Enhanced blue photoluminescence realized by copper diffusion doping of ZnO thin films

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Abstract: ZnO thin films with blue photoluminescence (PL) have been fabricated through Cu diffusion doping. A CuO_x-ZnO mixture, and Cu/ZnO double layer, films were prepared on amorphous SiO_x/Si substrates by pulsed laser deposition (PLD), and electron beam (e-beam) deposition, respectively. After sequential oxygen annealing, CuO_x-ZnO mixture films exhibited green emission centered at 523 nm. However, Cu/ZnO double layer films differed in producing a blue emission centered at 480 nm. Detailed analysis identified that this blue shift in the emission center resulted from increased blue emissions attributed to Cu dopants in the film by e-beam deposition. Luminescence intensity was increased to 6 cd/m^2 for a sample annealed at 700 °C. Color points were close to the locus of points following the line of a black-body-radiator on the CIE 1931 XY chromaticity diagram. The present results show that Cu-doped ZnO has strong potential as a cost effective phosphor for use in down converting LEDs.

OCIS codes: (310.6860) Thin films, optical properties; (250.5230) Photoluminescence; (300.2140) Emission; (330.1715) Color, rendering and metamerism; (999.9999) Zinc oxide.

References and links

1. Y. Shirasaki, G. J. Supran, M. G. Bawendi, and V. Bulović, "Emergence of colloidal quantum-dot light-emitting technologies," J. Nat. Photonics Rev. **7**(1), 13–23 (2012).
2. V. Wood, M. J. Panzer, J. Chen, M. S. Bardley, J. E. Halpert, M. G. Bawendi, and V. Bulvoić, "Inkjet-Printed quantum dot-polymer composites for full-color AC-driven displays," Adv. Mater. **21**(21), 2151–2155 (2009).
3. S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, and K. Leo, "White organic light-emitting diodes with fluorescent tube efficiency," Nature **459**(7244), 234–238 (2009).
4. D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase, and H. Waller, "Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine-trioctylphosphine oxide-trioctylphospine mixture," Nano Lett. **1**(4), 207–211 (2001).
5. K.-S. Cho, E. K. Lee, W.-J. Joo, E. Jang, T.-H. Kim, S. J. Lee, S.-J. Kwon, J. Y. Han, B.-K. Kim, B. L. Choi, and J. M. Kim, "High-performance cross-linked colloidal quantum-dot light-emitting diodes," Nat. Photonics **3**(6), 341–345 (2009).
6. D. Ratchford, K. Dziatkowski, T. Hartsfield, X. Li, Y. Gao, and Z. Tang, "Photoluminescence dynamics of ensemble and individual CdSe/ZnS quantum dots with an alloyed core/shell interface," J. Appl. Phys. **109**(10), 103509 (2011).
7. D. Feezell, J. Speck, S. DenBaars, and Sh. Nakamura, "Semipolar (2021) InGaN/GaN light-emitting diodes for high-efficiency solid-state lighting," J. Display Technology **9**, 190–198 (2013).
8. H. Zhao, G. Liu, J. Zhang, J. D. Poplawsky, V. Dierolf, and N. Tansu, "Approaches for high internal quantum efficiency green InGaN light-emitting diodes with large overlap quantum wells," Opt. Express **19**(S4 Suppl 4), A991–A1007 (2011).
9. H. Zhao, G. Liu, J. Zhang, R. Arif, and N. Tansu, "Analysis of internal quantum efficiency and current injection efficiency in III-nitride light-emitting diodes," J. Display Technology **9**(4), 212–225 (2013).

#196364 - $15.00 USD Received 27 Aug 2013; revised 20 Sep 2013; accepted 20 Sep 2013; published 24 Sep 2013

