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Color tuning of photoluminescence from ZnS nanobelts synthesized with Cu and Mn doping and without intentionally doping

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ABSTRACT

Unintentionally doped and Cu and Mn doped ZnS nanobelts were synthesized via the vapor phase transport method. The nanobelts have the single crystalline wurtzite structure. By modifying the mass ratio of source to dopant, the photoluminescence (PL) spectra from the Cu and Mn doped ZnS nanobelts can be tuned to center around 450 nm (blue) and 580 (orange), respectively. The PL spectra from the unintentionally doped ones synthesized in highly purified N_2 and N_2/H_2 gases center around 520 nm (green) and 660 nm (red), respectively. As far as we know, the blue colored PL of Cu doped ZnS nanobelts and the red colored PL of ZnS nanobelts are reported for the first time. In this way, the PL color from ZnS nanobelts can be tuned from blue to red. The ZnS nanobelts have potential application in the nano-multicolor displays.

1. Introduction

Semiconductor nanomaterials have been studied widely in recent years due to their various potential applications in nanodevices, such as field effect transistors, light emitting diodes and laser diodes [1–3]. As an important II–VI semiconductor, ZnS has received great attention for its potential optoelectronic applications [4–6]. ZnS doped with certain transition metals, such as Cu and Mn, can create new optically active luminescence centers, and has been used in phosphor and electroluminescence devices [7,8]. Various ZnS nanobelts have been synthesized in recent years, and their photoluminescence (PL) properties have been studied [9,10]. For the potential phosphor applications, it is important to find a way to tune the color of the PL from ZnS nanobelts.

In this work, we report the synthesis of unintentionally doped and Cu and Mn doped ZnS nanobelts via the vapor phase transport method. The unintentionally doped ZnS nanobelts are synthesized in N_2/H_2 (20 : 1) mix carry gas and highly purified N_2 gas, respectively. In this way, the PL color from ZnS nanobelts can be tuned from blue to red.

2. Experiments

The ZnS nanobelts were synthesized in a quartz tube (about 5 cm in diameter) placed in a furnace. The ZnS powders were used as the source. Silicon wafers thermally evaporated with Au catalyst, were used as the substrates. The source and the substrate were loaded on a quartz boat, which was then inserted into a quartz tube. The distance between the source and the substrates were 8–10 cm, and the temperature of the source and substrates were about 950 °C and 850 °C, respectively. The synthesis duration was around 30 minutes. The flow rate of carry gas is 80–100 sccm. For the synthesis of unintentionally doped ZnS nanobelts, N_2/H_2 (20 : 1) mix gas and highly purified N_2 gas were used as the carry gas, respectively. For the synthesis of Cu and Mn doped ZnS nanobelts, the $CuCl_2$ and $MnCl_2{\cdot}4H_2O$ dopants were placed upstream of the ZnS source, respectively. The distance between $CuCl_2$ and ZnS was about 40 cm, and the temperature of $CuCl_2$ was about 350 °C. While the distance between $MnCl_2{\cdot}4H_2O$ and ZnS was about 32 cm, and the temperature of $MnCl_2{\cdot}4H_2O$

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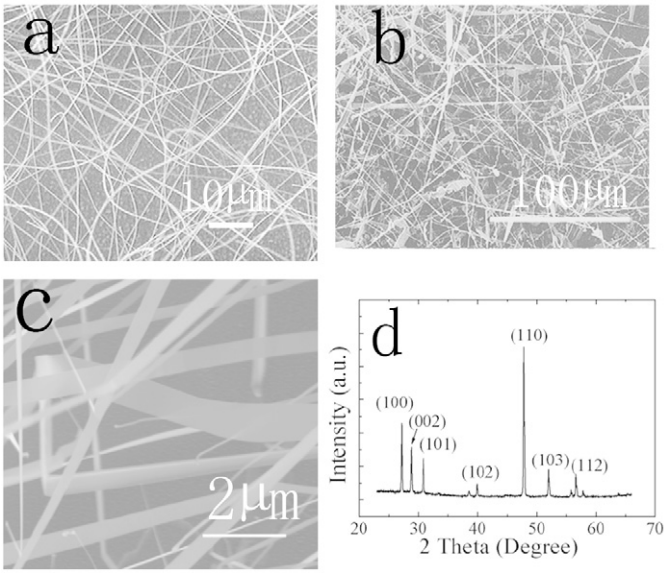

Fig. 1. The FESEM images with (a) unintentionally doped ZnS nanobelts grown in a highly purified N_2 carry gas, (b) Cu doped ZnS nanobelts, and (c) Mn doped ZnS nanobelts; (d) typical XRD pattern of the ZnS nanobelts.

was about 600 °C. The carry gas was highly purified N_2 gas. The as-synthesized products were characterized using an X-ray powder diffractometer (XRD) (Rigaku Dmax-2000), a field emission scanning electron microscope (FESEM) (AMRAY 1910 FE), and a high-resolution transmission electron microscope (HRTEM) (Tecnai F30) equipped with an energy-dispersive X-ray (EDX) spectroscope. Their PL spectra were measured using a micro-zone confocal Raman image system (HORIBA Jobin Yvon, LabRam HR800) equipped with a 40 × UV lens. A 325 nm He–Cd laser was used as the excitation source.

