Study of ZnO:Zn Phosphors Prepared by Sol-gel and Ion-implantation Techniques

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Abstract

ZnO thin films were firstly deposited on glass substrates by the sol-gel process, and then Zn ions with energy of 56 keV were implanted into the ZnO films to a dose of $1 \times 10^{17}$ cm$^{-2}$. The effects of ion implantation on the structural and optical properties of the ZnO films were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), photoluminescence (PL) and optical transmittance measurements. The results showed that the as-deposited films had hexagonal wurtzite structure with high c-axis preferred orientation and (002) peak disappeared after ion implantation. Both the near band edge (NBE) excitonic UV emission at 390 nm and the defect related deep level emission (DLE) centered at 470 nm in the visible region were greatly decreased after Zn ion implantation. The optical band gap redshifted from 3.10 to 3.04 eV after ion implantation.

Keywords: ZnO; Ion implantation; Sol-gel; PL; XRD

1. Introduction

Zinc oxide (ZnO), a wide band gap semiconductor, has received increasing attention in the research community due to its potential applications in optoelectronic devices in the blue and ultraviolet region. In recent years, many techniques have been employed to synthesize high-quality ZnO films, such as atomic layer deposition, radio frequency (RF) magnetron sputtering, chemical vapor deposition, pulsed laser deposition, plasma-assisted molecular beam epitaxy (MBE) [1-5]. For special applications, many dopants have been chosen to dope into ZnO films ion implantation, especially in the semiconductor industry, is a widespread tool for doping semiconductors. Advantages are the lateral selectivity of sample area and

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doping depth as well as an accurate dose control. In principal, every element from the periodic system can be implanted, what makes it a multipurpose and flexible tool for doping semiconductors. However, undesirable side effects are the implantation-induced damage and its effect on the structural and optical electrical properties of the semiconductor. As far as we know, studies on the effects of Zn-ion-implantation on the properties of ZnO films are very few. Zhao et al. have investigated the effects of excess Zn addition through ion implantation on the PL properties of ZnO bulk materials [6]. So, more studies on the effects of Zn-ion-implantation on the properties of ZnO films are necessary for further understanding of the recombination mechanisms responsible for the luminescence properties and potential optoelectronic applications of ZnO semiconductor films.

In this work, we prepared ZnO thin films by the sol-gel technique. The effects of Zn-ion-implantation on the structural and optical properties of ZnO films were investigated.

2. Experimental

First, ZnO thin films were prepared by the sol–gel method. Zinc acetate dihydrate (Zn(CH3COO)2·2H2O) was used as a starting material. 2-methoxyethanol and monoethanolamine (MEA) were used as a solvent and stabilizer, respectively. Zinc acetate dihydrate was first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate (Zn(CH3COO)2) was maintained at 1.0 and the concentration of zinc acetate was 0.35 M. The solution was stirred at 60 °C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was usually made 24 hours after the solution was prepared.

The solution was dropped onto glass substrates, which were rotated at 4000 rpm for 30 s. After depositing by spin coating, the films were dried at 300 °C for 10 min on a hot plate to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated twelve times. The films were then inserted into a furnace and annealed in air at 550 °C for 1 h. After annealing, the as-deposited films were subjected to ion implantation. Zn ions were implanted into the ZnO films at energy of 56 keV to a dose of 1\times10^{17} \text{cm}^{-2}.

After implantation, the structural and optical properties of the as-deposited and Zn-implanted films were measured. A BEDE-D1 X-ray diffractometer (XRD) was used to investigate the crystal orientation of ZnO films. The radiation source of is CuKα. The surface morphology of the films was observed through a JEOL JSM-5900LV scanning electron microscope (SEM). Measurements of optical transmittance were carried out using a SHIMADZU UV2550 spectrophotometer. The PL spectra were recorded using a SHIMADZU RF5301PC spectrophotometer at room temperature. The light source in the spectrophotometer is a xenon lamp operated at 345 nm wavelength with an output power of 150 W.

3. Results and discussions

Optical microscope observation shows that ZnO films have formed an interconnected structure. Wang et al. also observed similar interconnected microstructure in the ZnO:Al thin films prepared by direct current reactive magnetron sputtering[7]. SEM observation with electron energy of 20 keV has been performed to improve the resolution. Fig. 1 shows SEM images of ZnO films before and after 56 keV Zn ion implantation to a dose of of 1\times10^{17} \text{cm}^{-2}. It can be seen that the interconnected microstructure has been changed after ion implantation. The SEM images clearly indicate an increase in the thickness of the interconnected thread by a factor of ~2 following the ion implantation. Matsunami et al. observed ion-induced grain growth after He ion implantation into ZnO thin films prepared by off-axis RF magnetron sputter deposition method [8]. So, the increase in the thickness of the interconnected thread after ion
implantation may be due to ion-induced grain growth. However, the changes of grain size before and after Zn ion implantation cannot be observed in our SEM images because the grain size is too small.

Fig. 1. SEM images of ZnO films (a) as-deposited and (b) Zn-implanted ZnO.

