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Spectral features of $Zn_{1-x}Mg_xO$ thin films synthesized by the sol-gel route

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Abstract. $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films have been synthesized by sol-gel method on glass substrates. The structure, morphology and optical properties of the samples have been studied by X-ray diffractonmeter (XRD), scanning probe microscope, UV-visible spectrophotometer, fluorescence spectrophotometer and spectroscopic ellipsometer, respectively. The XRD result shows that all the films have hexagonal wurtzite structure, no phase segregation is observed. The surfaces of $Zn_{1-x}Mg_xO$ thin films are smooth and the root mean square (RMS) roughness of the samples is only several nanometers. The transmittance spectra reveal that all samples have high transmittance above 90%, with Mg doping content increase, the optical band gap increases from 3.27eV to 3.77eV. The photoluminescence spectra show that all samples have two emission peaks in ultraviolet and violet region, a blue shift of ultraviolet emission is observed. The refractive indexes of all samples decrease with the increase of wavelength ranging from 350nm to 900nm. The refractive index changes apparently by varying Mg content, which has potential application in research of optical materials and the design of optical devices.

Introduction

Znic oxide, as an important semiconductor material, has attracted great research interest among science and technology society due to its potential applications in ultraviolet photodetector [1], surface acoustic wave device [2], light emitting diode [3], solar cell window material [4] and other optical applications. Attempts have been made to modify or improve the properties of ZnO, such as adding dopants into ZnO to achieve multifunctionality. Among the different dopants, Mg doping has been greatly investigated because magnesium oxide has a high optical band gap of 7.8eV and the radii of Mg and Zn are similar [5]. Especially, the band gap of ZnO can be easily increased by Mg doping. What's more, Mg-doped ZnO has a lot of advantages in the application of ultraviolet photodetector [6, 7]. Many researchers have successfully synthesized Mg-doped ZnO thin films by various deposition techniques, such as pulsed-laser deposition (PLD) [8], chemical vapor deposition (CVD) [9], radio frequency magnetron sputtering [10], molecular beam epitaxy (MBE) [11] and sol-gel method [12]. Among these techniques, 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.

Refractive index is one of the fundamental properties for optical material, because it is closely related to the electronic polarizability of ions and local field inside material. In this article, $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films are prepared by sol-gel method. The dependence of structure, transmittance, luminescence and refractive index on Mg doping concentration is investigated.

Experiment

The $Zn_{1-x}Mg_xO$ thin films were synthesized by sol gel spin coating method. Zinc acetate dehydrate, monoethanolamine (MEA) and magnesium acetate 2-hydrate were dissolved in 2-methoxethanol to get ZnO solution. The Zn2+ ions concentration was maintained at 0.3mol/L, monoethanolamine was used as stabilizer. The molar ratio of monoethanolamine to the total metal ions was 1:1.The doping concentration was defined by 100% [Mg]/[Mg+Zn] and was kept at 0%, 5%, 10%, 20% and 30%, respectively. The resulting mixture solution was stirred for an hours at 60℃ and aged for one day at

room temperature. Mg doped ZnO thin films were prepared by spin coating method. The spin coating speeds were 1200 rpm for the first 10s and 3000 rpm for the next 20s. After spin coating process, the samples were dried at 300℃ for 10 minutes 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℃ for an hour in air.

The structure and morphologies of $Zn_{1-x}Mg_xO$ thin films were measured by X-ray diffractonmeter (Bruker D8 Advance) and scanning probe microscope (CSPM4000). The transmittance and photoluminescence spectra were measured by UV-visible spectrophotometer (UV-1201) and fluorescence spectrophotometer (RF-5301PC), respectively. The thickness and refractive index of the samples was measured by spectroscopic ellipsometer. All the measurements were carried out at room temperature in air atmosphere.

