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Thermal diffusion of Co into sputtered ZnO:Co thin film for enhancing visible-light-induced photo-catalytic activity

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ABSTRACT

ZnO has received a lot of attention in for the degradation and complete mineralization of environmental pollutants. In this study, efficient ZnO-based visible-light photocatalysts are synthesized via a low-cost method by increasing the Co concentration at the outermost surface of ZnO:Co thin film under an annealing process. The simply adjusted Co concentration gradient (≈1.5% increase) into the surface of ZnO:Co is driven by thermal diffusion. Co ions substitute Zn sites in the ZnO lattice. The band gap narrowed due to sp–d exchange interactions between the conduction band electrons and the d electrons of Co. The annealing process enhances the grain size and the degree of crystallinity of the diffused Co/ZnO:Co, which contributes to the absorption edge red-shift. Photocatalytic activities such as the photodegradation of methylene blue and the inactivation of bacteria are obviously enhanced. The proposed low-cost method significantly increases the efficiency of ZnO for the generation of the photocatalytic effect under visible-light exposure.

1. Introduction

Extensive effort has been directed towards the development of visible-light-driven photocatalysts [1] that bring about the photocatalytic effect under mild solar or indoor light, such as the visible-light-driven reactions of water and oxygen into hydroxyl radicals ($^{\bullet}OH$) and superoxide anions ($^{\bullet}O_2^-$) to harness solar energy [2–6]. Photocatalysts have also been applied to photo-degradation and sterilization [7–9]. Transition metal ions such as Cu, Co, Mn, and Ni can be doped into a zinc oxide (ZnO) structure for visible-light-driven photo-production [10]. High visible-light activity has been observed for Co-doped ZnO [11]; with an increase in Co content in ZnO, the absorption of visible light and the concentration of defects tend to increase [12,13]. For example, Co-doped ZnO achieves the highest rate of visible-light degradation of methylene blue (MB) because it has the highest number of surface oxygen defects [14]. Co-doped ZnO also exhibits better visible-light activity than those of Mn- and Ni-doped ZnO photocatalysts due to its better crystallinity and narrower band gap [10].

Titanium dioxide (TiO_2) in the anatase phase and ZnO both show high activity for organic matter degradation. However, they can only work under ultraviolet (UV) light (wavelength <387 nm) due to their wide band gap of 3.2 eV. The solar spectrum usually consists of 5–7% UV light, 46% visible light, and 47% infrared radiation. As a result, the development of photocatalysts that can yield high reactivity under visible light ($\lambda > 380$ nm) should allow outdoor sunlight and even interior lighting to be utilized for organic matter degradation [6,15]. ZnO, a typical n-type wide-band-gap semiconductor, plays an important role in many applications such as optoelectronics, energy conversion, photocatalysis, and gas sensing [16,17]. ZnO exhibits a more efficient photocatalytic effect than does TiO_2, the most intensively studied photocatalyst, in the photo-degradation of some organic compounds [18]. ZnO-based visible-light photocatalysts are inexpensive and easily prepared compared to TiO_2-based photocatalysts; however, the application of ZnO as a photocatalyst is limited due to its wide band gap (≈3.3 eV) and large excitation energy (≈60 meV at room temperature). Therefore, the development of visible-light-activated ZnO that retains its efficiency is desirable.

The structure of ZnO has been modified via doping with various metal or non-metal ions to enhance optical absorption and photocatalytic performance [19]. When Co ions substitute Zn ions in ZnO film, the photocurrent under visible-light exposure is greatly increased because two broad Co ions charge transfer bands occur within the visible energy range [20]. ZnO doped with a moderate concentration of Co can produce visible-light-driven oxygen evolution from water, which can improve hydrogen production under solar irradiation. The formation of photo-induced carriers is presumably responsible for the enhanced catalytic activity. In a study of Co doped into ZnO prepared by electrochemical synthesis, with $Zn_{1-x}Co_xO$, $0 \leqq x \leqq 0.068$, the optical band gap (E_g) value for $Zn_{0.979}Co_{0.021}O$ was 2.90 eV, which corresponds to the wurtzite

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phase of ZnO [21]. For the photocurrent properties of $Zn_{1-x}Co_xO$ samples, pure ZnO has been found to have the greatest photocurrent, which drops suddenly with an increase in Co content, even at a very low doping concentration under ultraviolet and visible-light illumination. A moderate concentration of Co should thus be doped into ZnO for photocatalytic applications [12].

Radio-frequency (RF) magnetron sputtering is the most commonly used method for obtaining well-adhered transparent thin films [22]. In the present study, for the deposition of ZnO:Co thin film, a sub-stoichiometric target with 2 wt% CoO in ZnO is applied for a stable deposition process [23]. Co is then thermally diffused into the sputtered ZnO:Co thin film, which drives the doped ions into substitutional sites and leads to atomic-scale random mixing with host atoms without the formation of a second phase, such as nanoparticles, clusters, and precipitates [24]. The visible-light-driven photocatalytic reactivity of the obtained Co-doped ZnO thin film is examined using MB degradation and bacteria inactivation tests. Co doping markedly restrains the photo-degradation of MB solution under visible-light exposure, since the substitutions in the ZnO lattice most probably act as trapping or recombination centers for electrons and holes [12]. Therefore, the content of thermally diffused Co into the sputtered ZnO:Co thin film that affects the visible-light-driven photo-catalytic reactivity is particularly emphasized.

