Low temperature growth and properties of ZnO nanorod arrays

Xiang Wu1,2, Huibo Chen2, Lihong Gong2, Fengyu Qu2 and Yufeng Zheng1

1 Center for Biomedical Materials and Engineering, Harbin Engineering University Harbin 150001, People’s Republic of China
2 Key Laboratory of Design and Synthesis of Functional Materials and Green Catalysis, Colleges of Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, People’s Republic of China
E-mail: wuxiang05@gmail.com and yfzheng@hrbeu.edu.cn

Received 15 March 2011
Accepted for publication 8 June 2011
Published 7 July 2011
Online at stacks.iop.org/ANSN/2/035006

Abstract
In this paper, well aligned ZnO nanorod arrays were synthesized by a simple hydrothermal route at a low temperature. The diameters of the as-synthesized products were 20–60 nm and the lengths were as much as several micrometers. The surfaces and tops of the nanorods were smooth. The as-grown nanorod arrays were investigated by x-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), photoluminescence (PL) spectroscopy and contact angle (CA) analysis. The as-grown nanorods were single crystalline structures with a wurtzite phase, and grew along the [0001] direction. The PL spectrum with only one strong peak at 383 nm shows good intrinsic emission.

Keywords: nanorods, hydrothermal growth, ZnO, optical property

Classification numbers: 4.00, 4.06

1. Introduction
In recent years, one-dimensional (1D) nanostructures, especially semiconductor 1D nanostructures, have been an increasing research focus due to their unique physical and chemical properties determined by their morphologies and dimensions [1–9]. Compared with two-dimensional (2D), three-dimensional (3D) and zero-dimensional (0D) nanostructures, 1D nanostructures have the following unique characteristics: large aspect ratio, single crystal structure and oriented growth [10]. Among various semiconductors, ZnO 1D nanostructures have attracted intense attention because of their distinctive geometries, excellent properties, and potential applications in nanodevices [11, 12]. ZnO is an important wide band-gap \( E_g = 3.37 \text{eV} \) semiconductor with a large exciton binding energy \( (60 \text{meV}) \) [13]. ZnO 1D nanostructures, especially nanorod arrays, have been investigated widely because of their applications in the fields of ultraviolet lasers [14], photodetectors [15], field effect transistors [16], solar cells [17] and nanogenerators [18].

ZnO nanorod arrays have been synthesized through a wide range of preparation methods, including thermal vapor deposition [19], metal-organic chemical vapor deposition (MOCVD) [20], pulsed laser deposition (PLD) [21] and the hydrothermal method [22, 23], etc. Among these methods, the hydrothermal route is a suitable choice because of its simple and inexpensive procedure, its easy control over the experimental parameters, and the resulting synthesis of a product with high yield and good crystal quality. In this work, we synthesized well aligned ZnO nanorod arrays using zinc acetate and ammonia as the raw materials and zinc foil as the substrate by a simple hydrothermal route at the low temperature of \( 130 ^\circ \text{C} \). The morphology, microstructure and growth mechanism of the as-grown products were studied. The PL property and the wettability of ZnO nanorod arrays were also measured.

2. Experimental
All reagents were analytically pure and used without further purification. A total of 5 mmol zinc acetate and an equal amount of hexamethylenetetramine (HMT) were dissolved in 30 ml deionized water. Then 1 ml ammonia was added...
and the mixture was stirred for 30 min. A zinc foil and the mixed solution were placed into a sealed autoclave and kept at 130 °C for 7 h. Then the autoclave was naturally cooled to room temperature. The zinc foil was removed and washed with deionized water several times, then dried at 60 °C for 5 h. The as-synthesized products were analyzed by scanning electron microscope (SEM, Hitachi-4800), transmission electron microscope (TEM, JEOL2010EX), x-ray powder diffraction (XRD, Rigaku Dmax-rB, Cu Kα radiation, λ = 0.1542 nm, 40 KV, 100 mA), PL spectroscopy (SPEX FL-2T2) and contact angle analysis (CA, Dataphysics OCA20).

3. Results and discussion

The as-synthesized ZnO nanostructures were first studied by SEM. Figure 1(a) is a general SEM image showing that a large quantity of nanorod arrays covered the entire zinc foil substrate. We noted that some nanoflowers are formed. This was because the density of the nanorods arrays in certain areas was not high. The diameter of the nanorod was about 20–60 nm, and the length was up to several micrometers. The top and surface of the nanorod were smooth. XRD was utilized to characterize the phase structure of the as-synthesized products. Figure 2 shows the XRD pattern of as-synthesized nanorod arrays. All diffraction peaks can be indexed to a hexagonal wurtzite structure of ZnO with lattice constants of a = 0.325 nm and c = 0.521 nm (JCPDS No. 36–1451), except for those marked with asterisks, which was from the Zn foil. No diffraction peaks from other impurities were detected.

TEM was used to further investigate the microstructure of the as-synthesized ZnO nanorod arrays. Figure 3(a) shows a bright field TEM image of a single ZnO nanorod. The diameter of the selected nanorod was uniform along the growth direction and was about 20 nm. The corresponding selected area electron diffraction (SAED) is shown in figure 3(b) and indicated that the nanorod grew along the [0001] direction, the fastest growth direction of ZnO. A high resolution (HR) TEM image in figure 3(c) shows the same result with the SAED pattern and indicates that the synthesized ZnO nanorod possessed a wurtzite single crystal structure.

