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Tunable visible emission and warm white photoluminescence of lithium-doped zinc oxide thin films

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Abstract Visible emission of Li-doped ZnO (LZO) thin films prepared by a sol–gel method has been tuned in a wide range from blue-green to yellow. Blue-green, yellow, and warm white emissions are observed as 5.0 at.% LZO thin films are annealed in N_2, air, and He, respectively. A strong dependence of the defect emission of LZO on annealing atmosphere suggests that the visible emissions of LZO are related to intrinsic defects rather than lithium impurities.

Introduction

Energy crisis in the past and upcoming decades urges the development of energy-saving technology. In the illumination industry, solid-state lighting devices in the form of light-emitting diodes (LEDs) have begun replacing incandescent and fluorescent lights in a number of niche applications due to their markedly enhanced electrical-to-optical energy conversion efficiencies [1]. Specially, there exists a need for white-light LEDs as a more efficient replacement for conventional lighting sources; and the most common approach to achieve white LEDs is to combine a white-light-emitting phosphor with a UV LED chip [2–4].

Zinc oxide (ZnO) has been extensively used as a bright green phosphor for vacuum fluorescent displays [5]. In addition to the green emission, violet [6], yellow [7], and orange-red [8, 9] emissions are also observed. Since these defect-related emissions are located in a wide range of the visible spectrum, great efforts have been made to modify and tailor the visible emissions. Doping ZnO with Li [10, 11] or Al [12] leads to the yellow luminescence, while co-doping ZnO with Li and Al gives off broad-band yellowish-white emission covering nearly the whole visible spectrum [13]. Synthesizing ZnO nanoparticles [14] or dispersing them in foreign matrix such as SiO_2 [15, 16], MgF_2 [17], and $BaTiO_3$ [18] represents another endeavour to modify the visible emissions of ZnO. Enhanced green emission [15], violet emission [16, 18], or broad-band blue-green luminescence [14, 17] has been achieved in these studies. In spite of great efforts made so far, the visible emissions from the modified ZnO were limited mainly to a narrow band in the spectrum and gave a colored emission.

In this work, we have demonstrated that the visible emissions of Li-doped ZnO (LZO) thin films can be tuned in a wide range from blue-green to yellow. Especially, we present here a warm white emission of the LZO films. The intense white emission of the LZO films may allow their possible application as a phosphor for white LEDs.

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Experimental

Preparation of LZO thin films

Li-doped ZnO thin films were prepared by a sol–gel process. Preparation of the precursor sol has been described in detail elsewhere [9]. Lithium was added as a dopant in the form of LiOH·H_2O at a dopant concentration of 0.5, 2.0, and 5.0 at.% (Li/Zn). Films were coated on silicon substrates via a dip coating method. After each coating, they were dried at 400 °C in air for 4 min. This process was repeated for six times to obtain a desired film thickness of about 300 nm, which was followed by further drying at 400 °C for 1 h to remove the residual organic compounds. To generate intense defect-related visible emission of the films and investigate the effect of annealing gas, the as-prepared films were finally annealed at 800 °C for 1 h in various gases including air, N_2, and He.

Characterization

The phase structure and purity of the as-prepared thin films were determined by X-ray diffraction (XRD) using a Philips PW3710 diffractometer with Cu*K*α radiation. Room-temperature photoluminescence (PL) spectra of the 800 °C-annealed LZO thin films was recorded by exciting the samples with a 325 nm He-Cd laser (IK3301R-G) at an output power of 30 mW.

Results and discussion

Figure 1 shows the XRD pattern of the as-prepared 5.0% LZO thin films. All diffraction peaks are identified as the hexagonal wurtzite structure of ZnO (JCPDS 36-1451), indicating that no impurities or secondary phases are formed in the range of Li doping concentration considered in this work.