10. G. Liu, J. Zhang, Ch.-K. Tan, and N. Tansu, "Efficiency-droop suppression by using large-bandgap AlGaInN thin barrier layers in InGaN quantum-well light-emitting diodes," IEEE Photonics Journal **5**(2), 2201011 (2013).
11. S. Choi, M.-H. Ji, J. Kim, H. J. Kim, and M. M. Satter, "Efficiency droop due to electron spill-over and limited hole injection in III-nitrid visible light-emitting diodes employing lattice-matched InAlN electron blocking layers," Appl. Phys. Lett. **101**(16), 161110 (2012).
12. S.-H. Yang, J.-S. Lin, F.-S. Juang, D.-C. Chou, M.-H. Chung, C.-M. Chen, and L.-C. Liu, "White light emitting diodes (LEDs) with good color rendering indices (CRI) and high luminous efficiencies by the encapsulation of mixed and double-deck phosphors," Curr. Appl. Phys. **13**(5), 931–934 (2013).
13. R. Wang, J. Zhang, X. Xu, Y. Wang, L. Zhou, and B. Li, "White LED with high color rendering index based on $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$ and ZnCdTe/CdSe quantum dot hybrid phosphor," Mater. Lett. **84**, 24–26 (2012).
14. J.-H. Kim, T.-H. Shin, K.-J. Yang, J. Jeong, and B. Choi, "Abstraction of blue photoluminescence in Al-doped ZnO nanoparticles prepared by electron beam deposition," Appl. Phys. Express **5**(1), 012603 (2012).
15. X. Peng, J. Xu, H. Zang, B. Wang, and Z. Wang, "Structural and PL properties of Cu-doped ZnO films," J. Lumin. **128**(3), 297–300 (2008).
16. Y. Yan, M. M. Al-Jassim, and S. H. Wei, "Doping of ZnO by group-IB elements," Appl. Phys. Lett. **89**(18), 181912 (2006).
17. L. Ma, S. Ma, H. Chen, X. Ai, and X. Huang, "Microstructures and optical properties of Cu-doped ZnO films prepared by radio frequency reactive magnetron sputtering," Appl. Surf. Sci. **257**(23), 10036–10041 (2011).
18. F. M. Li, L. T. Bo, S. Y. Ma, X. L. Huang, L. G. Ma, J. Liu, X. L. Zhang, F. C. Yang, and Q. Zhao, "Effects of the oxygen partial pressure and annealing atmospheres on the microstructures and optical properties of Cu-doped ZnO films," Superlattices Microstruct. **51**(3), 332–342 (2012).
19. F. Yang, S. Ma, X. Zhang, M. Zhang, F. F. Li, J. Liu, and Q. Zhao, "Blue–green and red luminescence from ZnO/porous silicon and ZnO:Cu/porous silicon nanocomposite films," Superlattices Microstruct. **52**(2), 210–220 (2012).
20. K. M. Safi, R. Vinodkumar, R. J. Bose, V. N. Uvais, and V. P. Mahadevan Pillai, "Effect of Cu on the microstructure and electrical properties of Cu/ZnO thin films," J. Alloy. Comp. **551**, 243–248 (2013).
21. Y. M. Tao, S. Y. Ma, H. X. Chen, J. X. Meng, L. L. Hou, Y. F. Jia, and X. R. Shang, "Effect of the oxygen partial pressure on the microstructure and optical properties of ZnO:Cu films," Vacuum **85**(7), 744–748 (2011).
22. J.-H. Jeon, S.-Y. Jeong, and Ch.-R. Cho, "Heteroepitaxial relation and optical properties of Cu-doped ZnO films grown by using pulsed laser deposition," J. Korean Phys. Soc. **54**(92), 858–862 (2009).
23. J. B. Kim, D. Byun, S. Y. Ie, D. H. Park, W. K. Choi, J.-W. Choi, and B. Angadi, "Cu-doped ZnO-based p–n hetero-junction light emitting diode," Semicond. Sci. Technol. **23**(9), 095004 (2008).
24. Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, "A comprehensive review of ZnO materials and devices," J. Appl. Phys. **98**(4), 041301 (2005).
25. M. D. McCluskey and S. J. Jokela, "Defects in ZnO," J. Appl. Phys. **106**(7), 071101 (2009).

1. Introduction

Phosphor nanoparticles have attracted much attention as down-converting materials for lighting devices, such as light-emitting diodes (LEDs), due to their low fabrication cost and high color-rendering index [1–6]. The recent major advances in III-nitride-based device technologies have resulted in significant progress in addressing internal quantum efficiency [7,8], and efficiency droop for light emitters [9–11]. White LEDs with a high color-rendering index are easily prepared by a capping of resin, which includes phosphor nanoparticles, on blue LEDs or UV LEDs [12,13]. From a material viewpoint, Cd-based semiconductor nanoparticles such as CdS, CdTe, and CdSe have been extensively studied; since their preparation is simple, and their luminescent quantum efficiency can be sufficiently improved by growing an inorganic shell of wide bandgap semiconductor around the particles [14]. In spite of good performances, these Cd-based materials are limited in their practical use because Cd is a controlled pollutant. Alternative Cd-free materials are therefore, required for practical application with phosphor nanoparticles in down-converting lighting devices.