Results and discussion

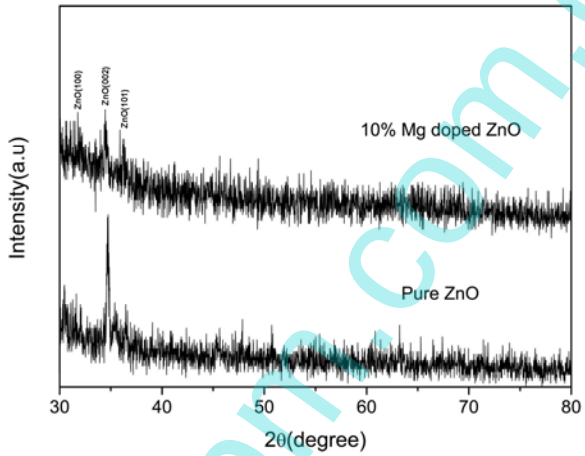

Fig. 1, X-ray diffraction patterns of pure and 10% Mg-doped ZnO thin films.

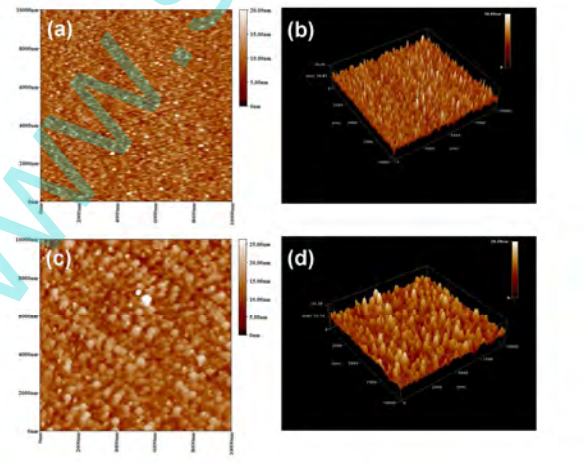

Fig. 2, Surface morphologies of Mg-doped ZnO thin films: (a) and (c), the 2D and 3D morphologies of pure ZnO, (b) and (d) the 2D and 3D morphologies of 30% Mg-doped ZnO.

Fig. 1 shows the X-ray diffraction patterns of $Zn_{1-x}Mg_xO$ (x=0 and 0.1, respectively) thin films using Cu-Kα radiation ($\lambda = 1.54056$ Å). It exhibits that all the diffraction peaks of both pure and 10% Mg doped ZnO thin films are corresponding to the hexagonal wurtzite structure ZnO. No peaks corresponding to magnesium metal clusters or magnesium oxides are observed on the patterns, which indicate that Mg ion has entered the ZnO lattice without changing their structures. With Mg doping

concentration increases, no obvious changes in the patterns are observed. The similar result was reported by Ding et al. [13]. The surface morphology micrographs of the samples are analyzed by scanning probe microscope over a 10000nm×10000nm area by contact mode. The results show that all samples have a very smooth surface with average highness about several nanometers. With Mg doping concentration increasing, the average particle size is gradually increased. The two dimensional (2D) and three dimensional (3D) surface morphology micrographs pure and 30% Mg doped ZnO thin films are illustrated in Fig. 2. The root mean square (RMS) roughness of $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films are 1.97nm, 1.93nm, 1.72nm, 1.26nm and 3.02nm, respectively. The small values of RMS roughness indicate that all the samples have flat and smooth surfaces. The similar results of surface morphologies of Mg doped ZnO thin films were reported by Liu et al. [14].

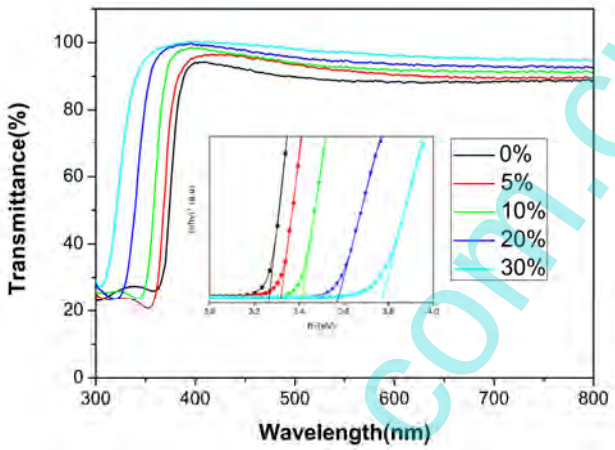

Fig. 3 Transmittance spectra of Mg-doped ZnO thin films with various Mg doping concentration. The inset shows the curve of $(\alpha h\nu)^2$ versus photon energy $h\nu$.