3. Results and discussion

Figs. 1(a), 1(b), and 1(c) show the typical FESEM images of the unintentionally doped, Cu doped, and Mn doped ZnS nanobelts, respectively. We can see that their lengths are hundreds of microns, and their widths and heights are hundreds and tens of nanometers, respectively. Fig. 1(d) shows a typical XRD pattern of the ZnS nanobelts. The peaks can be indexed as crystal planes of the wurtzite ZnS (JCPDS 75-1534). It is worth to be noted that no Cu or Mn related peaks can be found in the XRD patterns of Cu or Mn doped ZnS nanobelts. Fig. 2(a) shows a typical TEM image of the ZnS nanobelts. We can see that the nanobelt has a smooth surface. Fig. 2(b) is the HRTEM image of the nanobelt and the inset is the corresponding selected area electron diffraction (SAED) pattern recorded along the $[1\bar{2}10]$ zone axis. Corresponding Miller indices are labeled in the figure. The HRTEM image together with the SAED pattern demonstrates that the nanobelts are single crystalline wurtzite structure, and the growth direction is [0001].

To examine the element composition of the ZnS nanobelts, EDX measurements were performed on the nanobelts. Fig. 3(a) shows EDX pattern of an unintentionally doped ZnS nanobelt. The EDX data shows that the nanobelts are composed of Zn and S. Fig. 3(b) shows the EDX pattern of a Mn doped ZnS nanobelt. The atom percentage for Mn is about 3%. The Cu peak originates from the sample holder (copper grid coated with carbon film). It is worth to be noted that the content of Cu element in Cu doped ZnS nanobelt cannot be obtained correctly using EDX technique since extra Cu elements can come from the Cu grid.

Fig. 4(a) shows the PL spectra of Cu doped ZnS nanobelts. With the mass ratio of $CuCl_2$ to ZnS changing, the shape of the PL spectra changes. When $CuCl_2 : ZnS = 1 : 2$, two emission peaks can be found in the PL spectra. The main peak centers around 520 nm (green), and the peak locating at the left shoulder of the main one centers around 450 nm (blue), similar to that reported by Li et al. [10]. When the $CuCl_2 : ZnS = 1 : 1$, the intensity of the blue one becomes stronger than that of the green one. When the $CuCl_2 : ZnS = 2 : 1$, only the blue one remains. As far as we know, this is the first time that pure blue colored PL emission is observed from the Cu doped ZnS nanobelts. The blue emission can be attributed to the transition from the conduction band edge of ZnS to the deep trap energy levels formed by Cu^{2+} ions (t_2 state of Cu^{2+}) [11].

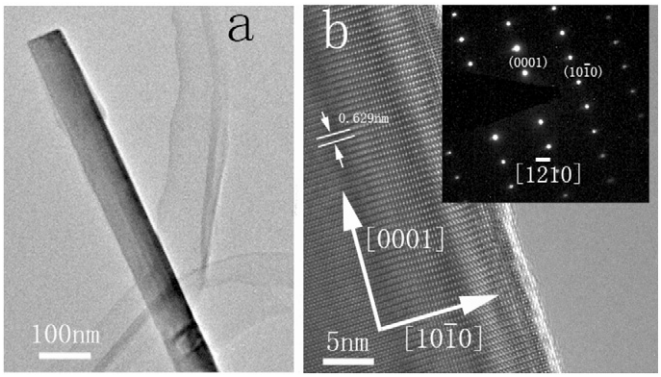

Fig. 2. (a) The typical TEM image of a ZnS nanobelt; (b) HRTEM image of the ZnS nanobelt. The inset is the corresponding SAED pattern recorded along the $[1\bar{2}10]$ zone axis.

Fig. 4(b) shows the PL spectrum of unintentionally doped ZnS nanobelts synthesized in highly purified N_2 carry gas. Only a green emission band centered 520 nm is observed. The green luminescence originates from the S species on the surfaces of the ZnS nanobelts [12].

In our case, 520 nm emissions were found from both Cu-doped samples and unintentionally doped sample under the same highly purity N_2 carry gas. We think this may be due to existence of excessive S elements on the surfaces of the nanobelts.

Room-temperature PL spectra from the Mn doped ZnS nanobelts are plotted in Fig. 4(c). When $MnCl_2{\cdot}4H_2O : ZnS = 1 : 1$, two emission peaks can be found in the PL spectra. The main peak centers around 590 nm, and the peak on the right shoulder of the main one centers around 660 nm. The 580–590 nm PL emission is a characteristic emission of Mn^{2+} ions in ZnS. It is associated with the emission via energy transfer from active states in the ZnS host lattice to the d electron states of Mn^{2+} [13]. The PL result demonstrates that the Mn^{2+} ions have entered into the ZnS crystal lattice structure. In recent years, several groups have investigated the PL properties from Mn doped ZnS nanobelts, and found that the emission band originated from the unexpected defect luminescent centers are usually unavoidable [14,15]. In this work, we find that when modifying the mass ratio of $MnCl_2{\cdot}4H_2O$ to ZnS to be 2 : 3, only one PL peak at 580 nm is observed, and the full width at half maximum (FWHM) of it is only about 50 nm, comparable to that of the Mn doped ZnS by post annealing reported by Li et al. [16].

Fig. 4(d) shows the PL spectrum of the unintentionally doped ZnS nanobelts synthesized in N_2/H_2 mix carry gas. There is only one red emission band centered at 660 nm. Red emission from the ZnS nanobelts has not been reported before. Some groups have reported the red PL of ZnS nanoparticles embedded in silica matrix, and suggest that it may be due to the formation of S vacancies on the surface layers of the ZnS particles [17,18].

In our case, the 660 nm emissions were found from both unintentionally doped sample but using mixed carry gas and Mn-doped samples ($MnCl_2{\cdot}4H_2O : ZnS = 1 : 1$). We think there are more S