

Structure and Optical Properties of Electrodeposited Nd-Doped ZnO Thin Films



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Abstract: Nd-doped ZnO thin films have been prepared by an electrodeposition method. The structure and the optical properties of the films were investigated. X-ray diffraction spectroscopy analysis indicates that the Nd doping can not disturb the structure of ZnO. No additional peaks are observed in the samples. The optical absorption spectra of Nd-doped ZnO thin films show that the absorbance peaks of the samples shift towards short wave length with the increase of Nd doping concentration. The photoluminescence spectra show that with the increase of concentration of Nd³⁺, visible emission is enhanced greatly and the intensity of ultraviolet emission is reduced.

Key words: Nd-doped ZnO; optical absorption; photoluminescence

Recently the optical properties of semiconductor crystals are extensively studied; in particular, high quality II-VI semiconductor samples have been prepared and their luminescence properties have been studied both experimentally and theoretically. Moreover ZnO is an important wide and direct band gap semiconductor with $E_g=3.3$ eV at room temperature. Because of its special characters, ZnO is often chosen as a host material for optoelectronic applications^[1-4]. In addition, ZnO has application potential in mercury-free fluorescent lighting, white light emitting diodes (LEDs) and liquid crystal displays (LCDs) in the near future. In order to enhance the luminescent properties of ZnO, the doped ZnO has been studied, such as transition metal doped ZnO and RE-doped ZnO^[5-10]. Rare earth (RE) ions are better luminescent centers than transition metal elements because their 4 f intra shell transitions originate narrow and intense emission lines. RE-doped semiconductors have applications in thin-film electroluminescent (TFEL) devices, optoelectronic or cathodoluminescent devices and so on^[11-14].

A variety of thin film deposition methods are employed to grow zinc oxide films, such as chemical vapor deposition (CVD)^[15], molecular beam epitaxy (MBE)^[16], pulse laser deposition (PLD)^[17], sol-gel technique^[18] and radio frequency sputtering^[19]. In the present work, we fabricated Nd-doped ZnO thin films by an electrodeposition method and studied their structure and optical properties.

1 Experiment

Zinc nitrate hydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 5 mmol], hexamethylenetetramine [$C_6H_{12}N_4$, 5 mmol], and the rare-earth nitrate [$Nd(NO_3)_3 \cdot nH_2O$] were taken according to required molar ratios (corresponding to 0, 0.5%, and 1%) and dissolved in 200 mL deionized water to grow $Zn_{1-x}Nd_xO(x, wt\%)$. The *n*-type (111) Si wafers with conductivity of $0.01 \Omega/cm^2$ were used as the substrates.

In general, the substrate was used as the cathode and a platinum sheet (99.999 % purity) was used as the anode. Prior to the electrodeposition, the Si substrates were

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ultrasonically cleaned in an acetone bath, and then immersed in a 5% HF solution for oxide removal. Thin indium films were evaporated on the rear of the Si wafers to form a good ohmic contact. The electrodes were placed parallel to each other separated by a distance of 2 cm. And the samples were labeled as A, B and C, corresponding to the increasing concentration of Nd, 0, 0.5% and 1%, respectively. The deposition was carried out at a constant potential of -1.0 V at 90 °C for 1 h.

X-ray diffraction (XRD) measurement was conducted on a Siemens D500 diffractometer using Cu $K\alpha$ radiation of 0.154 nm. A UV-360 Spectrophotometer (Shimadzu) was used for the optical characterization. PL (photoluminescence) spectra were measured using the 325 nm line of a He-Cd laser as an excitation source.

2 Results and Discussion

2.1 Structure of Nd-doped ZnO

Fig.1 shows the XRD patterns of the electrodeposited films. Compared with the pure ZnO, the addition of a small amount of neodymium ions into the precursor solution does not change the crystal structure of the samples. No additional diffractive peaks are observed, which means there are no impurity phases in the samples. No Nd_2O_3 , $Zn(OH)_2$ or other impurities are detected in the samples. Compared with standard ZnO XRD data, an obvious shift to lower angle side is observed for all the peaks in the XRD pattern, caused by doping of Nd^{3+} (0.0983 nm radius) into ZnO (0.0740 nm radius for Zn^{2+}) to enlarge lattice parameter of the crystal. This result indicates that Nd ions are doped into ZnO crystal lattice successfully with substituting positions of Zn ions.

Visualization of Nd incorporation into the ZnO lattice is realized using EDX, by which the correlation between the local microstructure and the chemical composition can be established. According to Fig.2, the Nd concentrations in the samples are calculated with $0wt\%$, $0.46wt\%$ and $0.87wt\%$ in sample A, sample B and sample C, respectively. And the rest is lost in the solution, not participating in the reaction.

