Synthesis and photoluminescence properties of Mn-doped ZnS nanobelts*

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Mn-doped ZnS nanobelts have been prepared through a thermal evaporation method at 1100°C. The synthesized nanobelts are characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), and photoluminescence (PL) spectroscopy. The results show that the nanobelts have an uniform single-crystal hexagonal wurtzite structure and grow along [0001] direction. Room-temperature photoluminescence reveals that the intrinsic PL of the nanobelts disappears and a new PL peak of the Mn-doped ZnS nanobelts emerges at 575 nm.

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Zinc sulfide (ZnS), a typical II–VI compound semiconductor with band-gap energy of 3.7 eV at room temperature and exciton binding energy of 39 meV, has attracted considerable attention due to its applications in flat-panel displays, electroluminescent devices, infrared windows, sensors and lasers[1-3]. Recently one-dimensional nanostructures such as nanowires, nanorods and nanobelts have been synthesized with high crystalline quality, which show unique electronic and optical properties[4-7]. The impurities in doped materials play an influential role in determining electronic and optical properties, which are critical for device development. For decades, manganese-doped zinc sulfide (ZnS:Mn) has been the most efficient electroluminescent (EL) phosphor material, and its synthesis and properties have been widely investigated[8-10]. Various synthesis techniques have been used to synthesize doped nanostructured materials, such as chemical reaction[11], ion implantation[12] and thermal evaporation at high temperature[13,14]. As reported by Geng et al.[14], the Mn-doped ZnS nanobelts show the defect-related emission around 450 nm and the yellow emission around 580 nm. In this letter, we report a simple thermal evaporation approach to synthesize Mn-doped ZnS nanobelts. Photoluminescence (PL) spectroscopy has been used to study the influence of the manganese doping on the optical properties of ZnS nanobelts at room temperature.

The sample was prepared in a horizontal quartz tube (outer diameter of 4.2 cm; length of 80 cm) which was mounted inside a high-temperature tube furnace. Zinc sulfide and manganese sulfide powders were placed into a ceramic boat, which was then loaded into the central region of the quartz tube. A silicon substrate coated with about 30 Å thick Au film was put into the tube at a distance about 30 cm from the ceramic boat. The presence of Au film on the silicon substrate is crucial to the nucleation of nanobelts during the early stage of growth, although Au is not found in the final product [15]. Temperature rose to 1100 °C with a rate of 40 °C/min. Carrier gas of 95% argon and 5% hydrogen was introduced, which flowed at a rate of 30 sccm and with a pressure of 100 mbar through the whole experiment. The 5% hydrogen used in this experiment prevented for the oxidation of the reactant. After 2.5 hours, the temperature was cooled to room temperature with a rate of 40 °C/min. White wool-like products were deposited on the silicon substrates.

Samples collected from the silicon substrates were characterized with X-ray diffraction (XRD) (Siemens D-500 with Cu $K\alpha$ radiation and a normal 2θ scan), scanning electron microscopy (SEM) (Philips XL 30 FEG), selected area electron diffraction (SAED) (JEM-200CX, operated at 200 kV) and high-resolution transmission electron microscopy (HRTEM) (CM200 FEG, operated at 200 kV). Photolumi-

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nescence (PL) measurements were performed at room temperature using Nd: yttrium-aluminum-garnet laser with a wavelength of 266 nm and a 6 ns pulse width as the excitation source and a 0.5 spectrometer (Acton Research Corp. Spectra Pro 500i) with an intensified charge coupled device (ICCD) camera (Roper Scientific) as the detection stage.

Fig.1 (a) and (b) show the SEM image for the high-density nanostructures grown on the silicon substrate. It reveals that the product consists of a large quantity of belt-like structures with an uniform width on silicon substrate, a typical length of ZnS nanobelts is in the range of tens of micrometers and the widths of them usually range from about 100 nm to 1 μm.

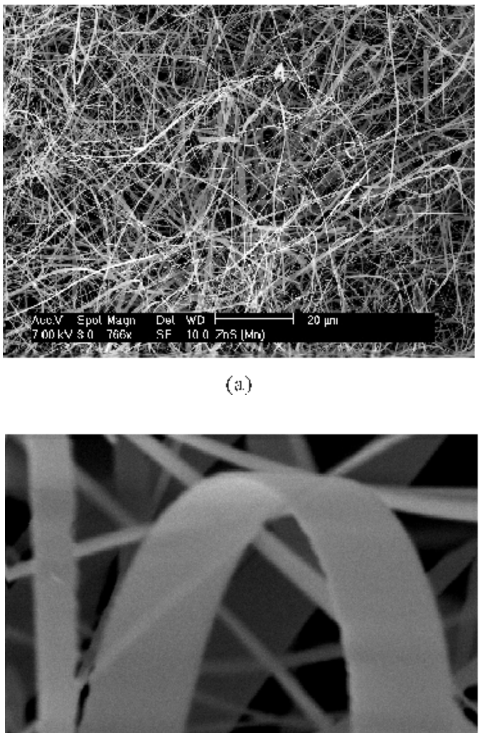

Fig.1 SEM images of Mn-doped ZnS nanobelts. (a) low magnification, and (b) high magnification

The structure and morphology of the Mn-doped ZnS nanobelts are further characterized by high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED), as shown in Fig.2. The transverse and longitudinal spacing of the crystallographic plane are 0.630 nm and 0.327 nm respectively, corresponding to (0001) and (01-10) lattice plane of hexagonal structure. The growth direction of the nanobelt is determined to be along [0001] direction. The HRTEM images also reveal that no obvious defects such as grain boundary, twin crystal structure or stacking fault are found. The corresponding SAED image of it is also shown in the inset of Fig.2. It also confirms that the nanobelt is single crystal with hexagonal structure and the growth direction of the nanobelt is [0001].