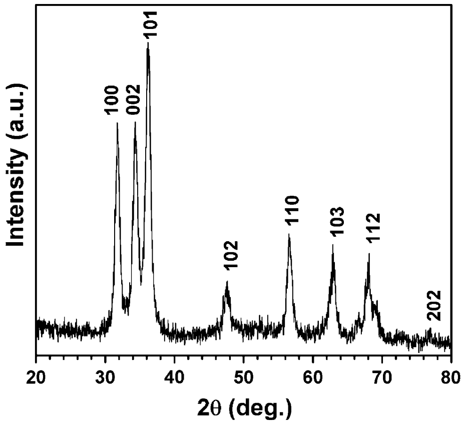

Fig. 1 XRD patterns of the as-prepared 5.0 % LZO thin films

Figure 2a illustrates the PL spectra of LZO thin films annealed at 800 °C in air. In addition to a weak band-edge UV emission located at around 382 nm, a strong visible emission is observed in all samples. Pure ZnO exhibits a blue-green emission with a peak centered at 500 nm. A green emission peak at 520 nm is obtained as 0.5% Li is incorporated into ZnO. An increase in Li doping concentration to 2.0 and 5.0% red-shifts the emission peak to 542 and 580 nm, respectively. In addition, the spectra are broadened as indicated by the appearance of a violet emission in the range of 400–450 nm. It is interesting to note that the luminescent spectrum of the 5.0% LZO annealed in air is similar to that of the 10% LZO prepared by spray pyrolysis [11]. The above results indicate that the visible emission of ZnO annealed in air can be tuned from blue-green to yellow as 0–5.0% Li is introduced into ZnO.

There is a big change in the shape of the visible emission of LZO films when the annealing gas is switched from air to N_2. As shown in Fig. 2b, all visible spectra in the blue-green range are quite similar in shape. The emission peak is slightly red-shifted from 500 to 506 nm with increasing Li doping concentration. Furthermore, the yellow emission of LZO is suppressed and the blue-green one is enhanced instead. In an attempt to balance the two emission bands, inert helium is used as the annealing gas. Rather surprisingly, an integration is achieved between the blue-green and yellow emissions (Fig. 2c). Additional 400–450 nm violet emission and 630–750 nm red emission of the He-annealed LZO may allow its potential application as a phosphor irradiating a warm white light. It is also seen in Fig. 2c that the emission intensity is enhanced at a higher Li content, while the spectrum shape is almost independent of the Li concentration.

Figure 3 depicts the Gaussian fit of the visible emission of 5.0% LZO thin films annealed in different gases. A broad emission of the air-annealed sample in Fig. 3a can be fitted into three bands: a moderate green emission, a strong yellow emission, and a weak red emission centered at 521, 587, and 636 nm, respectively. In contrast, a dominant blue-green emission and a weak yellow emission are Gaussian-resolved for the visible emission of the N_2-annealed sample (Fig. 3b). The results of Fig. 3a, b further confirm that switching the annealing gas from air to N_2 leads to a suppressed yellow emission and an enhanced blue-green emission. Figure 3c shows that a broad emission of the He-annealed sample can also be fitted into three bands, i.e., blue-green, yellow, and red, with the band intensities deceased in sequence. The Commission International de l'Eclairage (CIE) chromaticity coordinates of the emission spectra in Fig. 3 turn out to be (0.42, 0.44), (0.25, 0.45), and (0.36, 0.42), corresponding to yellow, cyan, and warm white, for the samples annealed in air, N_2, and He, respectively.

