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Effect of Nd doping level on optical and structural properties of ZnO:Nd thin films synthesized by the sol–gel route

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ABSTRACT

ZnO thin films with various Nd doping levels (0%, 1%, 3% and 5%, respectively) have been synthesized by the sol–gel method on glass substrates. X-ray diffraction (XRD) spectra and atom force microscope (AFM) studies reveal that all samples possess hexagonal wurtzite structure without any second phase. 1% Nd doped ZnO thin film has the best crystalline quality. With Nd concentration increases, the grain size reduces gradually. The optical measurements show that with Nd concentration increases, the absorption peak shifts to short wavelength, which indicates that the optical band gap of Nd-doped ZnO thin films increases. All samples have ultraviolet emission centered at 377 nm and strong green emission at 511 nm. The intensity of green emission gradually increases with Nd concentration increases. The emission mechanism is discussed in detail.

1. Introduction

ZnO has attracted more and more attention in recent years due to its unique physical properties and potential application in ultraviolet (UV) photoconductive detectors [1], surface acoustic wave devices [2], optoelectronic devices [3], light emitting diodes [4], and solar cells transparent electrodes [5]. ZnO is an n-type oxide semiconductor material with wide band gap energy of 3.37 eV, high exciton binding energy of 60 meV, a wide range resistivity (10^{-4}–$10^{12}\,\Omega\,cm$), high electron Hall mobility ($200\,cm^2\,Vs^{-1}$) and high transparency at room temperature [6]. Moreover, ZnO is a cheap, abundant, chemically stable and no toxin material with excellent radiation hardness. Various techniques have been applied to prepare ZnO thin films. For example, RF magnetron sputtering [7], chemical vapor deposition (CVD) [8], molecular beam epitaxy (MBE) [9], electrochemical deposition [10], pulse laser deposition (PLD) [11] and the sol–gel method [12] are widely used. Among these techniques, the sol–gel method attracts much attention due to some unique advantage including low cost, simple deposition equipment, easy adjusting composition and dopants, and fabricating large area films, etc.

Due to these unique properties mentioned above, synthesis of high quality, size and shape controlled ZnO thin film is very important for optoelectronic devices applications. In previous works, a lot of researches focus their attention on rare earth elements doped ZnO. To date, ZnO doped with Ce [13], Eu [14], Gd [15], Tb [16], Yb [17] and Er [18] has been intensively studied.

In this work, the interest is focused on Nd-doped ZnO thin film. Some experimental and theoretical research results about Nd-doped ZnO have been reported. Chao et al. [19] investigated the effect of annealing on the properties of Nd-coated ZnO nanoparticles by the sol–gel process. The Nd-doped ZnO nanoparticles show strong near-band-edge emission centered at 380 nm together with visible emission at 620 nm. Annealing caused re-crystallization and enabling an additional luminescence band centered at 899 nm. Zhou et al. [20] investigated the photocatalytic properties of Nd-doped ZnO nanoparticles. But the structural and visible emission properties associated with Nd doping concentration has been seldom investigated yet. For this purpose, Nd-doped ZnO films with various doping levels are prepared by the sol–gel method. The dependence of structural and optical properties on Nd doping concentrations is investigated.

2. Experiments detail

Nd-doped ZnO films were synthesized via sol–gel method. Commercially available zinc acetate 2-hydrate was dissolved in anhydrous ethanol to form ZnO solution. Ethanolamine was used as stabilizer. The total concentration of metal ions was maintained at 0.3 mol/L and the molar ratio of ethanolamine to the total metal ions was 1:1. The Nd doping ratio defined by [Nd]/[Nd+Zn] varied over a range of 0%–5%. The resulting mixture solution was stirred for two hours at 60 °C and aged for one day at room temperature to get a clear and transparent solution. The films were prepared by

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spin-coating method. The spin coating speeds were 1200 rpm for the first 10 s and 3000 rpm for the next 20 s. After spin coating process, the samples were dried at 300 °C for 10 min to evaporate the solvent and organic residuals. The process of spin coating and subsequent pre-heating treatment was repeated several times to obtain a desired thickness. At last, all the samples were annealing at 500 °C for an hour in air.

