Vol 16 No 9, September 2007
1009-1963/2007/16(09)/2769-04

Chinese Physics

© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Synthesis and photoluminescence study on ZnO nano-particles

Li Xiang(李 祥)[a)b)†], Zhai Fei-Fei(翟斐斐)[a)b)], Liu Ying(刘 颖)[a)],
Cao Mao-Sheng(曹茂盛)[a)], Wang Fu-Chi(王富耻)[a)], and Zhang Xi-Xiang(张西祥)[b)]

[a)] *School of Material Sciences and Engineering, Beijing Institute of Technology, Beijing* 100081, *China*

[b)] *Department of Physics, Hong Kong University of Science and Technology, Hong Kong, China*

(Received 9 December 2006; revised manuscript received 1 March 2007)

A new technique, namely low pressure sputtering, has been developed to fabricate Zn nanoparticles, with a subsequent oxidation to synthesize ZnO nanoparticles in the ambient atmosphere at 500 °C. The synthesized ZnO nanoparticle has a size of 6–8 nm with a preferred orientation of *c*-axis. The produced ZnO nanoparticles have a good UV photoluminescence (PL) emission energy of 3.349 eV with a significant enhancement of donor–acceptor pair emission located at 3.305 eV which implies a number of donor and acceptor bounded excitons existing in the synthesized ZnO nano particles. The near band edge PL emission of the fabricated ZnO is dominated by the bounded excitons at 10 K.

Keywords: sputtering, ZnO nanoparticle, photoluminescence
PACC: 6140M , 7280E, 8140R

1. Introduction

Zinc oxide (ZnO) has a band gap of 3.37 eV with a large excitonic binding energy of 60 meV, thus it is a promising candidate for future optical applications of UV light emitting devices. A great effort has been made to attempt to synthesize low-dimensional ZnO nanostructures by using different methods, including chemical vapour deposition,[1] thermal evaporation,[2,3] catalysis-assisted vapour-liquid-solid growth,[3−5] molecular beam epitaxy, metalorganic chemical vapour deposition and radio-frequency (RF) sputter.[6−9] Recently, several groups have reported a room temperature UV lasing and UV photoluminescence (PL) in ZnO nanowires and nanodots on different substrates.[6,7,10−13] Quantum-confinement-induced energy gap enhancement has been reported by using ZnO nanocrystalline with 20–60 nm grain sizes and lots of interesting phenomena have been found.[13−16] It has been found that the quality and shape of ZnO nanocrystal are essential to the applications in fabricating optical, optoelectronic and sensors devices.

Although a high-quality crystalline ZnO with a low-dimensional structure has been synthesized and strong UV photoluminescence has been observed at room temperature, most of the employed methods are concerned with molecular bean epitaxy (MBE) or metalorganic chemical vapour deposition (MOCVD) in which ultra vacuum, expensive substrate and high substrate temperature are required. Therefore, to avoid this disadvantage in applications, new methods to synthesize nanostructured ZnO materials with controllable size and shape in low dimensions are desired.

In this paper, a new method is presented to synthesize ZnO nanoparticles with a low pressure sputtering processing. The details of the experiments are described below.

2. Experiments

A new method of fabricating ZnO nanoparticles is presented in this paper. First, Zn nanoparticles are fabricated on p-type Si(111) substrate in a low pressure sputter system at room temperature in Ar atmosphere at 27–74 Pa, which is two orders of magnitude higher than that in the traditional sputtering processing (in traditional sputtering processing, the working pressure is 0.3–0.5 Pa). This new method has an advantage that the produced Zn is of large cluster and aggregated to nanoparticles. The produced Zn nanoparticles are black ash-like and then are oxidized in a 500 °C ambient for 2h. The structure and grain size of the produced ZnO films are studied by us-

†Corresponding author. E-mail: aihyoo@bit.edu.cn

ing x-ray diffraction (XRD) and the grain size of the synthesized ZnO nanoparticles is characterized with atomic force microscopy (AFM) with Digital Instruments Nanoscope IIIa and the scanning frequency is at 1.5 Hz. The photoluminescence of ZnO is studied at 10 K by using a Cd–He laser radiation. The laser beam was focused into a spot of about 3 μm in diameter using an objective lens.

