Effect of K-doping on structural and optical properties of ZnO thin films

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In this work, K-doped ZnO thin films were prepared by a sol–gel method on Si(111) and glass substrates. The effect of different K-doping concentrations on structural and optical properties of the ZnO thin films was studied. The results showed that the 1 at.% K-doped ZnO thin film had the best crystallization quality and the strongest ultraviolet emission ability. When the concentration of K was above 1 at.%, the crystallization quality and ultraviolet emission ability dropped. For the K-doped ZnO thin films, there was not only ultraviolet emission, but also a blue emission signal in their photoluminescent spectra. The blue emission might be connected with K impurity or/and the intrinsic defects (Zn interstitial and Zn vacancy) of the ZnO thin films.

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1. Introduction

ZnO is a direct wide-band-gap semiconductor material ($E_g = 3.37$ eV at room temperature [1]). It has a large exciton binding energy of 60 meV which makes the exciton hard to be thermally ionized. Therefore, ZnO is an ideal short-wavelength light-emitting material at room temperature or higher temperatures. With respect to the luminescent behavior of ZnO, as early as in 1969, R. Dingle at the Bell Telephone Laboratory had studied the green emission of Cu-doped ZnO [2]. Subsequently, in 1977, Powell and Spicer reported the first ultraviolet photoemission for (Cs) ZnO [3]. However, their work did not arouse widespread interest in ZnO. The turning point appeared in 1997 and 1998 when Tang, Zu [4,5], Bagnall [6] et al. reported the spontaneous and stimulated ultraviolet emission from ZnO thin films at room temperature. Afterwards, ZnO quickly attracted wide attention and ZnO still is a research focus in semiconductor field to this day.

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In order to obtain better crystallization quality and optical, electrical and ferromagnetic properties, researchers carried out doping in ZnO. For the first group elements, if the doped monovalent cations go into ZnO lattices to substitute for Zn^{2+}, it is possible to lead to p-type conduction. The realization of p-type conduction is very important for ZnO applications in optoelectronic devices, so many researchers have investigated the electrical property of the first group element-doped ZnO thin films [7–11]. However, there are few reports on photoluminescence of the first group element-doped ZnO thin films.

So far, ZnO has been studied mainly in the form of thin film. Various techniques such as pulsed laser deposition [12,13], magnetron sputtering [14,15], molecular beam epitaxy [16,17], sol–gel method [18,19] and so on have been applied to prepare ZnO thin films. In these techniques, the sol–gel method has been receiving high attention due to its many advantages such as low cost, simple deposition procedure, easier composition control, low processing temperature, easier fabrication of large area films, etc. In this work, we prepared K-doped ZnO thin films on Si(111) and glass substrates by sol–gel dip-coating method. Except for photoluminescence, we also studied the effect of K-doping concentration on structure and transmittance of the films. Compared with prior work of Kim et al. [11], we adopted different substrates, annealing temperature and atmosphere. Furthermore, we studied the photoluminescence of ZnO thin films at room temperature.

2. Experiments

Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), ethanol, monoethanolamine (MEA), and potassium acetate were used as the starting material, solvent, sol stabilizer and dopant source, respectively. According to a certain proportion, zinc acetate and potassium acetate were first put into ethanol at room temperature. Then the resulting mixture was stirred at 60 °C for an hour. When the mixture was stirred, MEA was put into it drop by drop. Finally, a clear and transparent homogeneous solution was formed. The Zn concentration was 0.3 mol/L and the concentration of K as a dopant was 0 at.%, 1 at.%, 2 at.% and 3 at.%, respectively, with respect to Zn. The ZnO sol was aged for 24 hours at room temperature and then ZnO thin films were prepared by the sol–gel dip-coating method. When the substrate was withdrawn from ZnO sol, it was placed in a furnace to be dried and given a pre-heat treatment at 300 °C. The procedure from dip-coating to drying was repeated for 6 times. Finally, the ZnO thin films were annealed at 500 °C in air for one hour.

The crystal phase and crystalline orientation of the ZnO thin films were investigated by X-ray diffractometer (Bruker D8 Advance). The surface morphologies were observed by scanning probe microscope (CSPM4000). The transmittance and photoluminescence of the ZnO thin films were measured by UV-visible spectrophotometer (Lambda 950) and fluorophotometer, respectively. The excitation source was a Xe lamp and the excitation wavelength was 325 nm. The thickness of the films was measured by an ellipsometer (TPY-2). They were 145, 141, 138 and 138 nm for the 0 at.%, 1 at.%, 2 at.% and 3 at.% K-doped ZnO thin films, respectively. All the measurements were carried out at room temperature in air.

