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Realization of strong violet and blue emissions from ZnO thin films by incorporation of Cu ions

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ABSTRACT

In recent years, Cu-doped ZnO materials have attracted wide attention due to some unique properties, such as p-type conduction, room-temperature ferromagnetism and plentiful luminescence behavior. In this work, Cu-doped ZnO thin films with different doping levels were prepared by sol–gel method. The structural, morphological features and the composition of the samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX), respectively. The optical properties were analyzed by the UV–visible transmittance spectra and fluorescence spectra. The Cu-doping in a low concentration does not influence the crystal phase of wurtzite ZnO and has a very small impact on c-axis preferred orientation of ZnO thin films. With the increase of Cu-doping concentration, the Cu ions are gradually changed from dominant Cu^{+} ions to dominant Cu^{2+} ions. Cu-doping in a low concentration caused strong blue-violet emissions in ZnO thin films. The violet emission is attributed to the transition of electrons from the conduction band to Cu^{+} acceptor levels, and the blue emission is ascribed to the transition of electrons from Cu^{2+} donor levels to Cu^{+} acceptor levels.

1. Introduction

In the last two decades, Zinc oxide (ZnO) has become one of the most widely studied wide bandgap semiconductors [1–6], mainly because it has some attractive features such as wide direct bandgap of ~3.37 eV, large exciton binding energy (~60 meV), a variety of morphologies, adjustable resistivity and so on. ZnO is considered to be one of the best candidate materials for the fabrication of short wavelength light-emitting devices and solid-state white light-emitting devices, so its luminescent properties have been attracting wide attention in the world [7–12]. Usually, ZnO shows a strong UV emission peak and a wide visible emission band. Now, for the study of ZnO luminescence, it is mainly concentrated on three aspects: (1) how to effectively improve the UV emission efficiency [13]; (2) exploring the visible emission mechanisms [7,8,14]; (3) controlling the visible emission behavior of ZnO materials [9–11,15], such as, making it emit violet, blue and red light at the same time, etc. If one wants to tailor the luminescent behavior of ZnO materials, doping is one of the most effective methods. For example, Drmosh et al. [16] deposited Cu-doped ZnO thin films with different doping levels by pulsed laser deposition, and they found that the near-band edge (NBE) emission centered at 393 nm disappeared and a violet emission centered at 423 nm occurred after Cu was doped into ZnO. Yu et al. [17] grew Cu-doped ZnO nanorods by a hydrothermal method; they found that the Cu-doping led to a stronger green emission in ZnO when the ZnO nanorods were excited by a UV light with a wavelength of 325 nm; however, the Cu-doping led to a weaker green emission in ZnO when the ZnO nanorods were excited by a UV light with a wavelength of 280.6 nm. Koshy and Khadar [18] observed that Cu-doping caused the UV emission of ZnO to decrease and led to visible emissions with multiple wavelengths including 410 nm and 423 nm. Sreedhar et al. [15] found that Cu-doping resulted in a stronger violet emission centered at 405 nm in ZnO thin film, but the NBE emission centered at 386 nm and the violet emission centered at 424 nm were hardly affected by Cu-doping.

Although some Cu-doped ZnO materials have been studied, the experimental results still show great divergence. For example, as for the solid solubility of Cu in ZnO, some researchers found that the solid solubility of Cu in ZnO was low [17,19], others found that the solid solubility of Cu in ZnO was high [15,20]. For another example, in regard to the effect of Cu-doping on the luminescence of ZnO, some researchers found that Cu-doping resulted in a green emission in ZnO and attributed the green emission to the Cu impurity related transitions

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[19,21], however, others found that Cu-doping did not cause green emission but led to other emissions like violet emissions [16]. In respect to the violet and blue emission mechanisms, there are also different views. Some researchers deem that the violet/blue emission is related to the intrinsic defects of ZnO and has nothing to do with Cu ions [16]. However, other researchers believe that Cu impurity is a luminescent center [18,22]. Therefore, it still needs more and deeper research on the physical properties of Cu-doped ZnO materials, which is important not only for the tailoring of the luminescent behavior of ZnO but also for obtaining stable Cu-doped p-type ZnO and disclosing the mechanism of room-temperature ferromagnetism in Cu-doped ZnO. In view of this, in this work, we carried out a systematic investigation on the effect of Cu-doping on the luminescent behavior of ZnO thin films.

In this work, Cu-doped ZnO thin films were prepared by sol–gel method. The choice of sol–gel method is because it has some advantages such as low cost, simple operation, easily achieving molecular level doping and good uniformity for the deposited films. However, the Cu-doped ZnO films prepared by the sol–gel method have been relatively fewly reported so far. We find that Cu-doping leads to a strong blue-violet co-emission in ZnO, and such strong blue-violet co-emission is rarely reported. The mechanisms behind the violet and blue emissions have been tentatively proposed. These results are beneficial for the development of blue-violet light-emitting diodes or flat panel displays.