The structure of Nd-doped ZnO thin films were studied by X-ray diffractometer (Bruker D8 Advance). The surface morphologies were observed by scanning probe microscope (CSPM4000). The absorption and transmittance spectrum of Nd-doped ZnO thin films were measured by UV–visible spectrophotometer (UV-1201). The photoluminescence spectra of Nd-doped ZnO thin films were measured by fluorescence spectrophotometer (FL3-TCSPC).

3. Results and discussion

3.1. The structure and morphology of Nd-doped ZnO thin films

Fig. 1 shows x-ray diffraction patterns of Nd-doped ZnO thin films. All the diffraction peaks of the samples correspond to wurtzite hexagonal crystal structure. No peaks corresponding to neodymium metal clusters or neodymium oxides are observed in the patterns, which indicate that Nd has entered the ZnO lattice without changing the crystal structure. It can be seen that all the films exhibit preferential c-axis (002) orientation perpendicular to the substrate. This is attributed to the lowest surface free energy of ZnO (002) plane. The other two peaks correspond to the (100) and (101) phase of ZnO. The full-width at half-maximum (FWHM) corresponding to (002) plane is firstly decreases and then increases with Nd doping concentration increasing (0.22, 0.16, 0.24 and 0.33, respectively). It exhibits that Nd doping strongly affects the peak intensity of ZnO (002) plane. When the doping concentration is 1%, the (002) plane of the pattern has the strongest intensity and narrowest FWHM, no other peak is founded, which means that 1% Nd doping effectively improve the crystalline quantity of ZnO thin films. With Nd doping concentration increasing above 1%, the intensity of (002) peak drops gradually, this behavior indicates that Nd^{3+} ions substitute for Zn^{2+} ions, restraining the crystal growth of ZnO. This is associated to the Nd doping concentration influence the stress in ZnO thin films [21]. The similar results were reported by Huang et al. [22]. From the above results, it can be concluded that a proper Nd-doping concentration can greatly improve the crystalline quality of ZnO thin films. But when doping concentration is above 1%, the crystallization quality degrades.

Fig. 2 shows the surface morphology micrographs of Nd-doped ZnO thin films measured by scanning probe microscope with contact mode. It exhibits that all samples have dense grains. The grains are basically round, which grow preferentially along the c-axis orientation perpendicular to the substrates. For the pure ZnO thin film as show in Fig. 2(a), the average grain size is about 59.85 nm and the lateral size distribution is not uniform. The grain size greatly reduces with Nd doping concentration increases. 1% Nd-doped ZnO thin film has uniform and dense grains, which means that the incorporation of 1% Nd effectively improve the crystalline property of ZnO films. This result is in good agreement with XRD results. With Nd doping contents increase above 1%, the grain distribution of the samples is not uniform and some particle agglomeration is founded. This may be due to the formation of Nd–O–Zn on the surface of the doped samples, which hinders the growth of crystal grains.

3.2. Optical properties of Nd-doped ZnO films

The absorbance spectra of Nd-doped ZnO films are shown in Fig. 3. It exhibits that all the films have high absorbance in the ultraviolet region. When the doping concentration is 1%, the