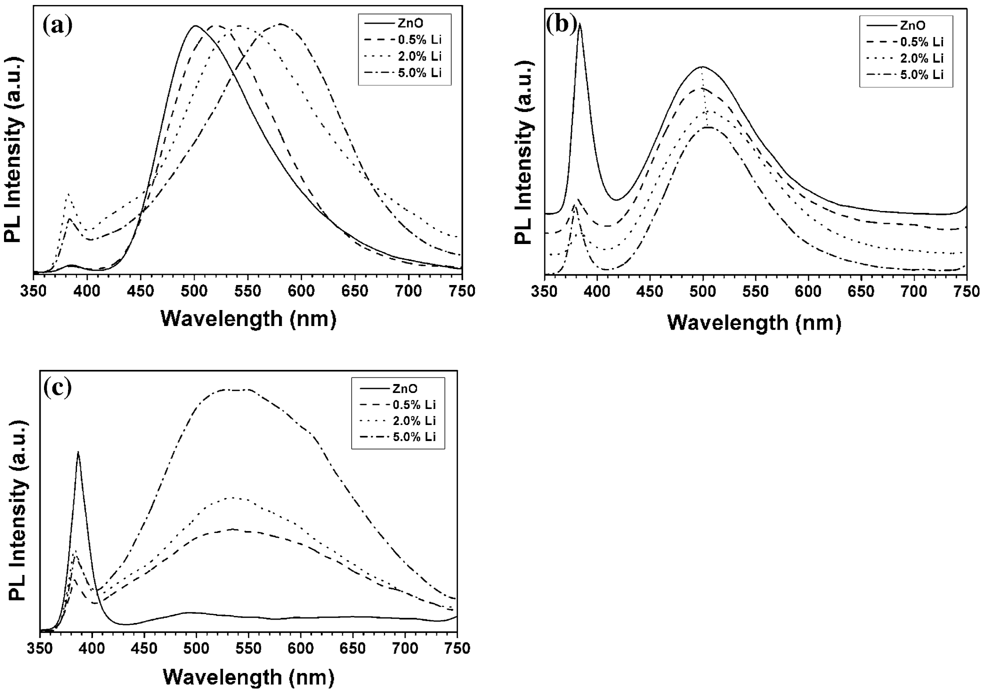

Fig. 2 Photoluminescence spectra of LZO thin films annealed at 800 °C in **a** air, **b** N_2, and **c** He

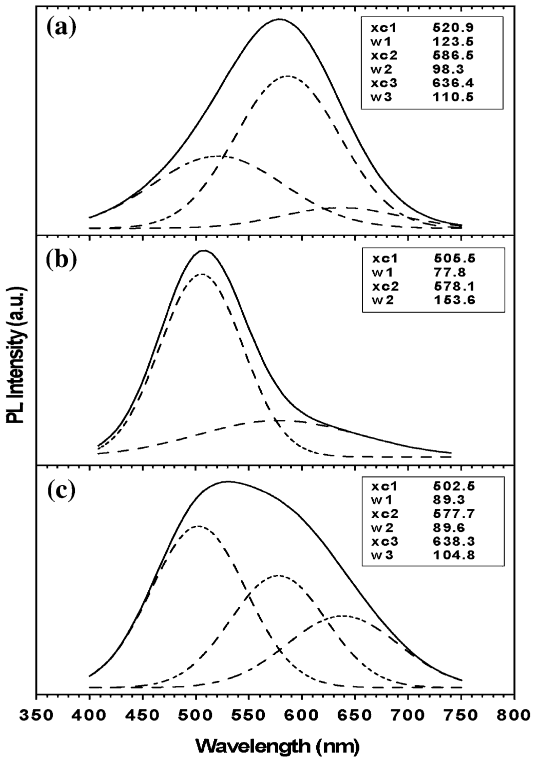

Fig. 3 Multi-peaks Gaussian fit of the visible emission of 5.0% LZO thin films annealed in **a** air, **b** N_2, and **c** He. *xc* stands for the peak position and *w* for the band width

In order to investigate the effect of annealing temperature on the PL properties of the LZO films, the samples are further annealed at a higher temperature of 900 °C in various gases. As illustrated in Fig. 4, the UV emission is markedly improved for the N_2- and He-annealed samples; however, it is almost unchanged for the air-annealed ones except for a slight red-shift of the band peak. The visible emission is suppressed for the N_2- and He-annealed samples, while it is enhanced for the air-annealed ones. A close look at Fig. 4c reveals that the visible emission still covers nearly the whole visible range despite its reduced intensity at 900 °C. Note also that when the annealing temperature is increased to 900 °C, the visible band of the N_2- and air-annealed samples is blue-shifted, which is centered at 495 and 550 nm, respectively. This result again confirms that the visible emission of LZO is strongly dependent on the annealing atmosphere, which locates at a lower wavelength for the N_2-annealed sample but at a longer wavelength for the air- and He-annealed samples.

