Research Article

Mg Doping Effect on the Microstructural and Optical Properties of ZnO Nanocrystalline Films

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Transparent $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x = 0.01, 0.03$, and 0.05) nanocrystalline films were prepared by sol-gel method followed by thermal annealing treatment of 700°C . Mg doping effect on the microstructural and optical properties of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films is investigated. From SEM images of all films, mean sizes of uniform spherical grains increase progressively. Pure wurtzite structure is obtained from the results of XRD. Grain sizes increase from 34.7 nm for $x = 0.01$ and 37.9 nm for $x = 0.03$ to 42.1 nm for $x = 0.05$ deduced from the XRD patterns. The photoluminescence spectra of the films show a strong ultraviolet emission and a weak visible light emission peak. The enhancement of ultraviolet emission and reduction of visible emission are observed due to the increase of Mg doping concentration and the corresponding decrease of oxygen vacancy defects. Besides, the characteristics of the dark/photo currents with $n\text{-Zn}_{1-x}\text{Mg}_x\text{O}/n\text{-Si}$ heterojunction are studied for photodetector application.

1. Introduction

The ZnO-based semiconductors have recently drawn much interest for the possible application in optoelectronics devices [1–3] due to the large direct band gap. These properties are important for application to commercial electronic products, such as photoconductors for electrophotography [4], varistors for electrical circuits [5], sensors for gas detection [6], and active layer for thin film transistors [7]. Highly conductive and optical transparent ZnO films in the visible range suitable for transparent electrodes in solar cell and liquid crystal display applications have been also reported [8, 9].

The ZnO-based thin films have been fabricated through various methods [10–12]. However, sol-gel spin coating method offers more merits due to ease-control of chemical composition and simpler method for large area coating at a low cost, compared with other high vacuum fabrication processes. For the application of ZnO-based semiconductors on electronic devices, one of the most promising methods is doping with elements from groups I and III and transitional

metals [13–15]. While the shift in PL and XRD versus Mg composition has been studied previously [16, 17], it becomes interesting to further explore the doping effect on the microstructural and optical properties of the ZnO-based films. In the present work, we survey the Mg-doping effect on the microstructural and optical properties of ZnO nanocrystalline films. In addition, the I - V characteristics of photodetecting devices with $n\text{-Zn}_{1-x}\text{Mg}_x\text{O}/n\text{-Si}$ heterojunction are studied.

2. Materials and Methods

$\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($x = 0.01, 0.03$, and 0.05) films were fabricated by sol-gel method. The source solutions were prepared by $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ (zinc acetate dehydrate), $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (magnesium acetate), $\text{C}_3\text{H}_8\text{O}_2$ (2-methoxyethanol), and $\text{C}_2\text{H}_7\text{NO}$ (ethanolamine). Zinc acetate dehydrate and magnesium acetate were firstly dissolved in 2-methoxyethanol in stoichiometric proportions. The concentration of metal ions was kept at 0.5 M . Then, ethanolamine

FIGURE 1: X-ray diffraction patterns of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with $x = 0.01$, $x = 0.03$, and $x = 0.05$.

was added into the solutions to form stable precursor solutions. After stirring at 150°C for 1 h on a hotplate, transparent solutions were obtained. The $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films were prepared by spin coating technique. Then, the samples were annealed by rapid thermal annealing treatment in air at the temperature of 700°C for 2 min with a heating rate of $600^\circ\text{C}/\text{min}$.

The crystal structure and grain orientation of ZnO films were determined by the X-ray diffraction (XRD) patterns using a Rigaku D/max 2200 X-ray diffractometer with Cu-K α radiation. The XRD data were recorded at room temperature under the 2θ range from 20° to 60° with a step width of 0.01° and a scan speed of $0.5^\circ/\text{min}$. Morphological characterization was observed using a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) at 3.0 kV. The transmittance spectra were obtained by JASCO V-670 spectrophotometer. Room temperature photoluminescence (PL) spectroscopy was applied for optical emission measurement from 330 to 645 nm and defect analysis using the He-Cd laser with wavelength 325 nm. Finally, the DC current-voltage (I - V) characteristics of $(\text{Zn}_{1-x}\text{Mg}_x\text{O} \text{ film})/(\textit{n}$ -Si substrate) structures were separately measured by an HP 4145 semiconductor parameter analyzer with the applied voltage from -5 V to 5 V under darkness and photo illumination using a solar simulator with power density $1000 \text{ W}/\text{cm}^2$ as the irradiation source.

3. Results and Discussion

Figure 1 illustrates the XRD patterns of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanocrystalline films. Based on the XRD patterns, all Mg-doped samples are found to have the same single polycrystalline phase with the wurtzite hexagonal structure of P63/mc. All samples exhibit the (002) preferred orientation, indicating c -axis orientation. The progressive narrowing of the XRD peaks with the increase of Mg concentration is related to the increase of the grain size of the nanocrystalline films. The

average grain size of the samples, obtained by the classical Scherrer formula, increases gradually from 34.7 nm for $x = 0.01$ and 37.9 nm for $x = 0.03$ to 42.1 nm for $x = 0.05$.