The transmittance spectra of $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films are illustrated in Fig. 3. The spectra show that all the samples have sharp ultraviolet absorption edge. The absorption edge of pure ZnO is centered at about 365nm, with Mg doping concentration increase from 5% to 30%, A blue shift of the band edge absorption is demonstrated. Surprisingly, the blue shift nearly linearly changes with the increase of Mg doping content. This phenomenon can be explained by the Burstein-Moss band gap widening and band gap narrowing due to the electron-electron and electron-impurity scattering. It is also observed that all samples are highly transparent in visible region. With Mg doping concentration increase, the transmittance in visible region is gradually increased, especially the 30% Mg doped ZnO is nearly 100% transparent in visible region. As our known, the transmittance is greatly connected with the light scattering of grain boundaries. With Mg doping concentration increase, the grain size is gradually increased, which make the grain boundaries in the films gradually decrease, thus lead to the increases of transmittance. The optical absorption coefficient α can be calculated from the transmittance by the following equation [15]:

$$\alpha = (\frac{1}{d})\ln(\frac{1}{T}), \quad (1)$$

where T is the transmittance, d is the thickness of the samples. The thickness of $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films are 96.18nm, 94.63nm, 101.5nm, 116.5nm, 112.6nm, respectively. ZnO is a wide band gap semiconductor material with direct band gap. The optical band gaps of the samples are determined with the following equation [16]:

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

where $h\nu$ is the photon energy, A is a constant, E_g is the band gap energy. By plotting $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ and linearly extrapolating to the energy axis. The band gaps of $Zn_{1-x}Mg_xO$ thin films are evaluated and showed in the inset of Fig. 3. The results show that the band gap of pure ZnO

is 3.27eV. With Mg doping concentration increase, the band gap of $Zn_{1-x}Mg_xO$ thin films almost linearly increases from 3.27eV to 3.77eV. This result is similar with the report by Wei et al. [17]. They synthesized Mg doped ZnO thin films and gave a relationship of Mg doping concentration and band gap of ZnO. The result showed that when the Mg doping concentration was lower than 70%, the band gap was linearly changed with Mg doping increase.

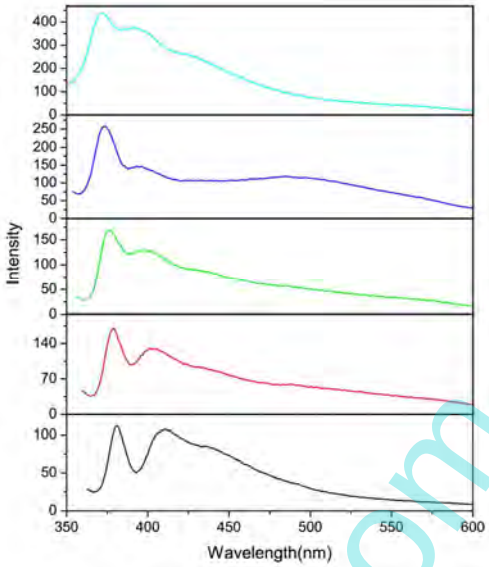

Fig. 4 Room-temperature photoluminescence spectra of Zn1-xMgxO thin films with various Mg doping concentration.

