

Structural and Photoluminescence Properties of Mn-doped ZnO Nanocolumns Grown by Cathodic Electrodeposition

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Abstract: Mn-doped ZnO nanocrystal was prepared on Si substrates by cathodic electrodeposition. X-ray diffraction (XRD) study suggests that the Mn ions are substituted for Zn position into ZnO crystal. Field-emission scanning electron microscopy (SEM) images show the column-like morphology of ZnO nanocrystal. In photoluminescence spectrum, the visible emission band is broadened because of the doping effect. The fitted result of the temperature-dependent PL spectra in the range from 122.8 K to 302.2 K indicates that Mn dopant could lead to the decrease of the exciton binding energy.

Key words: ZnO; doping; nanocrystal

One-dimensional (1D) nanostructures have attracted great interest in recent years, due to their unique and fantastic optical, electrical and mechanical properties as compared with bulk materials. They have great potential in fundamental studies and applications in nanodevices and functional materials^[1-6]. Up to now, many kinds of 1D semiconductor nanostructures have been synthesized. Among them, ZnO nanostructures are intensively studied, due to their wide band-gap of 3.37 eV and large binding energy of 60 meV, which makes them a promising material for UV photonic devices, sensors and piezoelectric devices. Different-shaped ZnO nanostructures have been fabricated by various synthesis methods, including chemical vapor deposition, thermal evaporation, aqueous solution deposition and pulsed laser deposition. The magnetic property of Mn doped ZnO nanostructures was also studied.

Compared with molecular beam epitaxy (MBE)^[7], pulse laser deposition (PLD)^[8], sol-gel technique^[9] and RF sputtering^[10] or chemical vapor deposition (CVD)^[11], electrodeposition is a simple and inexpensive technique. ZnO nanocolumns have been successfully synthesized by this method. In this paper, we present the results of

structural and optical properties studies of Mn doped ZnO nanocolumns electrodeposited onto p-type Si (111) substrates.

1 Experiment

The nanocolumns were electrodeposited from aqueous electrolytes, which contained ZnCl₂ (0.005 mol/L), Mn(CH₃COOH)₂ (0.00025 mol/L) and Zn(CH₃COOH)₂ (0.00025 mol/L). 0.1 mol/L KCl was introduced to ensure a good conductivity in the solution. The p-type (111) Si wafers with conductivity of 0.01 Ω/cm² were used as the substrates. In general, the substrate was used as the cathode and a platinum sheet (99.999% purity) was used as the anode. Prior to the deposition, the Si substrates were ultrasonically cleaned in an acetone bath, and then immersed in a 5% HF solution for oxide removal. Thin indium films were evaporated on the rear of the Si wafers to form a good ohmic contact. The electrodes separated with a distance of 2 cm were placed parallel to each other. The electrodeposition was carried out at a constant potential of -600 mV for 1 h at 60 °C.

X-ray diffraction (XRD) measurement was taken on a

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Siemens D500 diffractometer operating in the θ - 2θ Bragg configuration using Cu K α radiation of 0.15418 nm. The surface morphology was observed by a scanning electron microscope (SEM). PL spectra were measured using the 325 nm line of a He-Cd laser as an excitation source.

2 Results and Discussion

2.1 Structural properties of the Mn-doped ZnO

Fig.1 shows the XRD pattern of the as-grown sample. In the pattern, all the diffractive peaks belong to the wurtzite structure of ZnO. Compared with standard ZnO XRD data, a slight shift of 0.04 (± 0.01) degrees to lower angle side was observed for all the peaks in the XRD pattern. The lattice constants, a and c , could be calculated as 0.3265 and 0.5216 nm, respectively, which are bigger than those of pure ZnO ($a = 0.325$ nm, $c = 0.52$ nm). Since the Mn ionic radius (8000 pm) is larger than that of Zn (7400 pm). This result indicates that Mn ions are doped into ZnO crystal lattice successfully with substituting positions of Zn ions. According to the XPS results, the content of Mn ions in ZnO lattice could be estimated as 2%. The full width at half maximum (FWHM) of (101) diffractive peak is 1.85°, which means the size distribution of ZnO nanocrystal is large.

Fig.2 shows the typical SEM image of the electrodeposited Mn-doped ZnO sample. The sample is consisted of nanocolumns. The lengths of nanocolumns are around 500~600 nm with diameters of 200~300 nm. The nanocolumns are randomly grown on the substrate surface. And the hexagonal cross-section can also be observed clearly.

2.2 Optical properties of the Mn-doped ZnO

The Mn ions doping can also affect the PL properties of ZnO. The PL spectrum is shown in Fig.3, in which two emission bands could be observed. The emission band in the ultra-violet region could be considered as the near band edge exciton related emission. The emission center is located at 370 nm with the FWHM of 30 nm. The other broad emission is in the visible region, which is originated

