Article ID: 1000-7032(2010)02-0243-05

Electrical and Optical Properties of Li-doped ZnO Nanorods

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Abstract: Li-doped ZnO nanorods was grown on n-Si (111) substrate by chemical vapor deposition. XRD pattern showed that the nanorods are pure wurtzite ZnO of hexagonal crystal structure without any other oxide, such as Li_2O. Hall effect experiment under Van der Pauw configuration showed that Li-doped ZnO nanorods behave the p-type conductivity with hole concentration of 6.72×10^{16} cm^{-3} and a Hall mobility of 2.46 $cm^2 \cdot V^{-1} \cdot s^{-1}$. A neutral acceptor-bound exciton emission (A°X) was confirmed by the measurements of temperature-dependent photoluminescence (PL) spectra. The optical acceptor energy level is calculated to be about 142 meV.

Key words: ZnO nanorods; hall effect; PL

CLC number: O472.3; O482.31 **PACS**: 72.10.-d; 73.61.-r **PACC**: 7855; 8155 **Document code**: A

1 Introduction

One dimensional nanomaterials have attracted great interest because of their unique and fascinating optical, electrical, mechanical and thermoelectrical properties together with their wide uses in fundamental scientific research and potential technical applications[1]. Among these materials, ZnO is one of the most promising materials since it has a high mechanical and thermal stability, a wide bandgap (3.37 eV), and a large exciton binding energy (60 meV). Up to now, a number of ZnO nanomaterials with different morphologies and interesting structures, such as nanowires[2~4], nanorods[5,6], nanospheres[7,8], nanotowers[9], nanotetrapods[10] and nanocombs[11,12], have been successfully synthesized with different methods.

In order to realize nanosized ZnO electronic and optoelectronic devices, it is necessary to prepare both high-quality n-type and p-type ZnO. However, the growth of stable and reproducible p-type ZnO with high conductivity and high mobility is difficult because of its self-compensating effect, deep acceptor level and low solubility of acceptor dopants. It has been reported that Li-doped thin ZnO films behaved good p-type conductivity with high hole concentration by our previous studies and also by Ye, *et al*, indicating that Li is an optimal acceptor dopant for p-type ZnO[13, 14].

In this work, we reported the growth of Li-doped ZnO nanorods on the Si substrate by a chemical vapor deposition technique. The ZnO nanorods without any dopant under the same condition have also been grown for comparison. The optical properties of the Li-doped ZnO nanorods were also studied in detail.

2 Experiments

The n-type Si (111) wafer ($\rho = 0.001\ 7\ \Omega \cdot cm$) (2.0 cm × 1.0 cm in size) was used as substrate. It was cleaned in an ultrasonic bath with acetone and alcohol at room temperature, respectively.

Received date: 2009-11-25; **Revised date**: 2010-01-15

Foundation item: Project supported by the National Natural Science Foundation of China (10804071); the Natural Science Foundation of Shanghai (09ZR1420500); Shanghai Municipal Education Commission Project (sdj08013); Shanghai Dianji University Project (08C409) and Matched Foundation (08A128)

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Following that it was etched in diluted HF (10%) solution for 5 min, and then rinsed in deionized water and blown dry using high-purity nitrogen gas. ZnO nanorods were synthesized by chemical vapor deposition method in a horizontal tube furnace in air. The Zn-Li alloy with 2% Li was placed in a ceramic boat placed at the center of the tube furnace. The Si substrate was laid above the ceramic boat. The distance between the Zn source and the substrate was about 3 mm. The tube furnace was evacuated by using a mechanical rotary pump to remove the residual oxygen. The substrate was heated to an appropriate temperature of 600 ℃ at a rate of 10 ℃/min with a continuous flow of 200 sccm argon gas. About 2 min later, the mixed-gas of argon and oxygen with a ratio of 2∶1 was introduced into the system for growth about 20 min. The yellowish powder on the Si substrate was obtained after the furnace was cooled down to room temperature naturally (denoted as samples A). Under the same conditions, we conducted another experiment, the only difference was that the pure metal Zn without any dopant was used as Zn source (denoted as sample B).