Zinc Oxide (ZnO) is a wide bandgap (3.3eV) II-VI compound semiconductor, which can be considered as a potential candidate for down-converting phosphor materials. It contains no rare earth elements, or any controlled environmental pollutants. In addition, ultraviolet (UV) emission of ZnO can be rather easily shifted to the visible region by introduction of suitable impurities [15]. Cu, one of the Group-IB elements, has been known to cause ZnO emission in the light-blue range when used as a dopant [16]. A number of studies into the photoluminescence (PL) properties of Cu-doped ZnO have been reported, but few have clearly investigated PL centered on the blue range. L. Ma et al. have observed multiple peaks,

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including PL centered at blue and green, from Cu-doped ZnO films prepared by radio-frequency (RF) magnetron sputtering [17–21]. They attributed those peaks to energy levels formed by Zn interstitials, and oxygen vacancies. Similar results have been observed by using a variety of deposition methods, which includes pulsed laser deposition (PLD) [22], and plasma assisted molecular beam epitaxy (PA-MBE) [23].

In this article, we report the results of Cu-doped ZnO thin films with PL centered on the blue range (480 nm). The films were prepared through sequential electron beam (e-beam) deposition of ZnO and Cu, and then annealed at high temperature to induce oxidation and Cu diffusion. As reference samples, ZnO-CuO_x mixture films were prepared by PLD. To prevent crystallographic effects of the substrate on film growth, we used amorphous substrates that were intentionally not heated to investigate copper doping effects on the emission properties of ZnO. Results show that the homogeneous distribution of Cu impurity, and the diffusion path for oxygen gas, is decisive in suppressing the emissions attributed to oxygen vacancy, and promoting the blue emissions attributed to the Cu dopant. Color points of the blue emissions are in close proximity to the locus of points that follow the line of a black-body-radiator on the CIE 1931 X-Y chromaticity diagram.

2. Experimental

In order to investigate PL by Cu deposition doping of ZnO thin films, 200 nm thick Cu-doped ZnO thin films were prepared on thermally oxidized Si substrates (SiO_x/Si) by PLD. A cylindrical pellet (4x20 mm^2) of CuO_x-ZnO with a ratio of 1:99 wt% for the PLD target was prepared by spark plasma sintering at 750 °C under 30 MPa of pressure. The substrates were ultrasonically cleaned with acetone and alcohol in sequence for 15 min, and then dried in air. After transferring the substrate to a holder block, the vacuum chamber was pumped to $5x10^{-7}$ Torr in preparation for deposition. During deposition, there was no flow of oxygen. Cu-doped ZnO films were directly deposited by the irradiation of a KrF excimer laser (wavelength: 248 nm, energy: 400 mJ, and with a repetition rate of 2 Hz on target surface 5 cm from the substrate). Double layer films of Cu/ZnO were prepared by e-beam deposition to fabricate Cu-doped ZnO thin films by Cu diffusion. ZnO films with a thickness of 300 nm were deposited by using ZnO pellet sources (99.9999%, 2-5 mm) at 7 kV and 30 mA. Next, 40 nm thick Cu films were deposited in sequence by using a Cu grain source (99.9999%, 2-5 mm) at 7 kV and 120 mA. The base and working pressures were kept at $5x10^{-7}$ and $2x10^{-5}$ Torr, respectively. The films were annealed using a box furnace and an oxygen atmosphere for 90 min at 500, 700, and 850 °C, in order to promote oxidation and Cu diffusion into the ZnO matrix. PL and color properties were evaluated with a photospectrometer (Jasco FP-6000), and spectrometer (PR-655, Photo Research Inc.), respectively. Crystallography, cross-sectional structure, and the surface morphology of the films was measured with a powder X-ray diffractometer (XRD; Philips X'Pert APD), scanning transmission electron microscope (STEM; JSM-6701F), and atomic force microscope (AFM; XE-100), respectively.