3. Results and discussion

Figure 1 shows the high-angle x-ray diffraction spectrum of ZnO nanoparticles. The fabrication of this sample is carried out for 10 min in 54 Pa pressure Ar atmosphere with a sputtering power of 25 W, and then it was oxidized at 500 °C for 2h. In x-ray diffraction spectrum, the peaks appearing at the values of 2θ: 31.738°, 34.406°, 36.203°, 47.495°, 56.612° and 62.911° may be assigned to (100), (002), (101), (110), (110) and (103), respectively, indicating that it has a hexagonal structure of ZnO. As no Zn signal is detected, it is further confirmed to be completely oxidized. The inset shows the fine scanned XRD spectrum. The enhanced peak of (002) in the XRD spectrum indicates that ZnO has the tendency to grow in the *c*-axis orientation perpendicular to the substrate surface, which is consistent with the results in the previous reports.

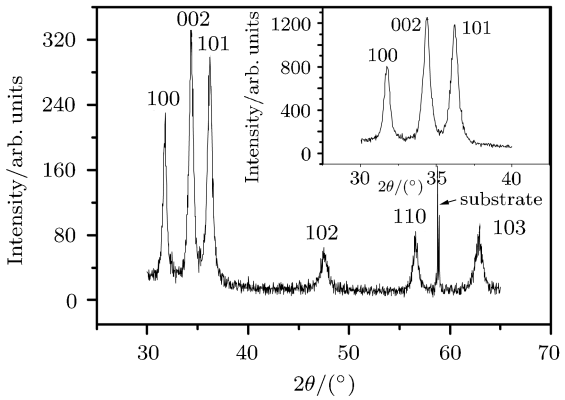


Fig.1. High-angle x-ray diffraction spectrum of the 770 K oxidized film. The average grain size of the ZnO nanoparticles is 8 nm with a preferred orientation of (002).

From the Bragg formula, the *c*-axis orientated space distance of the synthesized ZnO particles are calculated and the space distance is 0.2603 nm. The cell parameters of the synthesized ZnO calculated from XRD data are $a = 0.32517$ nm, and $c = 0.52191$ nm, which is little larger than that of the bulk one as reported by previous work.[17] The c/a of ZnO nanoparticles is 1.605 which is a little smaller than that of bulk one, which indicates a compression appearing in the *c*-axis direction in its crystalline cell. The compression of the ZnO crystalline cell can be due to the defects or interstitial Zn or O ion existing in the synthesized ZnO particles.

The grain sizes of ZnO nanoparticles are obtained by fitting the XRD data to the Scherrer formula $t = 0.9\lambda/B\cos\theta_{\rm B}$, where λ, $\theta_{\rm B}$, and B are the x-ray wavelength (1.54056 Å), Bragg diffraction angle, and line width at half maximum of (002) peak (34.406°), the obtained grain size of ZnO is 6.4 nm on average.

Figure 2 shows the morphology of the studied ZnO sample, which is obtained with atomic force microscopy system. From the images of AFM, it is clearly seen that the grain size of the studied sample is uniform and the statistic grain size of the sample is 7.4 nm consistent with its XRD calibration (see Fig.1). The PL spectrum of this sample is shown in Fig.3.

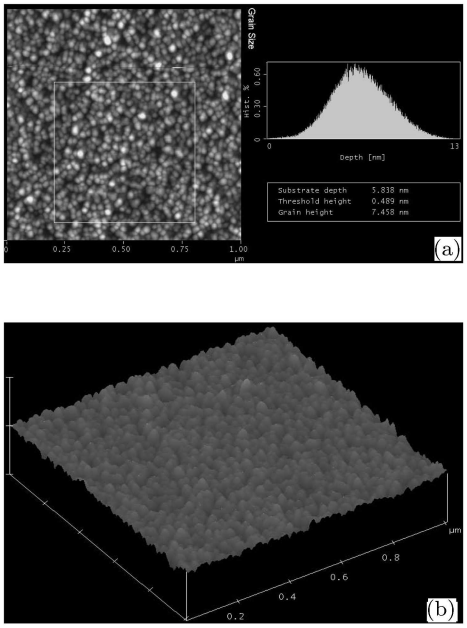


Fig.2. AFM morphology images of ZnO nanoparticles with an average diameter of about 7–8 nm.

Figure 3 indicates the PL spectrum of ZnO nanoparticles. The spectrum is measured at 10K in a wavelength range of 360–390 nm. A strong intensity of PL emission spectrum is observed with four prominent emission peaks located at 3.349, 3.305, 3.231 and 3.178 eV; a weak shoulder peak is also observed at 3.363 eV, which can be seen in Fig.4, more clearly. The full width at half maximum (FWHM) of the main

peak located at an energy of 3.349eV is 12 meV, while the peak located at 3.305 eV is much wider than that at 3.349 eV. The PL peak at 3.349 eV can be attributed to the emission of exciton bound to neutral donors. As is well known, the line-width of the exciton emission in low temperature PL is sensitive to compression and distortion as well as the local defects of ZnO lattice; the width of PL peak of our sample indicates that there exists some compression or torsion in the studied ZnO grains, which is also confirmed by the XRD results.