3. Results and discussion

3.1. Microstructure of the K-doped ZnO thin films

Fig. 1 shows X-ray diffraction patterns of the K-doped ZnO thin films prepared on Si(111) substrates. From the patterns, it can be seen that all the films have a diffraction peak corresponding to the (002) plane. This indicates that all the ZnO thin films are preferentially oriented along the *c*-axis perpendicular to the substrate. When the K-doping concentration is 0 at.%, 1 at.%, 2 at.% and 3 at.%, the diffraction peak lies at 34.94°, 34.86°, 34.85° and 34.88°, respectively. There is no second phase in these films from the patterns, possibly because of the low doping content [11]. What is more, K-doping almost does not affect the position of the (002) diffraction peak, but it strongly affects the peak intensity. When the doping concentration is 1 at.%, the diffraction intensity is the strongest. With the increase of K-doping concentration, the (002) peak intensity is dropping. This result is
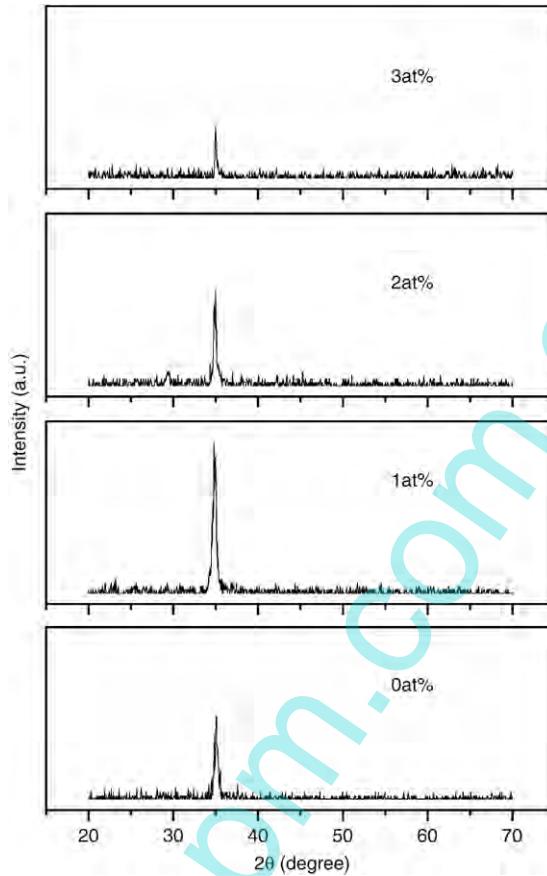
Fig. 1. X-ray diffraction patterns of K-doped ZnO thin films.