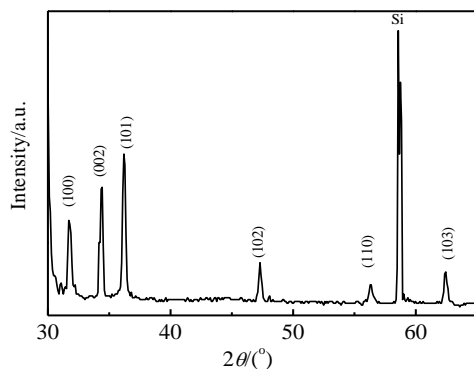


Fig.1 XRD pattern of the sample

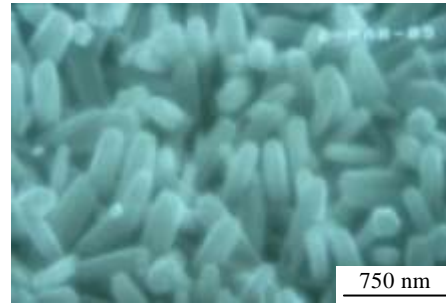


Fig.2 SEM image of the sample

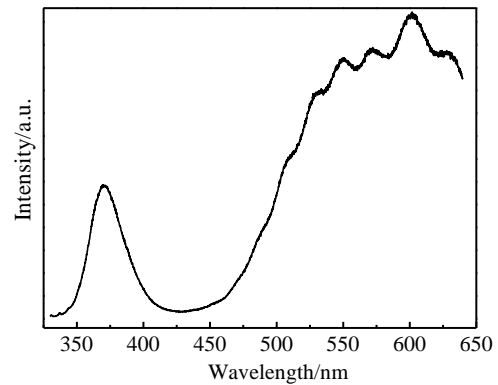


Fig.3 PL spectrum of the sample at room temperature

from the defect related deep level emission. Because of the Mn ions doping this emission band is broadened and red-shifted to low energy side.

Fig.4 shows the dependence of the PL spectrum of the sample in the temperature range from 122.8 to 302.2 K. As the temperature increases, the relative intensity decreases. The peak position shifts to low energy when the temperature increases from 122.8 K to room temperature (RT). This is because the bound excitons are thermally ionized and the carriers may take part in PL at high-temperature. The PL intensity decreases in the higher-temperature region, mainly due to thermally activated nonradiative recombination mechanism. This luminescence quenching is characterized by relatively high activation energy.

In order to study the influence of Mn doping on the band gap energy of ZnO, the PL integrated intensities of peak as a function of temperature are plotted in Fig.5. The experimental data could be fitted to the following formula:

$$I(T) = \frac{I_0}{1 + A \exp\left(-\frac{E}{k_B T}\right)} \quad (1)$$

where E is the activation energy of the thermal quenching process, k_B is Boltzmann constant, I_0 is the emission intensity at 0 K, T is a thermodynamic temperature and A is a constant. The solid line in Fig.5 is

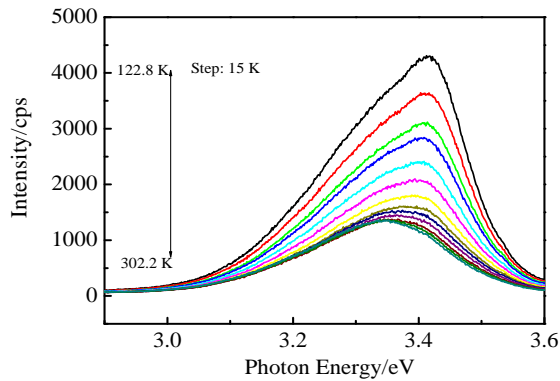


Fig.4 Dependence of the PL spectrums of the samples in the temperature range from 122.8 to 302.2 K

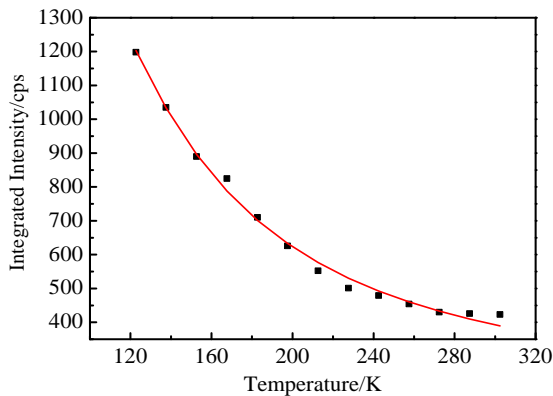


Fig.5 PL integrated intensities of peak as a function of temperature from 122.8 K to 302.2 K

the theoretical fit to the experimental data and we obtain $E = 31$ meV. This value is smaller than that of the free exciton in pure ZnO (59 meV), indicating that doping

Mn in ZnO nanocolumns could result in the decrease of the exciton binding energy.

3 Conclusions

1) Mn-doped ZnO nanocolumns have been fabricated by cathodic electrodeposition on Si substrates.

2) Mn ions have been doped into the lattice positions of Zn ions. Because of the doping, more defects are generated in the crystal, which induces that the visible emission band is broadened and shift to low energy side.

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电化学沉积 Mn 掺杂纳米 ZnO 的结构和光学性质研究

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摘要: 在Si衬底上用电化学沉积方法制备了Mn掺杂ZnO纳米晶, X射线衍射(XRD)的研究表明, Mn离子取代Zn离子进入到 ZnO晶格中。场发射扫描电子显微镜(SEM)图像显示, ZnO纳米晶形貌是柱状的。从光致发光谱可以看出, 由于掺杂效应导致可见发射带扩大, PL谱从122.8 K到302.2 K范围的拟合结果表明, Mn掺杂导致激子结合能的降低。

关键词: 氧化锌; 掺杂; 纳米晶

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