3. Results and discussion

3.1 Photoluminescence in the green range for Cu-doped ZnO thin films by pulsed laser deposition

Figure 1 shows PL spectra for films annealed in oxygen at 500, 700, and 850 °C. The peaks centered at 378 nm (3.28 eV) and 523 nm (2.37 eV), and deep level emissions start to appear in the sample annealed at 500 °C. The appearance of the emission peaks means that not just crystallization, but also oxidation, of the ZnO was improved by annealing at 500 °C. Further increase in the annealing temperature up to 850 °C enhanced the intensity of each peak. The peaks at 378 nm, and deep level emissions, are typical peaks of ZnO attributed to near band edge (NBE) and oxygen defects, respectively. The peak centered at ~523 nm (~2.37 eV) was mainly ascribed to Cu dopants in ZnO [16], which means that Cu atoms were successfully

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incorporated into ZnO during deposition. Figure 1 also shows that the peak centered at 523 nm (2.37 eV) slightly blue shifted to 517 nm (2.39 eV) by oxygen annealing at 700 and 850 °C. Looking more closely at the PL peak centered at 523 nm, it can be seen to consist of sub peaks attributable to Cu dopants and oxygen vacancies. The variation in the concentration ratio between the Cu dopant and oxygen vacancies was caused by the annealing conditions, and resulted in the change in intensity of the sub peaks. The center shifts towards blue as the sub peak in the blue range is dominant at higher annealing temperatures. This fact was recognized by full width at half maximum (FWHM) of the peaks measured at 93 nm. Typically, FWHM of monochromatic emission is known to be as low as several tens of nanometers [14].

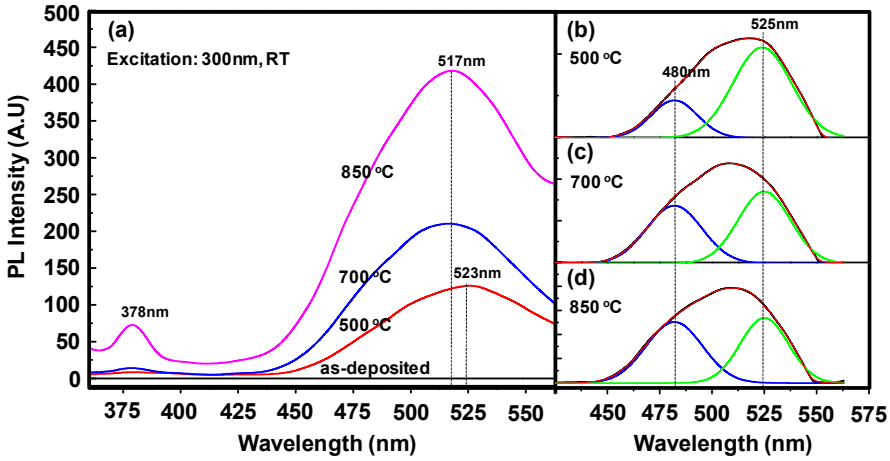

Fig. 1. PL spectra of Cu-doped ZnO thin films prepared by pulsed laser deposition (a) as-grown and after annealing at 500, 700 and 850 °C, and Gaussian fittings (b) 500 °C (c) 700 °C (d) 850 °C.

Peak properties for each temperature were analyzed in detail by Gaussian fitting, as shown in Figs. 1(b), 1(c) and 1(d). Two peaks, centered at 480 and 525 nm, appeared after oxygen annealing at 500 °C. The peak centered at 480 nm (2.58 eV) was considered to be the result of the formation of a shallow acceptor level, caused by Cu doping of ZnO. Yan et al. [16] explained that the high concentration of Cu atoms could be incorporated into ZnO, because of the low formation energy of substitutional Cu atoms. In this case, a defect band can form inside, and narrow, the ZnO bandgap. They calculated that Cu dopants form an acceptable level below 2.7 eV at the conduction band minimum of ZnO. This result is consistent with the present observation of blue emission at 480 nm.

When the samples were annealed at 700 and 850 °C, it was found that the emission intensity of each sub peak was enhanced. Moreover, the emission at 480 nm by Cu dopants became more dominant than the emission at 525 nm by oxygen vacancy (Figs. 1(c) and 1(d)), and the enhancement at 480 nm resulted in blue shift of the peak center at 523 to 517 nm.