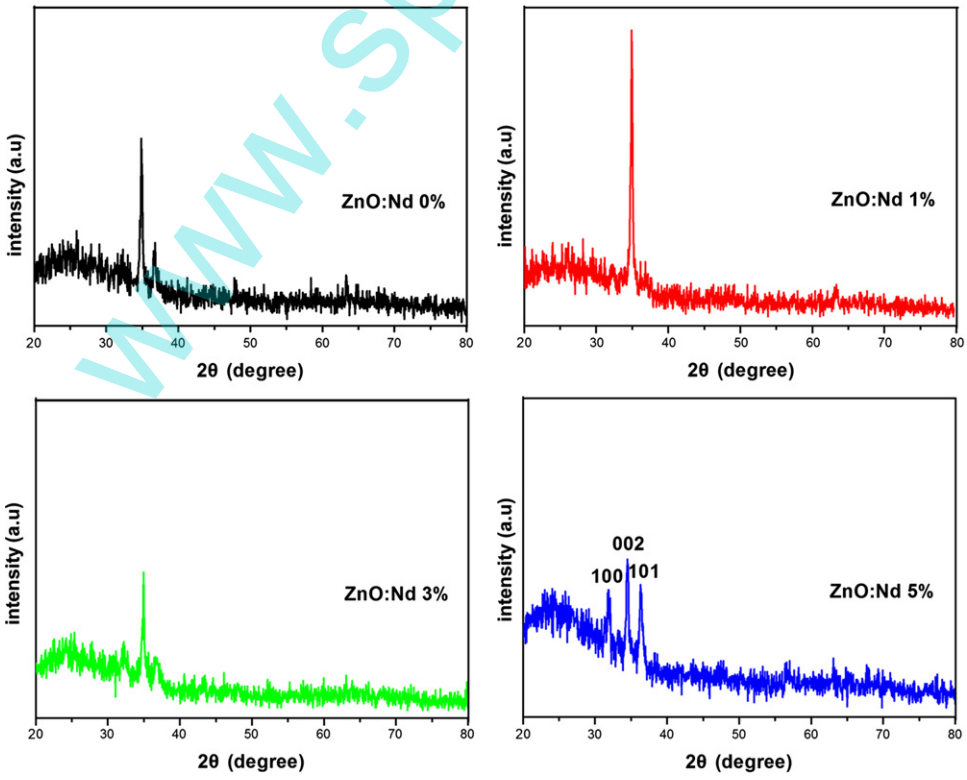

Fig. 1. X-ray diffraction patterns of Nd-doped ZnO thin films with various Nd doping concentration.