Based on the above experimental phenomena and analysis, the possible growth mechanism of ZnO nanorod
arrays is proposed as follows. First, ZnO nuclei form in the alkaline solution, then the obtained nuclei evolve into primary ZnO nanoparticles. As the reaction progresses, the nanoparticles attach together and further grow as the nanorods along the c-axis. Ultimately, hexagonal nanorods are obtained. The possible chemical reaction can be expressed as [24]

\[
\text{Zn}^{2+} + 4\text{OH}^- \leftrightarrow \text{ZnO}_2^{2-} + 2\text{H}_2\text{O},
\]

(1)

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \leftrightarrow \text{ZnO}_2^{2-} + 2\text{H}_2\text{O},
\]

(2)

\[
\text{ZnO}_2^{2-} + \text{H}_2\text{O} \leftrightarrow \text{ZnO} + 2\text{OH}^-.
\]

(3)

Optical properties and wettability of the as-grown ZnO nanorod arrays were also studied. Figure 4 shows a PL spectrum of the obtained ZnO nanorod arrays. Only a single wide emission peak centered at 383 nm was observed, which may be attributed to the recombination of free excitons through an exciton-exciton collision process [25]. No other peaks were found, illustrating that the as-synthesized ZnO nanorod arrays have a good crystal quality and stoichiometry.

The wettability of the solid surface was characterized by CA, which determines the angle between the solid and liquid surfaces. Nanostructures with hydrophobic surfaces are favorable for a number of applications, such as self-cleaning devices and solid lubrication systems that need a hydrophobic surface to decrease adhesion and friction. For ZnO 1D nanostructures, much effort has been focused on optical and electrical properties, but there are few reports regarding wettability [26, 27]. Figure 5 shows a water drop CA photograph of ZnO nanorod arrays. A contact angle of 110° illustrated that the as-synthesized ZnO nanostructures exhibited an excellent hydrophobic property and may be useful when applied in micro/nano systems as substitutes for some films for self-cleaning.

4. Conclusion

ZnO nanorod arrays with high yield have been successfully synthesized by a simple solution process at low temperature. The growth mechanism of the as-grown ZnO nanorod arrays is proposed based on these experimental results. The PL result indicates that the ZnO nanorods have a strong UV emission at 383 nm, while water drop CA data show that the as-produced nanorod arrays have favorable hydrophobic properties, making them potentially useful in applications involving photocatalysis or self-cleaning.

Acknowledgments

This work was sponsored by the Foundation for Key Project of Ministry of Education, China (No. 211046) and the Youth Skeleton Teacher Fund (10KXQ-07) of Harbin.
Normal University, Open Fund of State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Dong Hua University (K1012) and Program for Scientific and Technological Innovation Team Construction in Universities of Heilongjiang (No. 20011TD010).

References

[1] Wu X, Jiang P, Ding Y, Cai W, Xie S S and Wang Z L 2007 Adv. Mater. 19 2319
[2] Zhang J, Sun L, Yin J, Su H, Liao C and Yan C 2002 Chem. Mater. 14 4172
[3] Wu X, Qu F Y, Shen G Z and Cai W 2009 J. Alloys Compounds 482 L32
[4] Wu X, Sui J H, Cai W and Jiang P 2008 Chin. Phys. Lett. 25 737
[5] Khuc Q T, Vu X H, Dang D V and Nguyen D C 2010 Adv. Nat. Sci.: Nanosci. Nanotechnol. 1 025010
[6] Wu X, Zheng Y F and Qu F Y 2010 Adv. Nat. Sci.: Nanosci. Nanotechnol. 1 035005
[7] Gong L H, Wu X, Ye C, Qu F Y and An M Z 2010 J. Alloys Compounds 501 375
[8] Yu L J, Qu F Y and Wu X 2010 J. Alloys Compounds 504 L1
[9] Yu L J, Qu F Y and Wu X 2011 Appl. Surf. Sci. 257 7432
[10] Lin H P, Mou C Y and Liu S B 2000 Adv. Mater. 12 103
[11] Wu X, Jiang P, Cai W, Bai X D, Gao P and Xie S S 2008 Adv. Eng. Mater. 10 476
[12] Chen H B, Wu X, Gong L H, Ye C, Qu F Y and Shen G Z 2010 Nanoscale Res. Lett. 5 570
[13] Wan Q, Li Q H, Chen Y J, Wang T H and Lin C L 2004 Appl. Phys. Lett. 84 3654
[14] Huang M H, Mao S, Feick H, Yan H, Russo R and Yang P 2001 Science 292 1897
[15] Lu Y, Dajani I A and Knize R J 2006 Electron. Lett. 42 1309
[16] Suh D I, Lee S Y, Hyung J H and Lee S K 2008 J. Phys. Chem. C 112 1276
[17] Law M, Greene L, Johnson J C and Yang P 2005 Nat. Mater. 4 455
[18] Wang Z L and Song J H 2006 Science 312 242
[19] Park W I, Kim D H, Jung S W and Yi G C 2002 Appl. Phys. Lett. 80 423
[20] Kwak C H, Kim B H, Park C I, Seo S Y, Kim S H and Han S W 2010 Appl. Phys. Lett. 96 051908
[21] Bae J, Hong J I, Han W H and Snyder R L 2009 Chem. Phys. Lett. 475 260
[22] Lee J and Yoon M 2009 J. Phys. Chem. C 113 11952
[23] Wang B Q, Xia C H, Iqbal I, Tang N J, Sun Z R, Lv Y and Wu L 2009 Solid State Sci. 11 1419
[24] Liu B and Zeng H C 2004 Langmuir 20 4196
[25] Wong E M and Searson P C 1999 Appl. Phys. Lett. 74 2939
[26] Wu X, Cai W and Qu F Y 2009 Chin. Phys. B 18 1669
[27] Li G P, Chen T, Yan B, Ma Y and Wu T 2008 Appl. Phys. Lett. 92 173104