On the other hand, the above analysis indicates that the PL spectrum centered at 523 nm cannot be a single component in these films, because both oxygen defects and Cu dopants in ZnO films simultaneously increase with annealing temperature. We consider that the inhomogeneous distribution of Cu dopants in ZnO thin films is one of the main reasons for this. A target homogenously mixed with Cu and ZnO at an atomic scale is an ideal for producing thin films with uniform composition by PLD process, but it is nearly impossible to achieve practically as targets are fabricated with the more macroscopic methods of mechanical mixing and sintering. In addition, Cu atoms are oxidized in plume, as well as on the substrate surface, resulting in the formation of CuO_x during film deposition.

#196364 - $15.00 USD Received 27 Aug 2013; revised 20 Sep 2013; accepted 20 Sep 2013; published 24 Sep 2013

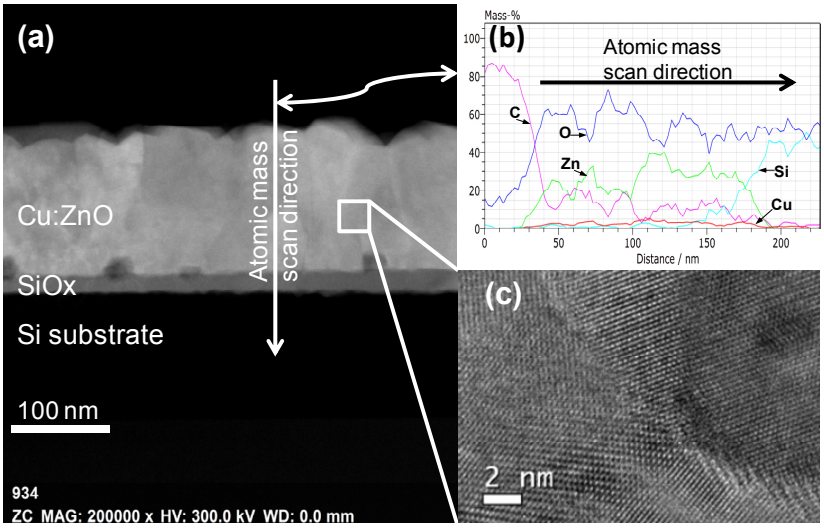

Fig. 2. Cross-sectional image and atomic mass profile of Cu-doped ZnO thin films by pulsed laser deposition (annealed at 850 °C) (a) low magnification (b) atomic mass-% profile (c) HR-TEM image.

This idea was supported with an atomic mass-% scan by STEM (Figs. 2(a) and 2(b)), which revealed that the distribution of Cu atoms in depth is not uniform after annealing at 850 °C. The HR-image also shows that the thin films form relatively dense structures (Fig. 2(c)). These are thought to be barriers for Cu and oxygen atoms to diffuse into the whole area of the ZnO film. As a result, it is concluded that Cu deposition doping of ZnO thin films by PLD is not an adequate method for enhancing Cu doping effects, and alternative approaches are needed that can distribute Cu atoms homogeneously into ZnO film.

3.2 Blue shift of photoluminescence in Cu-doped ZnO thin films by e-beam deposition

We considered the e-beam deposition method as a suitable technique for homogeneously distributing Cu dopants into ZnO thin films. With this, porous and amorphous films of ZnO can form while sustaining a low substrate temperature. The subsequent deposition of Cu dopants and oxygen annealing can promote homogeneous diffusion of Cu and oxygen atoms into the ZnO film. In this experiment, we deposited 340 nm thick Cu/ZnO double layer films on SiO_x/Si substrates by e-beam deposition. The films were deposited on the substrates through the sequential deposition of ZnO and Cu films at room temperature (RT).