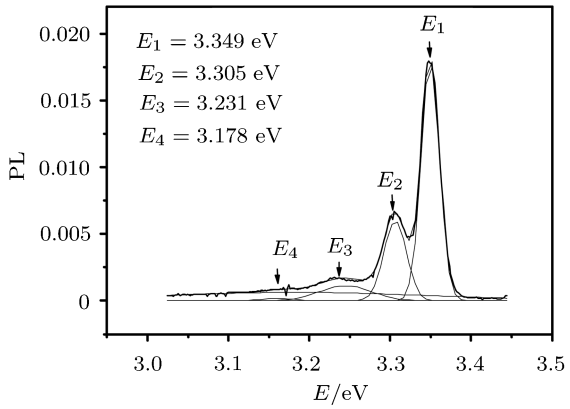


Fig.3. The photoluminescence (PL) spectrum of ZnO nanoparticles. This sample is prepared for 10 min in 53 Pa pressure Ar atmosphere with a sputtering power of 25 W and then oxidized at 500 °C for 2h. The spectra are measured at 10K in a wavelength range of 360–390 nm.

Based on the previous work, the peak at 3.305 eV may stem from the emission of donor–acceptor pair (DAP).[6] A weak peak at 3.231 eV is attributed to the phonon replica of DAP with a phonon energy of about 71 meV.[6,18] The weak peak at 3.178 eV could be the second phonon replica of DAP. The peak at 3.178 eV is quite weak and fat, and thus it is not possible to be assigned definitely. However, due to the defects or impurities in ZnO nanoparticles, this peak could result from several sub-peaks.[6,18]

The weak shoulder at 3.363 eV, which can be seen more clearly in Fig.4(a), can be attributed to free excitons emission, indicating that the synthesized ZnO particle has a good crystalline quality.[19]

Figure 4(a) shows the PL spectra of ZnO nanoparticles formed under different synthesis conditions and the spectra measured at a temperature of 10 K. The measured ZnO nanoparticles are oxidized from Zn nanoparticles at 500 °C, and the Zn particles are sputtered at different Ar pressures. A detailed Ar pressure dependence on the relative intensity between the peak at 3.349 eV (I1) and the peak at 3.305 eV(I2) is shown in Fig.4(b). By comparison, it can be seen that increasing Ar pressure in sputtering leads to an increase of the relative intensity of I1/I2 at pressures less than 53 Pa, and the relative intensity reaches its maximum at 54 Pa, and then decreases gradually with the further increase of Ar pressure. This behaviour can be explained as follows: at Ar pressures lower than 54 Pa, increasing the pressure can reduce the grain size of the produced Zn nanoparticles, consequentially, benefits the oxidation and formation of good-quality crystalline ZnO nanoparticles. At an Ar pressure of 54 Pa, the produced Zn reaches a smallest size, then the smallest and best-quality crystalline ZnO particles. After wards, with the further increase of Ar pressure, the size of produced Zn particles increases. In this case, the large Zn grain is difficult to oxidize completely, resulting in a number of O defects in the synthesized ZnO nanoparticles that can significantly enhance the intensity of DAP emission. Similar behaviour has been observed in Au granular films.

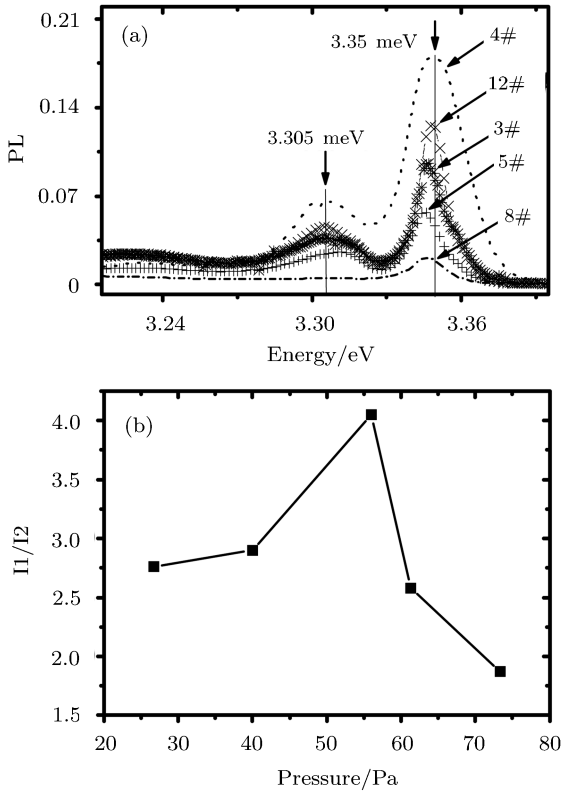


Fig.4. The PL spectra of ZnO nanoparticles prepared under different synthesis conditions, measured at a temperature of 10 K (a) and the corresponding PL peak intensity ratio against the sputtering pressure (b). I1 is the emission of neutral donor-bound excitons; I2 is of the DAP emission. The measured ZnO nanoparticles are oxidized from Zn nanoparticles at 500 °C, and sputtered in Ar atmosphere at different pressures.

