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Synthesis and photoluminescence of Y and Cd co-doped ZnO nanopowder

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Abstract: Y and Cd co-doped ZnO nanopowders were prepared via chemical precipitation method in order to modify the band gap and increase the luminescent intensity. The structures and optical properties of the as-synthesized samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). The effects of Y and Cd ions on the optical properties of the samples were studied. Doping of Y into ZnO evidently increases the intensity of UV emission, or co-doping of Y and Cd enhances the UV emission, narrows the band gap of ZnO and hence red shifts the UV emission at the same time. Therefore, Y and Cd co-doped ZnO nanopowders exhibit an intense violet emission in the room temperature PL spectrum, which could be a potential candidate material for optoelectronic applications.

Key words: ZnO nanopowders; chemical precipitation; optical properties

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1 Introduction

In the last few years, the hexagonal wurtzite ZnO, especial doped ones, has attracted numerous attention due to its unique optical properties and promise applications in optoelectronic devices [1−3]. In order to obtain properties expected, different kinds of dopants have been doped into ZnO lattice, such as rare earth elements [4,5], metals [6−10]. One important aim of doping elements into ZnO is called as “band gap engineering (or modification)”, i.e., increasing or decreasing the band gap energy of ZnO through doping specific elements, and hence the intrinsic UV emission of ZnO in its PL spectrum can be blue or red shifted to satisfy some specific applications [11,12]. For example, it was reported that doping Mg could effectively widen the band gap of ZnO as the oxide of Mg (MgO) shows a wide band gap [13], and doping Cd could narrow the band gap of ZnO for the same reason [14]. ZnO:Y thin films were prepared via sol−gel technique and it was found that the intensity of UV emission centered at 375−380 nm was enhanced by choosing appropriate annealing temperature without obviously position changing [15]. In our previous work [16], similar phenomena were observed. However, when the UV emission blue- or red-shifted, the emission intensity usually decreased. On the other hand, enhanced emitting intensity often existed without “band gap engineering”, that is, one disadvantage is that doping of heterogeneous element can induce various lattice defects or split band gap, which decreases the UV emission intensity or broadens the emission wavelength range. So, it is sometimes difficult to red or blue shift the UV emission without decreasing its luminescent intensity. Therefore, one potential aim on band gap modification is to hold or increase the emission intensity while the intrinsic emission is blue- or red-modified through doping or co-doping.

In the present work, we intend to add two elements of Y and Cd into ZnO crystalline lattice with an expectation that an intensive and red-shifted UV emission would be attained. Y and Cd co-doped ZnO powders were synthesized via chemical precipitation method and the photoluminescence properties were investigated.

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2 Experimental

In our experiments, all reagents were in analytical grade (purchased from Sinopharm Chemical Reagent Co., Ltd.) and used without further purification. Three powders of ZnO, $Zn_{0.97}Y_{0.03}O$ and $Zn_{0.94}Y_{0.03}Cd_{0.03}O$ were prepared by chemical precipitation method. The synthesized process of $Zn_{0.94}Y_{0.03}Cd_{0.03}O$ was as follows: $Zn(NO_3)_2·6H_2O$ and the stoichiometric quantities of $Y(NO_3)_3·6H_2O$ and $Cd(NO_3)_3·6H_2O$ were dissolved in deionized water with stirring to form main mixture solution. And a solution of NH_4HCO_3 was added into the main mixture solution gradually. The reaction between the two solutions lasted for 4 h until adequate white precipitate was formed. The white precipitate was filtered and washed with alcohol several times and then placed in a drying oven at 50 °C for drying. At last, the dried product was annealed at 400 °C for 2 h to form the final powder.

X-ray diffraction was employed to determine the phase structure on a D/max-Rigaku XRD diffraction spectrometer with a Cu K_α line of 1.5417 Å and a monochromator at 40 kV and 250 mA. X-ray photoemission spectroscopy (XPS) was used to investigate the energy states of yttrium and cadmium elements in the $Zn_{0.94}Y_{0.03}Cd_{0.03}O$ powder. The XPS spectra were obtained with an ESCALABMK II (Vacuum Generators) spectrometer using unmonochromatized Al K_α X-rays (240 W). Cycles of XPS measurements were done in a high vacuum chamber with a base pressure of 133.322×10^{-8} Pa. PL spectra were measured at room temperature with a fluorescence spectrophotometer using a He−Cd laser of a wavelength of 325 nm as the excitation light source. All powder samples for PL measurement had the same quality and were tested under the same condition.