The morphology and structure of ZnO nanorods were characterized using a field emission scanning electron microscope (FE-SEM; Philips XL30FEG) with an accelerating voltage of 5 kV and XRD measurement was performed by using a RigakuO/max-RA X-ray diffractometer with Cu Kαl radiation (λ = 0.154 18 nm). The electrical properties of ZnO nanorods were obtained by Hall measurements under the Van der Pauw configuration at room temperature. The temperature-dependent PL spectra were conducted on a 325 nm He-Cd laser with a liquid helium cooling system Jobin Yvon LabRAM HR800UV.

3 Results and Discussion

3.1 Morphology and Structure of ZnO Nanorods

Fig. 1(a) and (b) show the FE-SEM images of ZnO nanorod with Sample A and Sample B, respectively. From Fig. 1, it can be found that the synthesized Li-doped ZnO nanorods in sample A are about 50 nm in diameter and 1 μm in length, which are obviously smaller than the ZnO nanorods in sample B (about 300 nm in diameter and 10 μm in length). This implies that the ZnO nanorods growth behavior is associated with Li dopant. Further study of the mechanism is in progress.

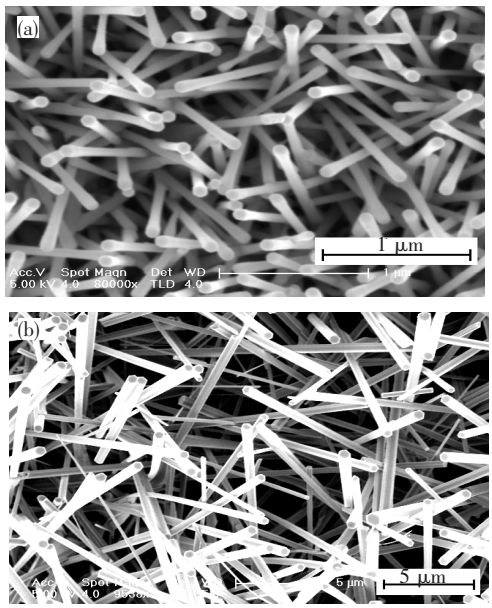

Fig. 1 SEM images of the Li-doped ZnO nanorods (a) and ZnO nanorods without any dopant (b)

The inset of Fig. 2 shows X-ray diffraction (XRD) patterns of ZnO nanorods with Sample A and Sample B, respectively. The dominant diffraction peaks of two samples correspond to diffraction of wurtzite hexagonal ZnO. There is no diffraction peak of any other oxide, such as Li_2O, in the XRD patterns. The (002) diffractive peak for sample A is located at 34.34°, which is larger than that of

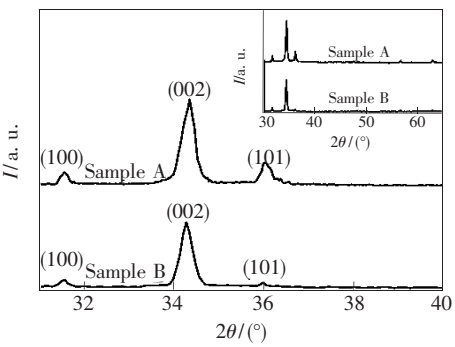

Fig. 2 XRD patterns of around the (002) peak of Sample A (ZnO nanorods with nominal Li content of 2%), and sample B (ZnO nanorods without any dopant), respectively. Inset is the corresponding XRD profile in diffraction angles (2θ) of 30° ~ 65°.

sample B at 34.27°, as shown in Fig. 2. Since the covalent radius of Li (0.123 nm) is a little smaller than that of Zn (0.125 nm), the increase of (002) diffraction peak of sample A compared to sample B indicates that Li atom substitutes for Zn lattice site in the ZnO. The full width at half-maximum (FWHM) for two samples is about 0.36°, which implies good crystallinity of ZnO nanorods (FWHM of ZnO substrate films is about 2°)[15].