2. Experiment

2.1. Fabrication of thermally diffused Co into sputtered ZnO:Co thin film

Two samples were sputtered using an RF magnetron sputter system (Helix, HLLS-87, Taiwan) onto Si (1 0 0) and used as references. For the first sample, a ZnO ceramic target (purity: 99.99%, Summit-Tech, Taiwan) was used to sputter ZnO thin film (denoted as ZnO); for the second sample, a thin film (denoted as ZnO:Co) was prepared using a sintered ceramic target with 98 wt% ZnO (purity: 99.99%, Summit-Tech, Taiwan) and 2 wt% CoO (purity: 99.99%, Summit-Tech, Taiwan). Fig. 1(a) shows the schematic design of the Co ingot (purity: 99.99%, Conyuan, Taiwan), which was slightly pressed upon ZnO:Co and then annealed, as illustrated in Fig. 1(b). The annealing process was performed at 900 °C for 2 h in air with a heating rate of 150 °C/h. Thermally diffused Co on ZnO:Co deposited on Si (1 0 0) (denoted as diffused Co/ZnO:Co) was thus prepared. For reference, an equally annealed ZnO:Co sample deposited on Si (1 0 0) (denoted as annealed ZnO:Co) was also prepared.

Quartz glass was used as the substrate for measuring the transmittance spectra and for the anti-bacterial test.

For the thin-film deposition, the ceramic target, with a diameter of ≈52 mm, to substrate distance was fixed at 7.5 cm. Before deposition, the Si (1 0 0) substrate was ultrasonically cleaned in acetone, rinsed in deionized water, and subsequently dried in a flow of nitrogen gas. An ultimate background pressure lower than 5.0×10^{-5} Pa was applied. During the deposition, the working gases (Ar and O_2) were independently fed into the reaction chamber through two installed mass flow controllers. The working pressure was maintained at ≈4.0 Pa. The Ar flow rate, RF magnetron working power, and deposition time were fixed at ≈28 sccm, ≈80 W, and 30 min, respectively. The thicknesses of all samples were controlled at ≈300 nm, as measured by an α-step surface profilometer (Alpha step, LA-Tencor, AS-IQ, USA).

2.2. Surface characterization

To determine the crystalline structures and crystal orientations of the as-prepared thin films, grazing incidence X-ray diffraction (GIXRD, Rigaku, RU-H3R, Japan) was employed. The GIXRD patterns were obtained by scanning in the 2θ range of 20–60°, with an incidence angle of 1° for thin-film samples deposited on the Si (1 0 0) substrate. The characteristic GIXRD patterns were utilized to calculate the average grain size using the Scherrer formula [25], as briefly described below.

$$D(\text{crystal}\quad\text{size}) = \frac{0.94\lambda}{\beta\cos\theta} \tag{1}$$

where $\lambda = 1.54$ Å and β is the full width at half maximum (FWHM) of the GIXRD peak. To estimate the values of the annealing temperature or the diffusion of the Co element with respect to the residual stress of as-deposited ZnO:Co, the stress (σ) can be calculated using [26]:

$$\sigma = -453.6 \times 10^9 \left(\frac{X_{\text{Lc}'} - X_{\text{Lc}}}{X_{\text{Lc}}}\right) \tag{2}$$

where X_{Lc} (0.5205 nm) [27] is obtained from the strain-free ZnO structure and $X_{\text{Lc}'}$ is the strain lattice constant, calculated as $\lambda/\sin\theta$, where θ is the diffraction angle obtained from GIXRD. The negative sign indicates that the films are in a state of tensile stress.

The absorption spectra of the films were measured using a UV/visible spectrophotometer (PerkinElmer, Lambda 35, USA) in reflection mode. For a direct band gap, the relation between $h\nu$ and α can be obtained by applying the Tauc model and the Davis and Mott model in the high-absorbance region [28]:

$$\alpha h\nu = D(h\nu - E_g)^n \tag{3}$$

where $h\nu$ is the photon energy, α is the absorption coefficient, E_g is the optical band gap, and D is a constant. For a direct transition, $n = 1/2$ or $2/3$; the former value was found to be more suitable for ZnO thin films since it gives the best linear curve in the band-edge region.

The quantified elemental information with depth profiling was obtained using X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI 5000 VersaProbe, Japan). XPS depth profiling was performed with a monochromatic Al-Kα source (25 W, $h\nu = 1486.6$ eV) and an energy resolution of ≈0.1 eV. All XPS depth profiling spectra were obtained at a take-off angle of 45° for each element.

The thin-film morphology was examined using scanning electron microscopy (SEM, JEOL, JSM-7001, Japan). The average particle size was obtained by an accessible computing program in SEM.

2.3. Photocatalytic assessment and anti-bacterial test

The photocatalytic effect was assessed by measuring the consumption of MB in water (≈0.75 mol/l with a color absorbance peak at 665 nm) [29]. The 24-point standard curve of absorbance at 665 nm (y) versus the concentration of MB in water (x in mol/l) was well fitted (i.e., $y \fallingdotseq 68.68x$). All the as-prepared samples were covered with MB in water in a closed system and irradiated by a 27-W fluorescent lamp for exposure durations of 1, 2, 3, 4, 8, 12, 18, and 24 h, respectively. The reaction rate can be simply expressed by a rate law; it is commonly expressed as: $r = -(d[C]/dt) = k\,[C]^n$, where r is the reaction rate, k is the reaction rate constant, and n is the order of the reaction. The photocatalytic oxidation of MB in water is a pseudo-first-order reaction [30]:

$$-\frac{d[C]}{dt} = k[C] \tag{4}$$

where C is the concentration of MB, C_0 is the initial concentration of MB, and k is the apparent rate constant of MB under photocatalytic oxidation in water. In terms of the conversion of MB (x, $x = (C_0 - C)/C_0$), Eq. (4) becomes:

$$r = \frac{dx}{dt} = -\frac{d(C/C_0)}{dt} = k(1-x) = k\left(\frac{C}{C_0}\right) \tag{5}$$