3 Results and discussion

X-ray diffraction patterns of the three as-synthesized powders (ZnO, $Zn_{0.97}Y_{0.03}O$ and $Zn_{0.94}Y_{0.03}Cd_{0.03}O$) are shown in Fig. 1. All the diffraction peaks correspond to the wurtzite structure of ZnO, without any secondary phases detected, which indicates that both Y and Cd elements have been doped into ZnO crystalline lattice. The Scherrer formula was used to estimate the crystallite sizes of these powders. The estimated average grain sizes are 38.9 nm, 13.9 nm and 12.9 nm, for ZnO, $Zn_{0.97}Y_{0.03}O$ and $Zn_{0.94}Y_{0.03}Cd_{0.03}O$, respectively. So these powders can be called as nanopowders. The evident reduction of grain size of the doped samples is attributed to the crystal lattice distortion caused by the doping of bigger radium Y and Cd ions into ZnO lattice, which restrains crystalline grains from growing up.

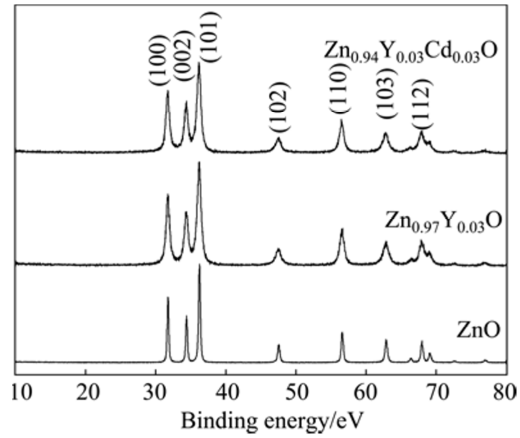

Fig. 1 XRD patterns of ZnO, $Zn_{0.97}Y_{0.03}O$ and $Zn_{0.94}Y_{0.03}Cd_{0.03}O$

In order to determine the chemical states of Y and Cd in the as-synthesized nanopowders, the XPS spectra of $Zn_{0.94}Y_{0.03}Cd_{0.03}O$ were measured and are shown in Fig. 2. Figure 2(a) depicts the XPS survey spectrum, in which all the peaks of Zn, Y, Cd, O and C elements are labeled, with the adventitious carbon C 1s peak at 285.0 eV used as reference for calibrating the binding energy. Figure 2(b) shows the XPS spectrum of Zn 2p in the Y and Cd co-doped ZnO particles. The binding energies of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ locate at 1020.7 eV and 1043.6 eV, respectively, and the peak separation between them is 22.9 eV, which is well located in the range of the standard reference value of ZnO [17]. It indicates that the majority of Zn ions mainly exist in the lattice of zinc oxide [18].

The spectrum of O 1s is shown in Fig. 2(c), and the peak located at 529.9 eV is attributed to O^{2-} ions at intrinsic sites, that is, O^{2-} ions are surrounded by zinc atoms with the full supplement of nearest-neighbor ones. The peak at 531.7 eV is usually attributed to the presence of loose oxygen on the sample surface of ZnO particle, i.e., adsorbed O_2 or H_2O [19,20]. As shown in Fig. 2(d), the spectrum of Y 3d has two peaks centered at 157.7 eV and 159.5 eV, which are attributed to the binding energy of Y $3d_{5/2}$ and Y $3d_{3/2}$, respectively. According to the stand binding energies of Y $3d_{5/2}$ at 156.6 eV and Y $3d_{3/2}$ at 157.4 eV, there are some shifts of 1.1 eV and 2.1 eV, respectively, in binding energy, which indicates that the binding energy of Y—O band doped in ZnO lattice is slightly different from that of pure Y_2O_3. Figure 2(e) depicts the XPS spectrum taken from Cd 3d regions, referencing that the binding energy of Cd 3d level in CdO is 403.0 eV [21]. The two peaks located at 404.9 eV and 411.8 eV are attributed to the binding energies of Cd $3d_{5/2}$ and Cd $3d_{3/2}$ respectively, i.e., the Cd—O bond in