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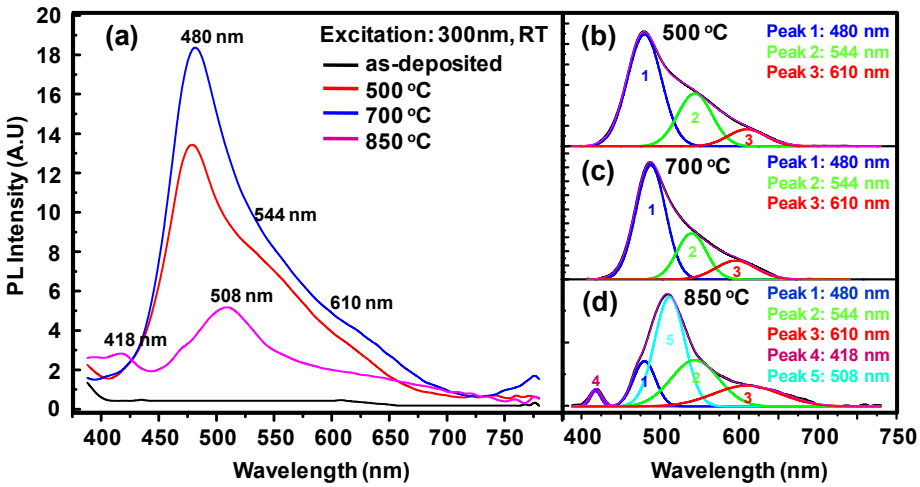

Fig. 3. PL spectra of the Cu-doped ZnO thin films prepared by e-beam deposition (a) as-grown and after annealing at 500, 700 and 850 °C, and Gaussian fittings (b) 500 °C (c) 700 °C (d) 850 °C.

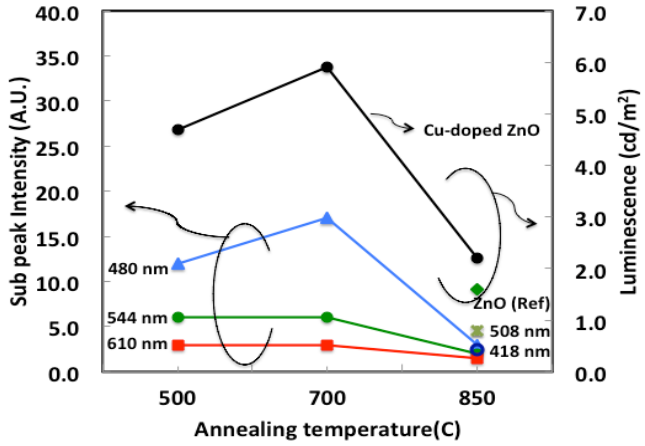

Fig. 4. The variation of sub peak and luminescence intensity in Cu-doped ZnO prepared by e-beam deposition according to annealing temperature.

The PL spectra of the annealed samples are shown in Fig. 3. A strong blue peak with shoulders, centered at 480 nm (2.58 eV), appeared in the sample annealed at 500 °C. The appearance of a single peak centered at 480 nm means that the effects of the Cu dopant, in terms of emission properties, were improved compared to those films produced by PLD (Fig. 1(a)). Further increase in the annealing temperature up to 700 °C enhanced the emission intensity by Cu dopants, but depressed the peak shoulder as shown in Fig. 3(c) and Fig. 4. This was considered a result of the promotion of Cu diffusion doping of ZnO thin film during annealing, however, when the annealing temperature was raised to 850 °C a new weak blue peak at 418 nm (2.96 eV), and a green emission band at 508 nm (2.44 eV), were observed. The strong blue peak intensity of 480 nm was also drastically decreased (Figs. 3(d) and 4).

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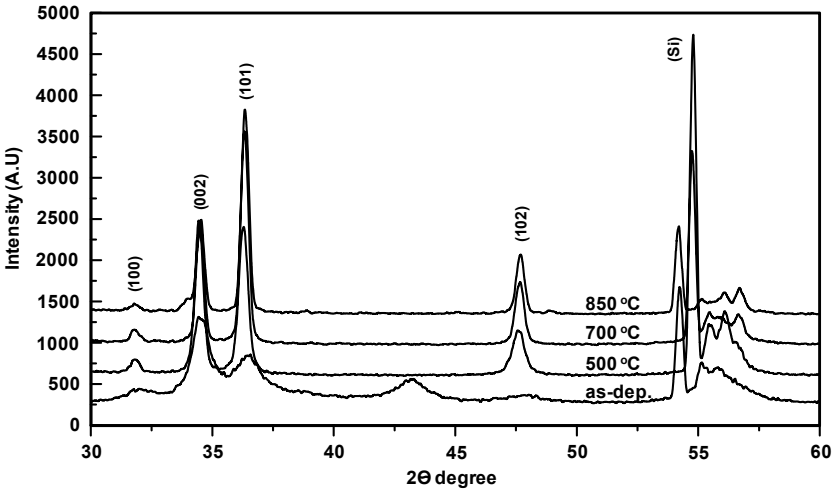

Fig. 5. XRD patterns of Cu-doped ZnO thin films on SiO_x/Si substrate by e-beam deposition (a) as-grown, and after annealing (b) 500 °C (c) 700 °C (d) 850 °C.