Fig. 2. XRD patterns of ZnO thin films before and after Zn ion implantation

Fig. 3. RT PL spectra of ZnO thin films before and after Zn ion implantation films

Fig. 4. Optical transmittance spectra of ZnO thin before and after Zn ion implantation

Fig. 2 shows the XRD patterns of the Zn-implanted (dose of $1\times10^{17}$ cm$^{-2}$) and as-deposited ZnO thin films. The as-deposited ZnO films have hexagonal wurtzite structure with c-axis preferred orientation. It can be seen from Fig. 2 that (002) diffraction peak disappears after ion implantation. Matsunami et al. found that the HWHM of (100) peak of ZnO films with a-axis preferred orientation slightly decreased after ion implantation up to a dose of $\sim 10^{17}$cm$^{-2}$ [8]. Moreover, the intensity monotonically decreased with increasing the implantation dose. Kono et al. observed that little changes were seen in HWFM for doses up to $1\times10^{16}$ cm$^{-2}$, which was defined as tolerance limit [9]. Earlier results showed that dynamic annealing takes place below the tolerance dose. A steady-state concentration of defects is reached when recombination of interstitial and vacancy becomes equal to the generation rate[10]. As the total dose increases, additionally created defects cause collapse of the damaged zone and create large disordered zone[10], effectively enhancing the damage creation. The dpa at the threshold dose of GaN is 10 dpa based on calculation using SRIM2000 and literature data [10, 11]. In the case of ZnO, dpa is determined to be 19 for Zn and 12 for O at maximum using SRIM2000 at the tolerance dose of $1\times10^{16}$ cm$^{-2}$ [11]. In our study, the total dose is above the tolerance limit for ZnO. So, (002) peak is greatly suppressed after ion implantation.

Fig. 3 shows the room-temperature PL spectra of as-deposited and Zn-implanted ZnO films. The spectrum of the as-deposited ZnO shows a near band edge (NBE) excitonic UV emission at 390nm and a defect related deep level emission (DLE) centered at $\sim 470$ nm in the visible region. NBE is originated from free-exciton recombination [12, 13]. DLE centered at $\sim 470$ nm is attributed to the electron transition from the conduction band to Zn vacancy ($V_{Zn}$) [14, 15]. $V_{Zn}$ is a deep acceptor and may act as compensating center in n-type ZnO [16]. Intrinsic point defects such as oxygen vacancy ($V_{O}$) [17],
interstitial Zinc (Zn\textsubscript{i}) and oxygen (O\textsubscript{i}) [18]. Zinc vacancy (V\textsubscript{Zn}) [19] and extrinsic impurities such as substitutional Cu [20] are proposed to explain DLE emission. However, only V\textsubscript{Zn} and V\textsubscript{O} are the two possible defects that are involved in DLE emission [6]. It is clearly seen that NBE and DLE are greatly decreased by the Zn ion implantation. It has been well known that the radiation damages induced by Zn ion implantation act as a non-radiative defect [21], so that PL emission is greatly decreased. In addition, we expect that some Zn ions may occupy the sites of V\textsubscript{Zn} in Zn-implanted sample during the ion implantation process. This leads to the decrease of V\textsubscript{Zn} concentration in the ZnO thin films, so that the DLE related with V\textsubscript{Zn} decreases after Zn ion implantation.

The optical transmittance spectra are employed to study the effects of Zn-doping through ion implantation on the optical properties of ZnO, as shown in Fig.4. The transmittances are about 70\% in the visible region for the as-deposited films. It can be seen that the transmittance in the visible region drops by \sim 10\% after ion implantation. In addition, the absorption edge redshifts after Zn ion implantation. This phenomenon can be observed clearly in Fig.5, which shows the relationship between absorption coefficient and photon energy. The optical bandgaps are analyzed by a conventional method [22,23]. After Zn ion implantation, the optical band gap redshifts from 3.10 to 3.04 eV. The redshift is about 0.06 eV. Matsunami et al. [8, 24] observed that the optical absorption edge redshifted to low energy and carrier concentration decreased after He and Ne ion implantations. Though an increase of Zn\textsubscript{i} concentration is expected in Zn-implanted films, Zn\textsubscript{i} is a fast diffuser, and is unlikely stable in n-type ZnO [16]. The redshift may be mainly due to the non-radiative centers created during the ion implantation process. The non-radiative centers can trap free carriers in the Zn-implanted films and results in a decrease of carriers’ concentration. So, the Fermi level drops, which results in the observed redshift.

4. Conclusions

We have prepared ZnO thin films on glass substrates by the sol-gel technique. Zn ions with energy of 56 keV to a dose of \num{1e17} cm\textsuperscript{-2} are implanted into the ZnO films. After Zn ion implantation, ZnO film showed a decrease in crystallinity and (002) diffraction peak disappears from the XRD patterns. Zn ion implantation at a dose of \num{1e17} cm\textsuperscript{-2} has the effects to decrease both the UV emission (NBE) and the visible emission (DLE) of ZnO thin films. The optical band gap of Zn-implanted films exhibited narrowing compared to the as-deposited films.

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