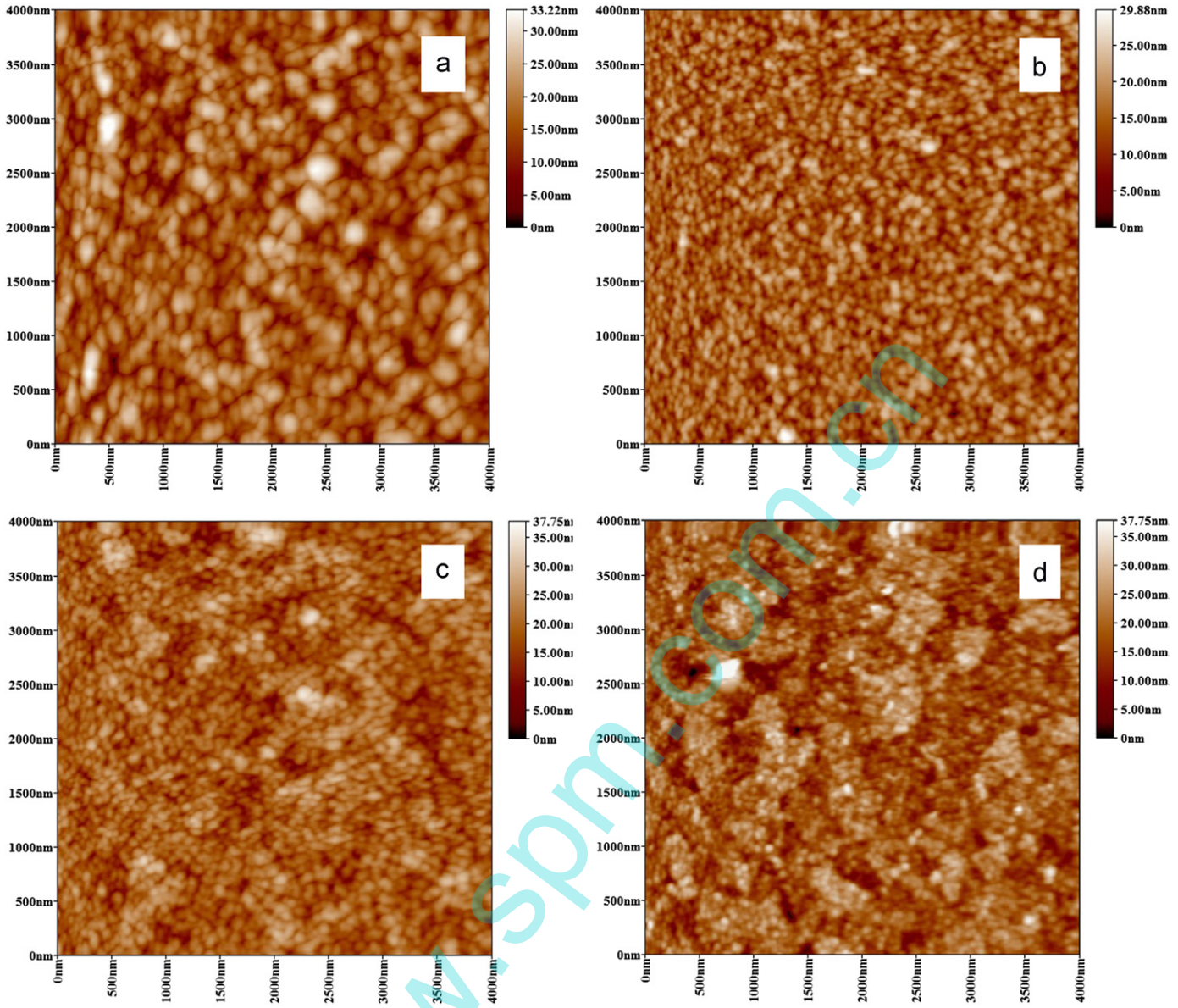

Fig. 2. Surface morphologies of (a) 0%, (b) 1%, (c) 3% and (d) 5% Nd-doped ZnO thin films.

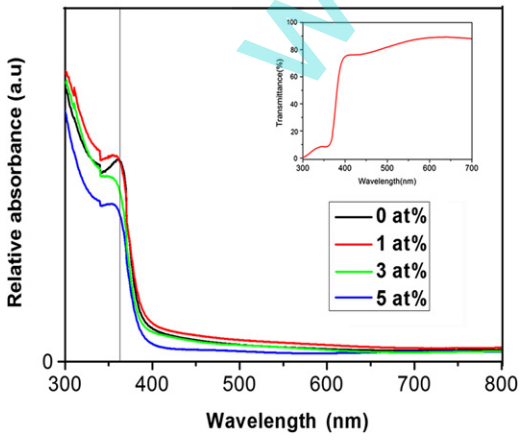

Fig. 3. Absorbance spectra of Nd-doped ZnO thin films with various Nd doping concentration. The insert show the transmittance of 1% Nd-doped ZnO thin film.

sample has highest absorbance intensity. With Nd doping concentration increases, the absorbance gradually decreases. It is obvious that, with Nd doping concentration increases, the absorbance peaks of the samples shift towards short wavelength. The optical band gap of Nd doped ZnO films are determined by applying the following formula [23]:

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (1)$$

where A is a constant, α is optical absorption coefficient, $h\nu$ is the photon energy and E_g is the optical band gap. The band gap of the films has been calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$ and by extrapolating the linear portion of the absorption edge to find the intercept with energy axis. The results show that the band gap of pure ZnO is 3.23 eV. When Nd doping concentration increases from 1% to 5%, the band gap is gradually increased. This is mainly attributed to the quantum size effect as well as the strong interaction between the surface oxides of Zn and Nd. The former reports of Nd dopant effect on optical band gap of ZnO are very