Figure 2 shows the surface morphology of FE-SEM images which reveals porously granular structure for all $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films. It is clear that the grain size increases progressively with the increase of the Mg concentration, which is consistent with the results indicated in Figure 1. Furthermore, the film thickness decreases from 132 nm for $x = 0.01$ and 124 nm for $x = 0.03$ to 105 nm for $x = 0.05$. It is for the reason that the film is gradually densified due to the increase of Mg doping concentration.

Figure 3 shows the PL spectra for all $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films. Two distinct emissions including an obvious ultraviolet (UV) emission and a weak green-yellow visible emission are observed. The UV emission originates from the exciton recombination corresponding through an exciton-exciton collision process [18]. The green-yellow emission is induced from the recombination of a photogenerated hole with an electron that belongs to a singly ionized defect, such as oxygen vacancy [19]. Gradual blue shift of the UV luminescence from 369.8 nm for $x = 0.01$ and 366.2 nm for $x = 0.03$ to 362.6 nm for $x = 0.05$ occurs with the increase of Mg doping concentration. Using the luminescence data, the band gaps, 3.35 eV for $x = 0.01$, 3.38 eV nm for $x = 0.03$, and 3.41 eV nm for $x = 0.05$, are calculated. As the Mg concentration increased, the results indicate a linear increase in the band gap due to the higher band gap of MgO (7.8 eV) than that of ZnO (3.3 eV). The intensity of the ultraviolet emission is strongly dependent on the crystalline quality of ZnO films [20]. Besides, the decrease of visible emission with increasing Mg concentration indicates the decrease of intrinsic defects [21]. The enhancement of ultraviolet emission intensity (I_{UV}) and reduction of green-yellow visible emission (I_{VIS}) are observed due to the increase of Mg doping concentration and the corresponding decrease of oxygen vacancy defects. The ratio of the emission intensities of visible to UV emission (denoted as $I_{\text{VIS}}/I_{\text{UV}}$) shows a decrease from 0.0876 and 0.0595 to 0.0488 of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films for $x = 0.01$, $x = 0.03$, and $x = 0.05$, respectively. The decrease of $I_{\text{VIS}}/I_{\text{UV}}$ ratio with increasing Mg concentration of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films shows a decrease of defects and an enhancement of crystallinity of the ZnO films, which is consistent with the result observed from XRD patterns.

Figure 4 shows the I - V characteristics of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films deposited on n -type Si substrates for photodetector application, which was measured separately under dark (dark current, I_{dark}) and photo illumination (photo current, I_{photo}). The previous report elsewhere [22] stated that zinc oxides usually exhibit n -type semiconductor nature due to in situ defects. The PL results reveal the decrease of defects with Mg doping increase. We may continuously deduce the results of the decrease of carrier concentration, the increase of resistivity, and the decrease of both I_{dark} and I_{photo} currents. The measured (I_{dark} , I_{photo}) at 5 V are ($4.12 \mu\text{A}$, $5.52 \mu\text{A}$), ($4.02 \mu\text{A}$, $5.12 \mu\text{A}$), and ($3.80 \mu\text{A}$, $4.84 \mu\text{A}$) for $x = 0.01$, $x = 0.03$, and $x = 0.05$, respectively. The variation of UV photo-induced current defined as $(I_{\text{photo}} - I_{\text{dark}})/I_{\text{dark}}$ decreases from

FIGURE 2: SEM images for $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films of (a) $x = 0.01$, (b) $x = 0.03$, and (c) $x = 0.05$. Left and right columns show the cross-section and top view, respectively. The scale bars denote 100 nm.

34% and 28% to 27%. The results reveal the possibility of ZnO-based semiconductors for photodetector application.

4. Conclusions

The Mg-doped ZnO nanocrystalline films were separately deposited by sol-gel spin coating method for comparison of microstructural and optical properties. XRD patterns

show that all compositions are found to exhibit the same wurtzite hexagonal structure with group space $P6_3/mc$. FE-SEM images show the grain size increases and the thickness decreases of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with the increase of Mg doping concentration. The results of photoluminescence spectra show a linear increase of band gap and a decrease of defects. I - V curves with the dark and photo illumination of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ film/ n -Si structures reveal the possibility of ZnO-based semiconductors for photodetector application.

FIGURE 3: Photoluminescence spectra of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with $x = 0.01$, $x = 0.03$, and $x = 0.05$.

FIGURE 4: Dark/photo I - V curves of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with (a) $x = 0.01$, (b) $x = 0.03$, and (c) $x = 0.05$.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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