structural, optical and surface analyses have been carried out. We have also studied the reuse-ability of the as-deposited Co:ZnO thin films.

2. Experimental details

2.1. Sample preparation

Pure ZnO and Co incorporated thin films have been grown on a glass substrate by using DC/RF sputtering technique. The substrate was cleaned several times by acetone and ethanol mixture (1:1) then dried using nitrogen gas before inserting inside the RF chamber. High purity targets (99.99%) of ZnO (3×0.6 in.) and Co metal (3×0.6 in.) were used to deposit the required materials. Table 1 represents the experimental conditions for the samples preparation.

2.2. Characterizations

X-ray diffraction technique (Ultima-IV; Rigaku, Japan) was applied to perform the structural analyses. The XRD analyses were performed via PDXL software. The optical response of the as-deposited thin films was studied via UV–vis spectrophotometer (PerkinElmer, Lambda 750). To acquire the surface morphology, we have employed the atomic force microscope (omicron VTA-AFM). The AFM analysis was done with attached software to obtain grain size and surface roughness. The XPS (PHI 5000 Versa Probe II, USA) linked with multipack software was used for the compositional analysis. While, the film thickness of the deposited thin films were measured using DektakXT(Bruker Germany)surface profiler.

2.3. Photocatalytic activity

The methylene blue (MB) organic waste dye was used to study the photocatalytic response. The observations were made in a glass reactor consisting 100 ml of 1×10^{-5} M MB dye. The reactor contained tungsten lamp (500 W) as visible light source and was fixed vertically over the distance of 30 cm. The irradiation time was three hours for all samples. To study the degradation process of MB, we have taken 3 ml of the MB dye solution after every thirty minutes and carried the visible measurements for the studied dye. The following equation was used to calculate the degradation percentage [14]:

$$Degradation\ (\%) = \frac{C_o - C_t}{C_o} \times 100, \quad (1)$$

Where, $C_\circ$ and C_t represent the initial concentration and the concentration of MB with a given time respectively.