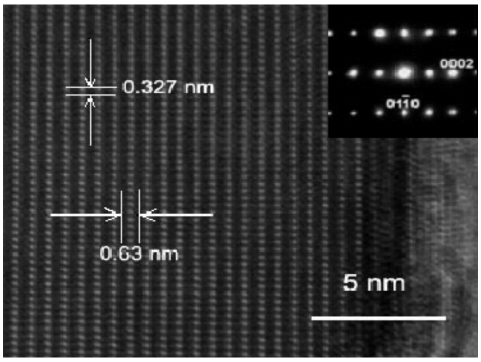

Fig.2 HRTEM image of Mn-doped ZnS nanobelt of the edge (SAED pattern is shown in inset)

Fig.3 shows the XRD spectrum from 10° to 70° of the Mn-doped ZnS products. The indexes of the peaks are labeled according to the hexagonal structure of ZnS. The lattice constants are a = 3.822 Å and c = 6.620 Å respectively. They are consentient with those listed in the JCPDS card No. 79-2204. No obvious manganese is detected.

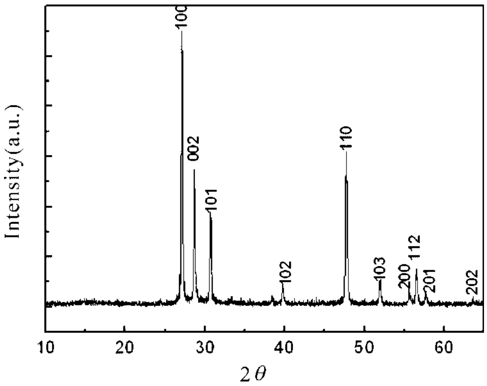

Fig.3 XRD spectrum of Mn-doped ZnS nanobelts

Fig.4 shows the room temperature photoluminescence spectra from a large quantity of undoped ZnS nanowires and the mixture of Mn-doped ZnS nanobelts and nanowires, and Mn-doped ZnS nanobelts. Fig.4 (a) shows the PL spectrum of the undoped ZnS wires, the emission band around 325 nm, which corresponds to the recombination of free excitons of ZnS[16]. Fig.4 (b) and (c) exhibit PL spectra of the Mn-doped ZnS products, the intrinsic PL of the ZnS disappears and a new PL peak emerges at 575 nm.

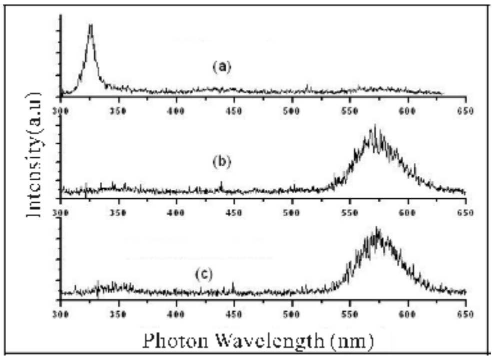

Fig.4 (a) Photoluminescence spectrum of ZnS nanowires, (b) Photoluminescence spectrum of mixed Mn-doped ZnS nanobelts and nanowires, and (c) Photoluminescence spectrum of Mn-doped ZnS nanobelts.

The transition mechanism for Mn-doped ZnS has been thoroughly discussed by Calabrese et al.[17]. The subsequent transfer of electrons and holes into the electronic level of the Mn ions leads to the characteristic emission of Mn^{2+} in ZnS. This observed yellow emission in the photoluminescence of bulk Mn-doped ZnS is associated with the Mn^{2+} $^4T_1$-$^6A_1$ transition and its peaks are around 585 nm at room temperature [18]. In contrast, few defect-related luminescences are discovered, which indicates the Mn^{2+} ions are homogeneously doped into the ZnS nanobelts. Therefore, we can obtain pure emitting yellow light materials.

In conclusion, a simple thermal evaporation approach is developed to synthesize high-quality Mn-doped ZnS nanobelts. The HRTEM image indicates that the nanobelts are single crystals, it has perfect microstructure, and no defects such as dislocation are observed. The XRD spectrum indicates that the lattice constants are a=3.822Å and c= 6.620Å respectively. The study of the PL spectra of the nanobelts at room temperature reveals that the Mn-doped ZnS nanobelts can emit pure yellow light, which promises valuable application of the prepared Mn-doped ZnS nanobelts in optical devices.

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