Moreover, with the variation of oxidation temperature, the PL characteristics of the synthesized ZnO nano-particles are changed. When the oxidation temperature is lower than 250 °C, no UV PL emission is observed from the synthesized ZnO samples at 10 K, when the oxidation temperature is at 300 °C, UV PL emission can be observed from the synthesized samples at 10 K. And it is found that the optimal oxidation temperature is 500 °C. If the oxidation temperature is higher than 600 °C, no UV PL is observed at 10 K, which can be explained as follows: when the oxidation temperature is higher than 600 °C, the produced ZnO particles has a number of O defects which quench the bound edge emission, consequently, no UV PL emission is produced. This explanation can be confirmed by the PL measurement of the sample in a range of 360–600 nm, and an enhancement of green PL emission spectra is observed at 2.35 eV, which is attributed to the Vo defects in the ZnO crystal.

4. Conclusions

ZnO nanoparticles with good UV PL emission at 10 K have been synthesized by using the oxidation of Zn nanoparticles in the ambient atmosphere. Our study indicates that ZnO nanoparticles can be fabricated by employing low pressure sputtering. Optimal sputtering condition is found to produce nanoscale Zn particles and then successfully synthesize ZnO nanoparticles. The near band edge emissions studies indicate the bounded excitons emission is dominant at 10K, while the DAP emission is significantly enhanced, which further implies that defects in the synthesized ZnO act as donors and acceptors. The details of donors and acceptors should be further investigated and their study is now underway.

References

[1] Wu J J and Liu S C 2002 *Adv. Mater.* (Weinheim, Germany) **14** 215

[2] Huang M H, Wu Y, Feick H, Tran N, Weber E and Yang P 2001 *Adv. Mater.* (Weinheim, Germany) **13** 113

[3] Cho S, Ma J, Kim Y, Sun Y, Wong G K and Ketterson J B 1999 *Appl. Phys. Lett.* **75** 2761

[4] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 *Science* **292** 1897

[5] Zhang L L, Gao C X and Chen J G 2005 *Chin. Phys.* **14** 1221
Yao B D, Chen Y F and Wang N 2002 *Appl. Phys. Lett.* **81** 757

[6] Zhang B P, Binh N T and Segawa Y 2004 *Appl. Phys. Lett.* **84** 586

[7] Liu H X, Zhou S M, Li S Z, Hang Y, Xu J, Gu S L and Zhang R 2006 *Acta Phys. Sin.* **55** 1398 (in Chinese)
Kim T W and Kawazoe T 2004 *Appl. Phys. Lett.* **84** 3358

[8] Yu S F, Yuen Clement, Lau S P and Lee H W 2004 *Appl. Phys. Lett.* **84** 3244

[9] Shen G Z, Cho J H and Lee C J 2005 *Chem. Phys. Lett.* **401** 414

[10] Shan W, Walukiewicz W, Ager III J W and Yu K M 2005 *Appl. Phys. Lett.* **86** 191911

[11] Ko H J, Chen Y F, Zhu Z and Yao T 2000 *Appl. Phys. Lett.* **76** 1905

[12] Djurisic A B and Leung Y H 2004 *Appl. Phys. Lett.* **84** 2635

[13] Hur T B, Heang Y H and Kim H K 2005 *Appl. Phys. Lett.* **86** 193113

[14] Matsumoto T, Kato H, Miyamoto K and Sano M 2002 *Appl. Phys. Lett.* **81** 1231

[15] Park W I, Yi G C, Kim M and Pennycook S J 2003 *Adv. Mater.* **15** 526

[16] Lin B X, Fu Z X and Jia Y B 2001 *Acta Phys. Sin.* **50** 2208 (in Chinese)

[17] Reeber R R 1970 *J. Appl. Phys.* **41** 5063

[18] Zeuner A, Alves H and Hofmann D M 2002 *Phys. Status Solidi* B **234** R7

[19] Jung S W, Park W I, Cheong H D, Yi G C and Jang H M 2002 *Appl. Phys. Lett.* **80** 1924