different from that of Kim et al. [11] who found that when the K-doping concentration was 2 at.%, the (002) diffraction peak was the highest. This difference is possibly connected with the use of different substrates, different annealing temperature and atmosphere. From the above result, it is apparent that 1 at.% K-doping greatly improved the crystallization quality of the ZnO thin film, but crystallization quality dropped when K-doping concentration was above 1 at.%. Fig. 2 shows the surface morphology micrographs of the ZnO thin films prepared on Si substrates. A scanning probe microscope was used to observe the surface morphologies of the films over a 4000×4000 nm area by contact mode. All the thin films have granular and uniform grains. For the pure ZnO thin film, the in-plane average grain size is about 95 nm. Although its grain sizes are uniform, there are some pores on the surface, which suggests that the pure ZnO thin film has a relatively loose structure and its density is not high enough. After 1 at.% K is doped, the in-plane average grain size increases to 108 nm and there is no pore on the surface, which means the incorporation of K improved the density of the ZnO thin film. This result is in agreement with the analysis of X-ray diffraction patterns. That is to say, 1 at.% incorporation of K greatly improved the crystallization quality and density of ZnO thin film. According to presumption of Kim et al. [11], when the concentration of K is below 2 at.%, K ions are not substituted in Zn^{2+} sites. They possibly exist in the vicinity of the oxygen vacancies (V_O), so they prevent lattice distortion by the V_O, which somewhat enhances the crystallinity. However, with the increase of K content, the grain sizes of the films gradually decrease again. The grain sizes are 97 and 93 nm for the 2 at.% and 3 at.% K-doped ZnO thin films, respectively. The similar phenomena have been reported in Al-doped ZnO thin films [20,21]. Lin et al. [20] found that as the concentration of Al rose, the crystallite size
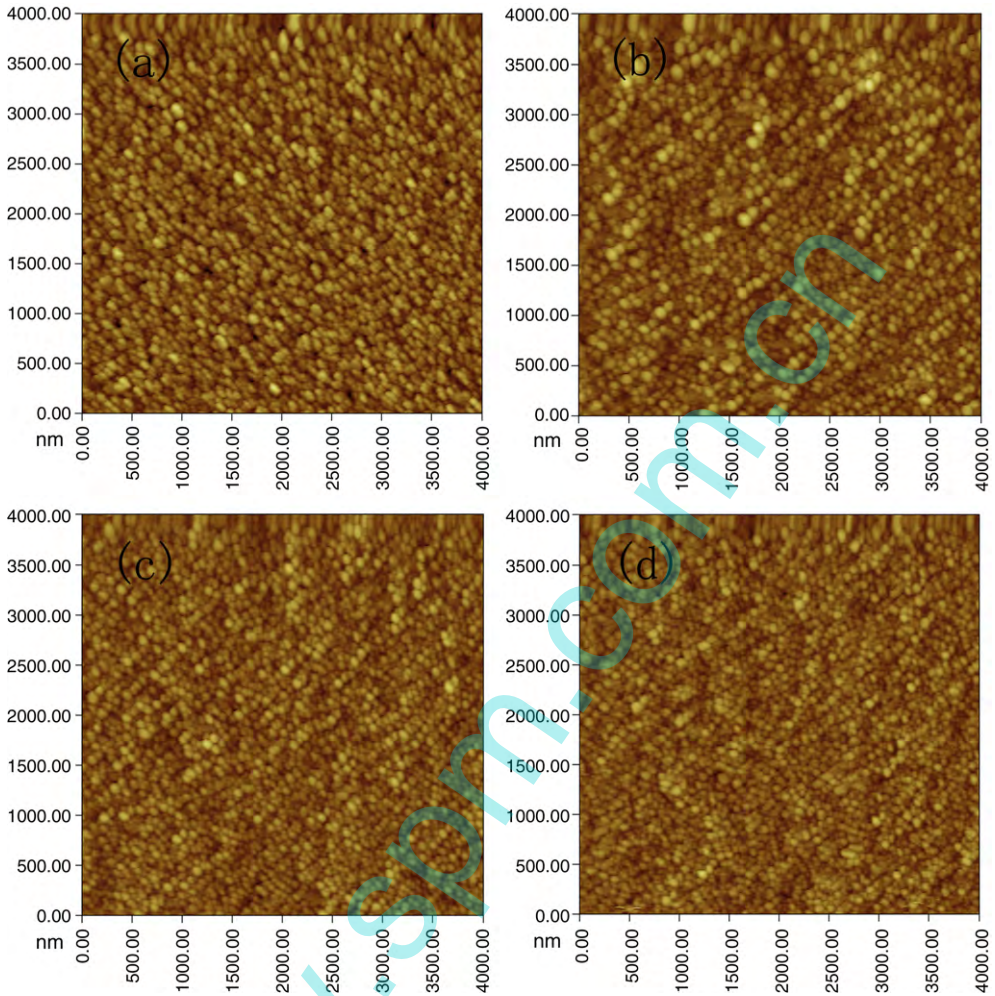
Fig. 2. Surface morphologies of (a) 0 at.%, (b) 1 at.%, (c) 2 at.%, and (d) 3 at.% K-doped ZnO thin films.

became distinctly smaller. They attribute this phenomenon to the nucleation mechanism of the ZnO phase. However, Zhou et al. [21] think it is due to a high difference in ionic radius between zinc and aluminum. For our films, we think the decrease of the grains is attributed to the nucleation mechanism of the ZnO phase. The increase of K concentration will enhance the nucleation of the ZnO phase and results in a smaller grain size as a consequence [20].

3.2. Optical properties of the K-doped ZnO thin films

ZnO thin film is a transparent conductive thin film in the visible region, so it can be used as a window material and transparent electrode. Fig. 3 shows the transmittance spectra of the K-doped ZnO thin films prepared on glass substrates. For all the films, they have high transmittance in the visible region. The 1 at.% K-doped ZnO thin film has the highest transmittance and 3 at.% K-doped ZnO thin film has the lowest transmittance in the visible region. The transmittance of ZnO thin film has much to do with its crystallization quality. From Fig. 2, it can be seen that with the increase of K concentration, the grain sizes gradually decrease, which makes grain boundaries in the film increase
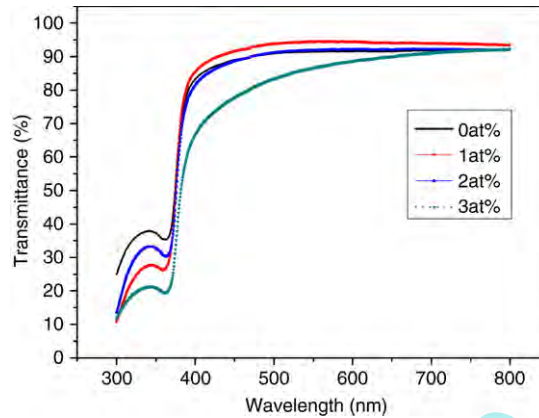
Fig. 3. Transmittance spectra of K-doped ZnO thin films.