3.2 Electrical and Optical Properties of ZnO Nanorods

The electrical properties of both Sample A and Sample B are listed in Table 1, which gives that the sample A grown with Li dopant shows p-type conduction, while the sample B grown without Li dopant shows n-type conduction. It is noted that both sample A and B are prepared under the same condition. This implies that the p-type conductive behavior of the sample A is associated with Li dopant, which is due to the fact that Li atom can replace Zn site in the Li-doped ZnO nanorods to form acceptor dopants.

Table 1　Electrical properties of Li-doped and undoped ZnO nanorods prepared by chemical vapor deposition

Sample	Li contentat(%)	Type	Resistivity(Ω · cm)	Mobility ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	Carried concentration(cm^{-3})
A	2	p	37.84	2.46	6.72×10^{16}
B	0	n	0.026	4.73	7.16×10^{18}

Fig. 3 shows the PL spectra of the sample A and sample B in the ultraviolet region at 20 K, respectively. It can be seen that the emission bands located at 3.306, 3.234, and 3.162 eV can be observed in the both samples. The obvious differences between two samples are the emission bands located at 3.351 and 3.364 eV. In Sample B, the emission band located at 3.364 eV is ascribed to the donor-bound exciton[13].

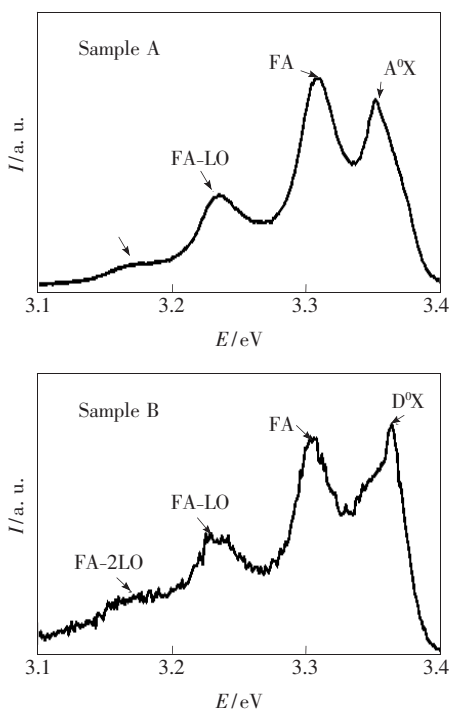

Fig. 3　The PL spectra at 20 K for the sample A and sample B, respectively (λ_{ex} = 325 nm).

In order to investigate the origins of the emission bands of Sample A, the temperature-dependent PL measurements from 20 to 300 K were performed. The spectra are shown in Fig. 4 (a). For the emission band located at 3.351 eV, an obvious temperature-dependent blueshift from 3.351 eV at 20 K to 3.358 eV at 80 K can be observed, and then this

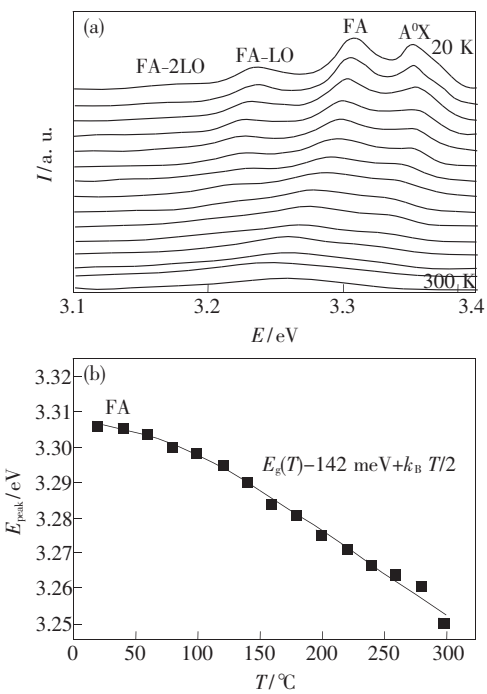

Fig. 4　The temperature-dependent PL spectra in the temperature range 20 ~ 300 K in the ultraviolet region for Sample A (a). Temperature-dependent peak positions and their fitting curves for the emission bands located at 3.306 eV (b).