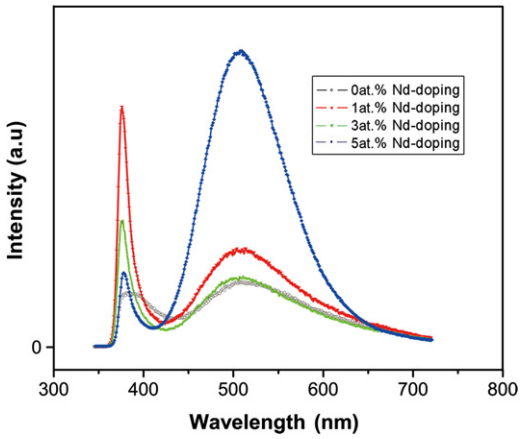

Fig. 4. Room-temperature photoluminescence spectra of Nd-doped ZnO thin films with various Nd doping concentration.

different. For example, Zhou et al. [20] prepared Nd-doped ZnO nanoparticles with various Nd doping concentration by the sol–gel method and found that the band gap was gradually increased with Nd doping content increasing. But Liu et al. [24] found that Nd doping can effectively decrease the band gap of ZnO. The differences of former reports are closely associated with the growing temperature and annealing environment. The inset in Fig. 3 shows the transmittance of 1% Nd-doped ZnO thin film, it is obvious that the film has high transmittance in the visible region.

The photoluminescence spectra of Nd-doped ZnO thin films excited by 325 nm at room temperature are shown in Fig. 4. It exhibits that all the samples have strong ultraviolet emission centered at 377 nm and broad green emission centered at about 511 nm. The ultraviolet emission results from excitonic recombination corresponding to the near edge emission of ZnO [25]. The ultraviolet emission is closely connected with the density of free exciton in ZnO thin films. It is clear that the intensity of ultraviolet emission is obviously enhanced when ZnO thin film is doped with 1% Nd. This is because 1% Nd doping improves the crystalline quality of ZnO, thus increases the density of free exciton. What is more, 1% Nd doped-ZnO has the biggest ratio of ultraviolet emission intensity to visible emission intensity, which confirms that 1% Nd doped effectively reduces the defects in ZnO crystal, thus improve the crystalline quality. However, when the Nd doping is above 1%, the intensity of ultraviolet emission is reduced. The possible reason is because of the decrease in crystalline quality of ZnO thin films. The similar results were also found on Mg [26] and Al [27] doped ZnO nanostructures. 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. Li et al. [28] investigated the annealing effect on morphologies and photoluminescence properties of ZnO nanocombs. They attributed the strong green emission to oxygen vacancies. Lv et al. [29] prepared Na-doped ZnO thin films. They attributed the green emission to electron transition from the level of ionized oxygen vacancies to the valence band. It can be seen that with Nd doping concentration increases, the green emission intensity gradually increases. The possible reason is that, with the Nd doping concentration increases, the oxygen vacancies in ZnO thin films is greatly increased, thus the opportunity of electron transition from the energy level of oxygen vacancies to the valence band is increased.

4. Conclusions

The structural, morphological, and optical properties of Nd-doped ZnO thin films prepared by the sol–gel method are investigated. XRD spectra indicate that all the films exhibit wurtzite hexagonal crystal structure. The surface morphology is investigated by scanning probe microscope. The results show that the surface particles density is increased. The absorption band edge of the films shifts to short wavelength, which indicates that the band gap of the films is increased. The photoluminescence spectra measurements show that all the samples have ultraviolet emission centered at 377 nm and green emission centered at 511 nm. The intensity of ultraviolet emission is greatly enhanced when Nd doping concentration is 1% and the green emission intensity is gradually increased with Nd doping concentration increasing.

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