greatly. The increase of grain boundaries intensifies the light scattering, which will lead to a decrease of transmittance. Optical band gap of ZnO thin films can be obtain by applying the following two formulas (1) and (2) [22]:

$$T = (1 - R)^2 \exp(-\alpha d) \tag{1}$$

$$\alpha h\nu = D (h\nu - E_g)^{\frac{1}{2}}. \tag{2}$$

In the formula (1), T is the transmittance of the ZnO thin film, R is its reflectivity, α is the absorption coefficient and d is the film thickness. In the formula (2), $h\nu$ is the photon energy, D is a constant and E_g is the optical band gap. According to (1) and (2), we calculated the absorption coefficient $\alpha \sim \ln T$ as well as $\alpha h\nu \sim (h\nu - E_g)^{\frac{1}{2}}$. Then the plot of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ can be obtained. Extrapolation of linear portion to the energy axis at $(\alpha h\nu)^2 = 0$ gives the E_g value. By the above process, we obtained the E_g values 3.36 eV, 3.39 eV, 3.38 eV and 3.30 eV for the 0 at.%, 1 at.%, 2 at.% and 3 at.% K-doped ZnO thin film, respectively. The change of E_g possibly reflects the different states of K in ZnO thin films [11].

Fig. 4 shows the photoluminescent spectra of the K-doped ZnO thin films prepared on Si substrates. From the spectra, it can be seen that there is an ultraviolet emission peak centered at 381 nm and a very weak yellow-green emission band centered at 560 nm for the pure ZnO thin film. As for the ultraviolet emission, it is generally considered it results from the transition of electrons between valance band and conduction band or/and recombination of a free exciton. However, the emission mechanism of yellow-green is controversial as yet. After 1 at.% K is doped in ZnO thin film, its ultraviolet emission is getting stronger and at the same time a blue emission centered at 470 nm occurred. When the content of K increases, the ultraviolet emission reduces but the blue emission has a little increase. With regard to blue emission of ZnO thin films, it has been observed in some research work. For one example, Peng et al. [23] prepared Cu-doped ZnO thin films on Si(111) substrates by RF sputtering technique and found the films had a strong blue emission. They ascribed the blue emission to the Zn interstitial (Zn_i) and Zn vacancy (V_{Zn}) level transition. For another example, Maiti et al. [18] prepared Mn-doped ZnO thin films on glass substrates by sol–gel dip-coating method and found the films had a blue emission centered at 466 nm. They thought the blue emission was connected with a defective structure of the films. For the third example, Wei et al. [24] prepared ZnO thin films on sapphire substrates by pulsed laser deposition and found the films had a blue emission centered at 459 nm. They attributed the blue emission to the electrons transition from the donor energy level Zn_i to the acceptor energy level of V_{Zn}. In the above three examples, the first and second are the blue emission of doped ZnO thin films and the third is the blue emission of pure ZnO thin films. For our ZnO thin films, pure ZnO thin film has almost no blue emission, but the blue emission signal is observed in K-doped ZnO thin films. When the concentration of K is 3 at.%, the blue emission is the strongest and the quality of the ZnO thin film
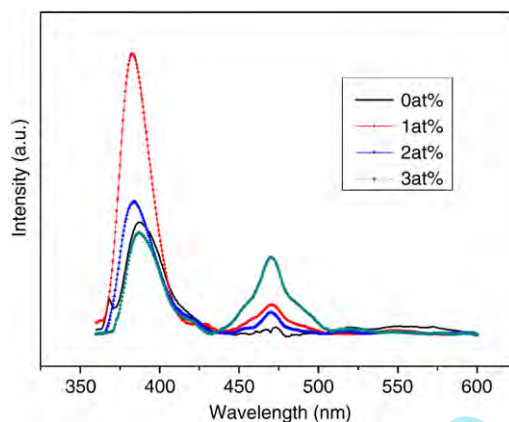
Fig. 4. Photoluminescent spectra of K-doped ZnO thin films.

is the worst compared with others. Therefore, it is difficult to ascertain whether K impurity or defect structure is the dominant factor that leads to blue emission. In here, we speculate the blue emission is associated with both of these factors.

4. Conclusions

In this work, we prepared K-doped ZnO thin films on Si and glass substrates by a sol–gel dip-coating method. The structural analyses show that 1 at.% K-doping greatly improved the crystallization, increased the density and eliminated pores on the surface of the film. When the doping concentration was increased, the crystallization quality dropped and grain size decreased. The optical measurement results show that all the ZnO thin films had high transmittance in the visible region; 1 at.% K-doped ZnO thin film had the highest transmittance and the strongest ultraviolet emission. For the K-doped ZnO thin films, except ultraviolet emission, they had a blue emission centered at 470 nm. The blue emission may be connected with K impurity or/and the intrinsic defects (Zn_i and V_{Zn}) of the ZnO thin films.

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