emission band shows the temperature-dependent redshift, which is a result of a transition from acceptor-bound exciton emission (A°X) to free exciton (FX) emission as temperature increases[13]. Therefore, this emission band can be attributed to A°X. The temperature-dependence of the emission bands located at 3.306 eV position fits well in an equation for a radiative electron transition from conduction band to acceptor (FA) given by

$$E_{FA}(T) = E_g(T) - E_A + k_B T/2,$$

where $E_{FA}(T)$ is the temperature-dependent FA transition energy, E_A is the acceptor energy level, and k_B is the Boltzmann constant. The acceptor energy level is calculated to be 142 meV, as shown in Fig. 4(b), the value is slightly smaller than that of Sample A[16], which may be due to the smaller diameter of ZnO nanorods.

Since the energy difference between 3.162, 3.234 eV and 3.306 eV are 72 and 144 meV, which are equivalent to one and two longitudinal optical (LO)-phonon energy of ZnO, respectively. Therefore, these two emission bands are ascribed to FA-1LO and FA-2LO.

4 Conclusion

The p-type ZnO nanorods with hole concentrations of 6.72×10^{16} cm^{-3} and mobility of 2.46 cm^2 · V^{-1} · s^{-1} is fabricated on n-Si(111) substrate by chemical vapor deposition using Li as dopant. The Li-doped p-type ZnO nanorods are of pure wurtzite ZnO crystal structure, and no other oxide, such as Li_2O. The measurements of temperature-dependent PL spectra show that a neutral acceptor-bound exciton emission (A°X) is found. The optical acceptor energy level is calculated to be about 142 meV.

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Li 掺杂 ZnO 纳米棒的导电和发光特性

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摘要: 利用气相输运方法,在(111)面硅衬底上制备了名义上原子数分数为 2% 的 Li 掺杂的 ZnO 纳米棒(样品 A)。作为比较,我们在相同的生长条件下制备了没有任何掺杂的 ZnO 纳米棒(样品 B)。XRD 分析测试表明:样品 A 和样品 B 中的 ZnO 纳米棒具有纤锌矿六边形结构,没有其他氧化物,例如 Li_2O。Hall 效应测量表明:样品 A 导电类型为 p 型,空穴载流子浓度为 6.72×10^{16} cm^{-3},空穴载流子迁移率为 2.46 $cm^2\cdot V^{-1}\cdot s^{-1}$。样品 B 为 n 型,电子载流子浓度为 7.16×10^{18} cm^{-3},电子载流子迁移率为 4.73 $cm^2\cdot V^{-1}\cdot s^{-1}$。低温光致发光光谱测试表明,样品 A 和样品 B 发光峰明显的区别是位于 3.351 eV(样品 B)和 3.364 eV(样品 A)处。根据文献报道,在没有掺杂的 ZnO 中,3.364 eV 发光峰源于施主束缚激子发光。通过变温光致发光光谱的测试,证明了在样品 A 中,位于 3.351 eV 的发光峰源于受主束缚激子发光,其光学受主能级位于价带顶 142 meV 处。

关　键　词: 氧化锌纳米棒; 霍尔效应; PL

中图分类号: O472.3; O482.31　　**PACS:** 72.10.-d; 73.61.-r　　**PACC:** 7855; 8155　　**文献标识码:** A

文章编号: 1000-7032(2010)02-0243-05

收稿日期: 2009-11-25; **修订日期:** 2010-01-15

基金项目: 国家自然科学基金(10804071); 上海市自然科学基金(09ZR1420500); 上海市教委高校选拔优秀青年教师培养基金(sdj08013); 上海电机学院博士科研启动基金(08C409)和配套基金(08A128)资助项目

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