2. Experiments

The Cu-doped ZnO thin films were deposited by sol–gel method. Firstly, ZnO sols were prepared using zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$), copper acetate ($Cu(CH_3COO)_2{\cdot}H_2O$), anhydrous ethanol, monoethanolamine (MEA) as precursor, dopant, solvent and stabilizer, respectively. In the ZnO sols, the molar ratio of zinc acetate to MEA is 1:1; the Zn^{2+} concentration is 0.3 mol/L; the doping level of Cu (Cu/Zn) is 0, 1, 2, 3 and 4 at.%. These ZnO sols are aged at room temperature for 24 h and then ZnO thin films are deposited by spin-coating these sols on substrates. When one spin-coating process is finished, the sol film will be dried by an infrared lamp for 5 min and then be preheated at 270 °C in a muffle furnace for 3 min in order to evaporate the solvent and remove organic residuals. The procedures from spin-coating to preheating treatment are repeated several times to obtain a desired thickness for the ZnO films. At last, the ZnO thin films are annealed at 500 °C for 1 h in air atmosphere. The thickness of the films is measured by an ellipsometer using a light source with a wavelength of 632.8 nm, which is all about 100 nm.

The crystal phase and crystalline orientation of the Cu-doped ZnO thin films were determined by an X-ray diffractometer (SmartLab). The surface morphologies of the samples were observed by a field emission scanning electron microscope (S4800). The surface roughness of the films was measured by an atomic force microscope (CSPM4000). The composition and the chemical bonding states of the constituent elements of the films were analyzed by an X-ray photoelectron spectrometer (Thermo escalab 250Xi). The optical transmittance of the samples was measured by a double beam spectrophotometer (Cary5000). The photoluminescence spectra were recorded by a spectrometer (LabRAM HR800) using a He-Cd laser as the excitation source with a wavelength of 325 nm.

3. Results and discussion

3.1. The structure, morphology and chemical composition of the Cu-doped ZnO thin films

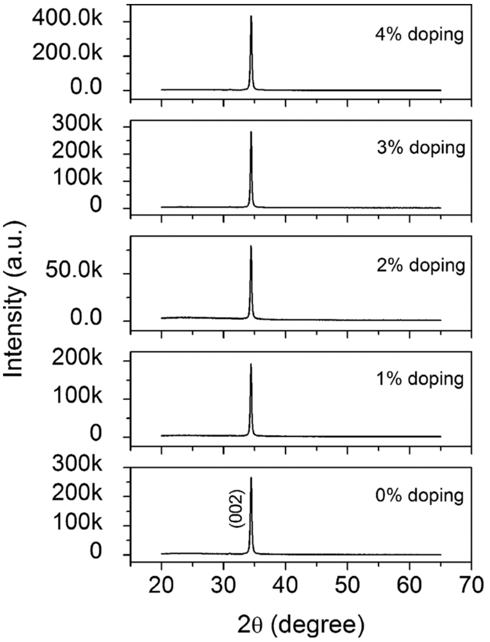

Fig. 1. XRD patterns of the samples.

Fig. 1 shows the XRD patterns of Cu-doped ZnO thin films with different doping concentrations. All the films only show a strong (002) peak, indicating that all the samples are crystallized in a wurtzite phase and ZnO grains are oriented preferentially along the c-axis direction which is perpendicular to the substrate surface. As for the 0, 1, 2, 3 and 4 at.% Cu-doped ZnO thin films, their (002) peak is located at 34.43°, 34.42°, 34.41°, 34.42° and 34.44°, respectively. With the increase of Cu-doping concentration, the (002) peak first moves toward the smaller angle direction, and then moves to the large angle direction. The similar phenomenon was also observed in other Cu-doped ZnO materials [16]. The change in the position of the (002) diffraction peak should be caused by the variation in valence state of the doped Cu ions. It well known that for Cu^+, Cu^{2+} and Zn^{2+} ions, their ionic radii are 0.096 nm, 0.072 nm and 0.074 nm, respectively. If numerous Cu^+ ions enter ZnO lattices and substitute Zn^{2+} ions, the lattice constant c will increase since the ionic radius of Cu^+ is larger than that of Zn^{2+}. Accordingly, the interplanar spacing d along the c-axis direction will also increase. From the Bragg equation: $2d\sin\theta = n\lambda$, we can know that when the interplanar spacing d increases, the diffraction angle θ will decrease; that is to say, the (002) peak will shift towards the smaller angle direction. If numerous Cu^{2+} ions enter ZnO lattices and substitute Zn^{2+} ions, the opposite phenomenon will occur. Based on this, we can infer that Cu ions should be mainly present in +1 valence state in ZnO when Cu-doping concentration is lower than 3 at.%; however, Cu ions would be mainly present in +2 valence state in ZnO when Cu-doping concentration is higher than 3 at.%. The similar variation of Cu valence state with the increase of Cu-doping concentration in ZnO has been also reported by others. For example, Jongnavakit et al. [23] deposited Cu-doped ZnO thin films by sol–gel method with the doping concentration in the range of 0.1–1.0 mol% and mainly investigated the photocatalytic activity of the samples. They found that the valence state of Cu ions was gradually changed from +1 to +2 with the rise of Cu-doping concentration. They deem that if numerous Cu^+ ions substitute Zn^{2+} ions, lots of holes will be produced, which make the system be less stable as the net charge is not zero. It is possible that more generated Cu^{2+} ions allow the system to be more stable at higher Cu-loadings [23]. It should be pointed out that the valence state of Cu ions in ZnO is not only influenced by the doping concentrations but also many other factors such as deposition method, annealing temperature, growth temperature, etc. In addition, it should be noticed that the difference of ionic radius between Cu^{2+} and Zn^{2+} is very small. Therefore, the effect of low concentration Cu^{2+} ions substitution for Zn^{2+} ions has little effect on the lattice constant, crystal quality and growth orientation of ZnO [20,24]. For example, Khan and Ghosh [20] prepared Cu-doped