The room temperature photoluminescence spectra of $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films (excited wavelength was 325 nm) are illustrated in Fig. 4. It can be seen that all samples have a strong ultraviolet emission and a weak violet emission. It is well known that the ultraviolet emission is usually attributed to the near-band-edge emission with free exciton recombination. With Mg doping increase, the ultraviolet emission peaks of $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films are 381 nm, 379 nm, 377 nm, 374 nm and 372 nm, respectively. This blue shift of ultraviolet emission usually attributes to the increases of band gap in ZnO crystal. It is also observed that the intensity of ultraviolet emission is enhanced slightly with Mg doping increases. The similar result was reported by Zhao et al. [18]. Surprisingly, the sample of 20% Mg-doped ZnO thin film exhibits a wide green emission band. It is commonly acceptable that the green emission is attributed to oxygen vacancy [19] in ZnO crystal. What's more, all the samples have a weak violet emission, which may ascribe to electron transition from the bottom of conduction band to the shallow acceptor level formed by Zn vacancies [20].

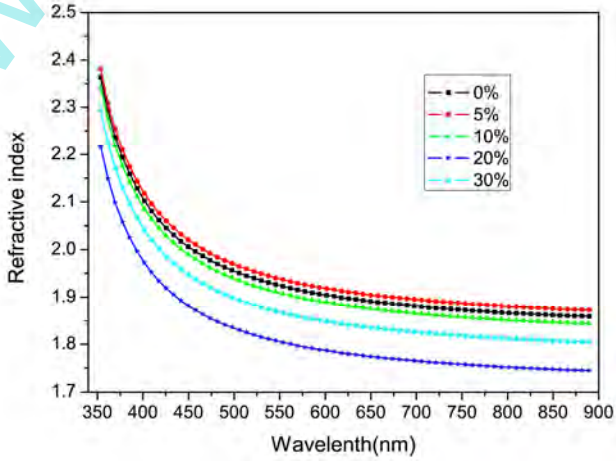

Fig. 5 Refractive index of Mg-doped ZnO thin films with Mg doping concentration of 0%, 5%, 10%, 20% and 30% respectively.

The refractive index plays an important role in the research for optical materials and it is significant for optical communication and optical devices design. Fig. 5 shows the derived value of refractive index of $Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films measured by spectroscopic ellipsometer. It exhibits that the refractive index of all samples decreases with the increases of wavelength ranging from 350nm to 900nm. It can be seen that with Mg doping increases, the refractive index changes greatly, but there is not a regular changes observed. In previous reports, the reasons for the changes of refractive index are very differences. Zhang et al. [21] investigated oxygen particle pressure and substrate temperature on optical property of $Mg_xZn_{1-x}O$ thin films prepared by magnetron sputtering and found that the refractive index increased with substrate temperature increasing. They attributed this to the changes of the film compactness and Mg/Zn ratio. Lu et al. [22] synthesized Na-doped ZnO thin films by sol-gel method and found that refractive index decreases with Na doping concentration. They attributed this to the different structure and density of the films. Mekhnache et al. [23] prepared ZnO thin films on various substrates. They attributed the differences of refractive index to the films thickness and compactness. In our work, the refractive index changes are suitable with the tendency of film thickness changing, and it is shown that the changes of refractive index have little relationship with Mg doping concentration. It can be concluded that the changes of refractive index are closely related to the film thickness. What's more, the surface structure is closely related to the light scattering property, which may play a key role in the changing of refractive index.

Conclusion

$Zn_{1-x}Mg_xO$ (x=0, 0.05, 0.1, 0.2 and 0.3, respectively) thin films have been successfully synthesized by sol-gel method. Structure and morphology studies show that all the films have hexagonal wurtzite structure; no phase segregation is observed. The surfaces of the samples are smooth and the root mean square (RMS) roughness of them is only several nanometers. The optical measurements reveal that all samples have high transmittance above 90%, with Mg doping content increases, the optical band gap increases from 3.27eV to 3.77eV. All samples have two emission peaks in ultraviolet and violet region, a blue shift of ultraviolet emission is observed. The refractive index of all samples decreases with the increases of wavelength ranging from 350nm to 900nm. The refractive index of the samples changes apparently with Mg doping concentration increase. This is associated with the film thickness and surface structure. It has potential application in research of optical materials and the design of optical devices.

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