Fabrication and Optical Properties of La-doped ZnO Thin Films

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Abstract. La-doped ZnO thin films were deposited on the substrates of slide glass and Si by sol-gel method. The La/Zn ratio was 1%, 2%, 3%. All the samples were characterized by X-ray diffraction (XRD), atomic force microscope (AFM), ultra-violet spectrometer (UVS) and photoluminescence (PL). All the samples have nice wurtzite structure. The morphology of the samples have flat surface. The peak of UV luminescence had a blue shift with the increase of La/Zn molar ratio.

1. Introduction

ZnO is a semiconductor material with wide band gap and wurtzite structure, its band gap is about 3.37 eV and its exciton binding energy is up to 60 meV at room temperature, is attracting more attention because of its good optical and electrical properties. Doping different metal atoms or ions into ZnO can change the structure and band gap of ZnO, endowing doped ZnO with new characteristics that is different from the ZnO dilute. Rare earth-doped ZnO is a research focus in recent years, but doping rare earth with the sol-gel method is rare. This experiment, adapting the gel-sol method, grows La-doped nanoZnO thin films in the Si film (P type 100 direction) and ordinary glass plate, which aims to study the effects from La with different concentrations on the ZnO thin films, such as, the structure, UV transmittance and surface morphology, luminescence resulting at room temperature[1-5].

2. The Experiment

(CH₃COO)₂Zn·2H₂O and La(NO₃)₃·6H₂O were weighed by electronic balance according to the Molar Ratio and dissolved in ethylene glycol, then added with metal ion equimolar monoethanolamine. Putting them in the reaction kettle and stirring for 1 hour at 60°C, which finally forms the colorless transparent homogeneous solution. Then painting films evenly after 72-hour aging and placing the samples in the box-type resistance furnace for annealing. the films on simple glass substrates were annealed in air at 550°C for 1 hour, and the films on Si substrates were annealed at 900°C for 1 hour, respectively. The annealing temperature for ordinary glass substrate and Si substrate is 550°C and 900°C respectively, and the annealing time is 1 hour. Later, cooling them in the furnace to room temperature. At last, La-doped ZnO thin films with the doping concentration of 1%, 2%, 3% were obtained.

3. Results and Discussion

3.1 The crystal structure of La-doped ZnO thin films

The XRD patterns of La-doped ZnO thin films has been depicted in Figure 1. All of the samples showed that La-doped ZnO thin films were still had the polycrystalline hexagonal wurtzite structure and had no obvious preferential orientation. These thin films, as a result of different preparation methods and experimental conditions, differ from those La and Nd doped ZnO thin films made by Wen Jun. Fig.1 also shows that with the increase of doping concentration, the diffraction peaks obviously move toward the large angular direction, which indicates that the C axis of La-doped ZnO thin films shortens[6,7].

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3.2 The transmission spectra of La-doped ZnO thin films

Fig.2 is the transmission spectrum of the different doping concentration samples with glass slide as the substrate annealed at 500°C. All of the data were collected at room temperature. Fig.2 (a) shows that transmissivity decline sharply around the 380nm UV, besides, there are obvious ultraviolet absorption edge, and the transmission side appears obvious blue shift with the increase of doping concentration, which indicates that the doping of rare earth La can enlarge the gap width of ZnO\(^{8-10}\). Fig.2 (b) refers to the specific band gap width of La-doped ZnO thin films. The band gap width of the 1% sample is 3.32eV, the 2% sample 3.40eV, and the 3% sample 3.36eV. It is clear that La-doped ZnO thin films can better regulate the the band gap width of ZnO thin films.

Fig.2  Transmission spectra of La-doped ZnO thin films annealed at 500°C.

(a) Wavelength and transmittance diagram
(b) Photo Energy and transmittance rate diagram
3.3 Surface Morphology of La-doped ZnO thin films

The AFM images of La-doped ZnO thin films annealed at 900°C for 1 hour were showed in Fig.3. La-doped ZnO thin film samples of different concentrations appear to be granular, and the growth of particles is relatively uniform, which has a great relationship with the selection of Si substrate and higher annealing temperature.

![AFM images of ZnO samples annealed at 900°C](image)

Fig.3  AFM images of ZnO samples annealed at 900°C

3.4 Photoluminescence Properties of Samples

Fig.4 illustrates the room-temperature PL spectra of the ZnO samples annealed at 900°C. La-doped ZnO thin films have better luminescent properties, besides, the ultraviolet luminescence peaks shift toward short wavelength with the increase of doping concentration, which is consistent with the phenomenon observed through the transmission spectrum.

![PL spectra of samples obtained at 900 °C](image)

Fig.4  PL spectra of samples obtained at 900 °C;
4. Conclusions

La-doped ZnO thin films of different concentrations are prepared by sol-gel method. Analysis through XRD, UV-S, AFM and PL spectrum shows that the La-doped ZnO thin films of different concentrations have hexagonal wurtzite structures. What’s more, the surface was smooth, the particle is uniform and the ultraviolet luminescence peaks are enhanced significantly and shift toward short wavelength with the increase of doping concentration.

References