For detailed analysis, we investigated the crystallography and cross-sections of the films. Figure 5 shows the XRD patterns of Cu-doped ZnO films both before and after annealing. The diffraction patterns indicate that all samples have a single-phase wurtzite hexagonal ZnO structure. There are no additional characteristic peaks related to Cu/CuO_x, or any other secondary phases distinguishable within the detection limit. These results lead to the conclusion that the green shift after annealing at 850 °C resulted from deep level emission ascribed to oxygen defects, and by the presence of Zn vacancies such as vacancy complexes [24,25].

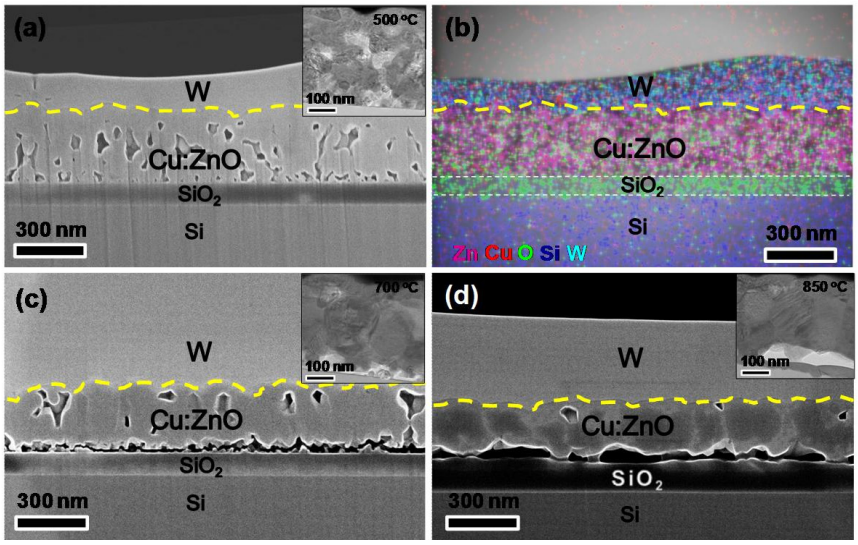

Fig. 6. Cross-sectional STEM images and EDX elemental mapping of Cu-doped ZnO thin films on SiO_x/Si substrate by e-beam deposition, after annealing at (a) 500 °C and (b) corresponding EDX mapping (c) 700 °C (d) 850 °C, inserts are HR-TEM images.

Detailed analysis by STEM revealed that the films produced by e-beam deposition have a porous structure after annealing at low temperature, which is favorable to the diffusion of oxygen and Cu atoms, but the films have denser structure after annealing at 850 °C. Figures

#196364 - $15.00 USD Received 27 Aug 2013; revised 20 Sep 2013; accepted 20 Sep 2013; published 24 Sep 2013

6(a) and 6(b) show a cross-sectional image, and corresponding EDX mapping, for Zn, Cu, and O, respectively. This demonstrates that Cu atoms diffused homogenously at 500 °C. It is known that the density of the film increases with annealing temperature (Figs. 6(c) and 6(d)). The voids in the film completely disappeared after annealing at 850 °C, with the structure becoming similar to that of the bulk material. From this structural evolution of the films, it is believed that Cu atoms could chemically bond with oxygen atoms in ZnO, because sufficient oxygen gas could not be provided through such a dense film structure at ambient temperature. Therefore, oxygen vacancies and Zn interstitials prevail, which results in a further decrease in bandgap by the generation of impurity energy levels after annealing at 850 °C. Consequently, Cu doping effects disappear, and the emission peaks become nearly identical to those of ZnO ascribed to Zn vacancies [25].