It has been reported that the yellow emission of LZO is ascribed to shallow donor—lithium acceptor pair (DAP) transitions [10]. Recently, both theoretical calculation [19] and experimental investigation [20] have, however, shown that lithium acceptors (Li_{Zn}) possess a shallow energy level, which is experimentally determined to be as small as 150 meV [20]. Accordingly, Li-involved DAP transitions give only a near-band-edge UV emission [20]. On the other hand, a yellow emission is commonly observed in undoped ZnO, which is normally attributed to the intrinsic defects of oxygen interstitials (O_i) [7]. Other visible emissions such as green and red emissions are also found to be related to intrinsic defects of oxygen vacancies (V_O) and O_i [8]. The defect emission of LZO exhibiting strong dependence on annealing atmosphere in our work suggests that the visible

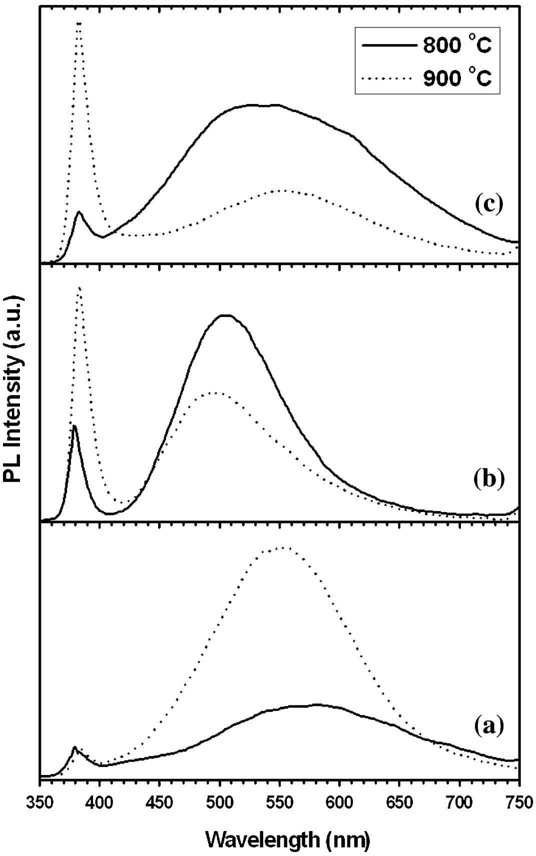

Fig. 4 Photoluminescence spectra of the 5% LZO thin films annealed at 900 °C in **a** air, **b** N_2, and **c** He. PL spectra of the 800 °C-annealed 5% LZO thin films were also included for comparison

emissions of LZO would be related to intrinsic defects rather than lithium impurities. Further work is necessary to clarify the exact role of lithium in the development of visible emissions of LZO.

Conclusion

We have investigated the effect of annealing gas on the photoluminescent properties of LZO thin films. The visible emission of ZnO annealed in air is found to be tunable from blue-green to yellow by simply changing Li doing concentration. Switching the annealing gas from air to N_2 leads to a suppressed yellow emission and an enhanced blue-green one. Integrated blue-green, yellow, and red emissions are obtained for He-annealed samples, emitting a warm white light with a CIE chromaticity coordinate of (0.36, 0.42) and thus making them a possible candidate as a phosphor for white LED. A strong dependence of the defect emission of LZO on the annealing atmosphere in our work suggests that the visible emissions of LZO may be related to intrinsic defects such as V_O and O_i rather than lithium impurities.

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