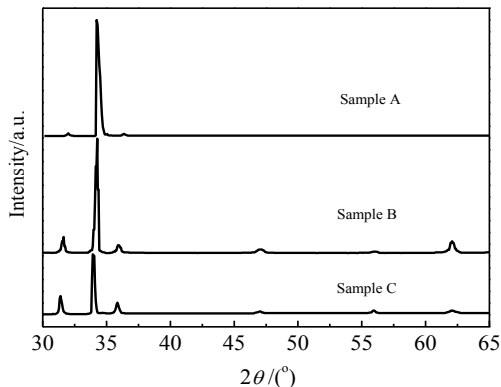


Fig.1 XRD patterns of Nd doped ZnO (0, 0.5%, 1%) thin films

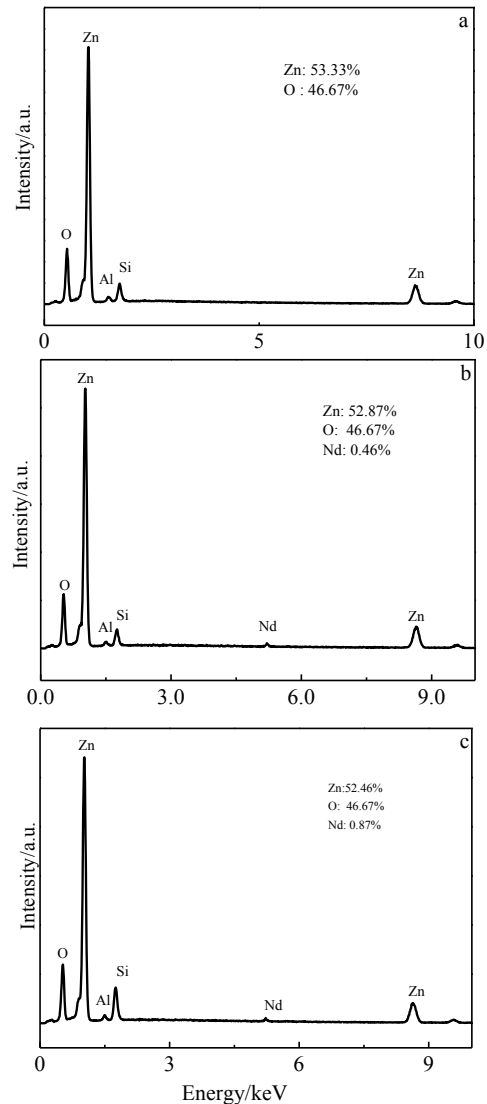


Fig.2 EDX spectra of Nd doped ZnO thin films: (a) sample A, (b) sample B, and (c) sample C

2.2 Optical properties of the Nd-doped ZnO

The optical absorption spectra of the Nd doped ZnO samples were measured at room temperature. The shifts of band edges with different Nd compositions are shown in Fig.3. The band gap transition for the pure ZnO is observed at 3.26 eV. With Nd doping concentration increasing, the band gap gradually increases. This is mainly attributed to the quantum size effect as well as the strong interaction between the surface oxides of Zn and Nd. It is exhibited that all the films have high absorbance in the ultraviolet region. With the increase of Nd doping concentration, the absorbance gradually decreases. It is obvious that, with the increase of Nd doping concentration, the absorbance peaks of the samples shift towards short wave length.

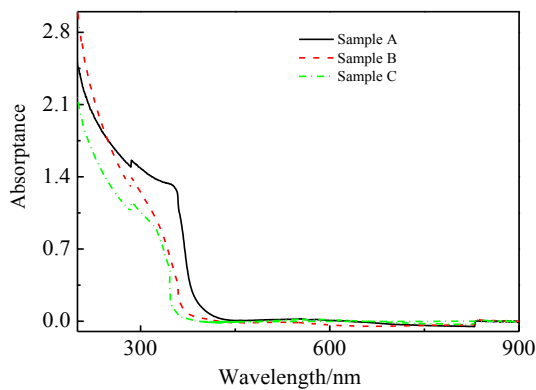


Fig.3 Room temperature optical spectra of ZnNdO films with different Nd concentrations

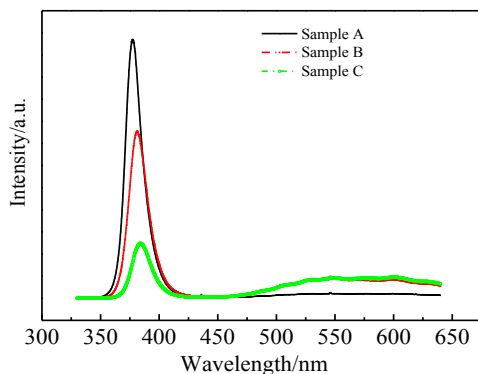


Fig.4 Room temperature PL spectra of ZnNdO films with different Nd concentrations

The PL spectra of Nd-doped ZnO thin films excited by 325 nm at room temperature are shown in Fig.4. It is exhibited that all the samples have strong ultraviolet emission centered at 377 nm and broad green emission centered at about 560 nm. The ultraviolet emission results from excitonic recombination corresponding to the near edge emission of ZnO^[20]. The ultraviolet emission is closely connected with the density of free exciton in ZnO thin films. PL properties of Nd³⁺ doped ZnO were studied, when the doping concentration was varied from 0.5% to 1%. As the concentration of Nd³⁺ is increased, visible emission is enhanced greatly. However, with the Nd doping concentration increasing, the intensity of ultraviolet emission is reduced. The possible reason is the decrease in crystalline quality of ZnO thin films, which might increase the content of oxygen vacancies. The visible emission is generally referred to as a deep-level or trap- state emission, which is usually due to oxygen vacancies, Zn vacancies and Zn interstitials. So it can be seen that with Nd doping

concentration increasing, the green emission intensity gradually increases. The possible reason is that, with the Nd doping concentration increasing, the oxygen vacancies in ZnO thin films are greatly increased, and thus the opportunity of electron transition from the energy level of oxygen vacancies to the valence band is increased.

3 Conclusions

1) Nd doped ZnO thin films can be prepared by the electrodeposition method.

2) Nd ions are doped into ZnO crystal lattice with substituting positions of Zn ions. When Nd doping concentration increases from 0.5% to 1%, the band gap is gradually increased.

3) As the concentration of Nd³⁺ is increased, visible emission is enhanced greatly. However, with the increase of Nd doping concentration, the intensity of ultraviolet emission is reduced.

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