3.3 Color property of blue enhanced photoluminescence in Cu-doped ZnO thin films

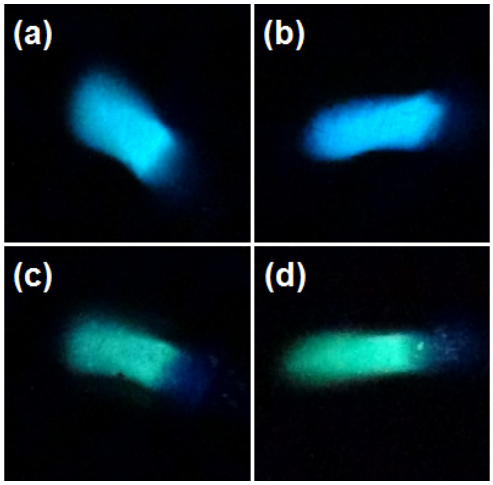

Fig. 7. Photo images of photoluminescence in Cu-doped ZnO and pure ZnO thin films by e-beam deposition, after annealing at (a) 500 °C (b) 700 °C (c) 850 °C (d) 850 °C (pure ZnO, reference sample).

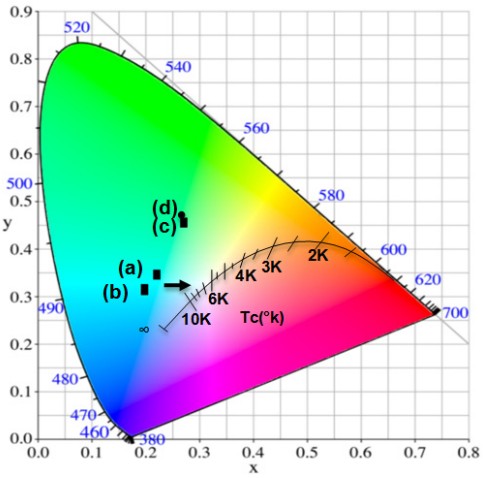

Fig. 8. CIE coordinates of photoluminescence in Cu-doped ZnO and pure ZnO thin films, after annealing at (a) 500 °C (b) 700 °C (c) 850 °C (d) 850 °C (pure ZnO, reference sample).

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Figure 7 shows photo images of PL in Cu-doped ZnO thin films. The images for blue emission at Figs. 7(a) and 7(b) are not distinguishable with the naked eye. However, Fig. 7(c) shows that the color is shifted to green, and the intensity is drastically decreased. More specifically, the intensity decreased from 6 cd/m^2 at 700 °C, to 2.2 cd/m^2 at 850 °C (Fig. 4), which is nearly the same as for ZnO thin films annealed at 850 °C (Figs. 7(d) and 4). Figure 8 shows the color coordinates of PL on the CIE 1931 X-Y chromaticity diagram. Color points of the sample at 500 and 700 °C (Figs. 8(a) and 8(b)) were evaluated as (0.254, 0.3485) and (0.2522, 0.3483), respectively. It is known that these points are in close proximity to the locus of points following the line of a black-body-radiator. This is because the emission peaks at 480, 544 and 610 nm are mixed (Figs. 3(b) and 3(c)). The points are also located to the left hand side of daylight, with a color temperature of 6000~6500 K, meaning that daylight can be mimicked by a combination of Cu-doped ZnO and red phosphor. The color point at 850 °C (Fig. 8(c)) was found to be close to that of ZnO (Fig. 8(d)), with values of (0.2819, 0.3663) and (0.2552, 0.4754), respectively.

4. Conclusion

In summary, we fabricated ZnO films with blue PL by Cu diffusion doping. PL centered on the green range of 523 nm in Cu-doped ZnO thin films, produced by conventional PLD consisted of sub peaks at 480 and 525 nm. Cu-doped ZnO thin films with PL centered at 480 nm were achieved by preparing double layer films of Cu/ZnO with a porous structure by e-beam deposition and sequential annealing, in order to promote Cu diffusion at high temperatures. The color points of blue emission were located in close proximity to the locus of points following the line of a black-body-radiator, this is because small amount of the deep level emissions at 544 and 610 nm is mixed. These results mean that white light with a color temperature of 6000~6500 K can be produced by a combination of Cu-doped ZnO and red phosphor, and Cu-doped ZnO therefore has strong potential as a cost effective phosphor for use in down converting LEDs, including white LEDs and laser diodes. The present results also imply that Cu-doped ZnO can respond to shorter wavelengths than deep blue, potentially allowing cost effective blue and white LEDs to be produced from UV and deep-blue LEDs. In addition, the fabrication of visible-light LEDs can be simplified by using ZnO-based UV LEDs.

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