Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 2435–2439

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fabrication of ZnO nanodisks from structural transformation of ZnO nanorods through natural oxidation and their emission characteristics

M. Israr-Qadir[a,*], S. Jamil-Rana[a], O. Nur[a], M. Willander[a], L.A. Larsson[b], P.O. Holtz[b]

[a]*Department of Science and Technology, Campus Norrköping, Linköping University, SE-601 74 Norrköping, Sweden*
[b]*Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden*

Received 14 July 2013; received in revised form 3 August 2013; accepted 5 August 2013
Available online 19 August 2013

Abstract

An environmentally benign natural oxidation based synthetic technique has been developed to grow and transform the ZnO nanorods into nanodisks at a very mild temperature of 55 °C with excellent features of its novelty and reproducibility. Metallic zinc foil and formamide solution have been utilized as substrate and reacting solution, respectively, for the growth of ZnO nanostructures. The optimized values of temperature, concentration of formamide and the reaction time are achieved to obtain the controlled and desired nanoscale morphologies. Detailed mechanism of the structural transformation of the nanorods into nanodisks has been discussed. Strong ultraviolet emission peak along with the much weaker deep level defects related emission has been realized in the microphotoluminescence spectrum. A visible red-shift and decrease in the intensity of ultraviolet peak are observed with increasing range of temperature from 20 to 300 K.

Keywords: Zinc oxide; Formamide; Natural oxidation; Nanodisks; Emission characteristics

1. Introduction

Controlled synthesis of nanoscale structure is intimately associated with the exploration of their novel phenomena and potential applications. Morphological dimensions of the nanostructures are significantly important and expectations towards the exceptionally improved functional properties increase at the scale roughly between 1 and 100 nm. The aim to achieve these properties has entailed the tremendous interest for the fabrication of the nanoscale morphologies with high crystalline quality, purity and in particular growth orientation [1]. Amongst the various fascinating materials, ZnO is a distinct low cost material having the most plenteous nanostructures and exhibits its capability to be utilized for the miniaturized nanodevice applications. In addition, the ease of the fabrication of ZnO nanostructures of any shape and on any surface brings it to the forefront in the fields of fundament laboratory research and industrial technology. In recent years, ZnO nanostructures have become the center of an intensive interest due to its broad range of applications; such as, dye-sensitized solar cells, field emission, sensors, piezoelectric generators, hydrogen storage devices and light emitting diodes [2–7]. In many applications, the properties of ZnO nanostructures have a strong dependence on its crystallography, surface area and morphology. The growth habit and morphology of ZnO nanostructures are crucially important for practical applications and have strong dependence on the growth parameters, such as, reaction time, temperature, concentration of the solution, reagents stoichiometry and the pH value of the solution.

In the recent decade, one dimensional ZnO nanostructures with different morphologies, such as nanowires, nanorods and nanotubes [2,4,8] have proved their potential for the usefulness in the progression towards efficient nanodevices. Besides these nanostructures, various two and three dimensional nanostructures e.g. nanoplates, nanodisks, nanosheets, thin films and tetrapods are also being synthesized [9–13]. Till date, miscellaneous attractive ZnO morphologies have been synthesized

*Corresponding author. Tel.: +46 11 36 34 41; fax: +46 11 36 32 70.
E-mail address: miqadir30@gmail.com (M. Israr-Qadir).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.08.017

by using diverse methods, for instance chemical vapor deposition, thermal evaporation, vapor liquid solid and solution approaches [14–18]. The majority of these growth techniques require expensive equipments, hard growth conditions and pretreatment of the substrate, while the rest of them need external additive precursors, e.g. citrate ions, iodide and polyethylene glycols to get the desired nano/microstructures [16,18,19]. Here, we report a controlled and reproducible solution methodology for the large scale production of ZnO nanorods and their transformation into nanodisks on zinc foil via natural oxidation of metallic zinc. In addition, this simple, low cost and environmentally friendly technique has the huge potential to produce various ZnO nanostructures of diverse shape and size without any additive precursors or pretreatment of the substrate. Till date, the structural transition from ZnO nanorods to nanodisks has not been reported in the literature through a single step strategy while working at low temperature conditions or without using any external precursor. Moreover, the emission properties of the ZnO nanodisks have been analyzed through microphotoluminescence (μ-PL) for the temperature range of 20–300 K.

2. Experimental

For the preparation of ZnO nanostructures with various morphologies, two pieces of zinc foil ($1 \times 1\ cm^2$) substrates were cleaned in ethanol solution using ultrasonication bath. Both substrates were immersed perpendicularly to the bottom of a vial in a 3 ml of 15% formamide aqueous solution. The sample vial was sealed and then placed in a preheated oven at a constant temperature of 55 °C. The substrates were then rinsed thoroughly in ethanol and dried in air for further characterization. Time dependent experiments were carried out to optimize the reaction duration as well as to elucidate the transformation mechanism of ZnO nanorods into nanodisks.

3. Results and discussion

The morphological changes, dimensionality and density of the ZnO nanostructures are examined by using scanning electron microscopy (SEM), Fig. 1(a–c). Fig. 1a shows a panoramic view of the ZnO nanorods on zinc foil substrate covering the whole area with uniform density, smoothness of the top surface and equal length. It is observed that the average diameter and length of the nanorods after 18 h reach the values up to ~400 nm and 2 μm, respectively. The synthesis mechanism of ZnO nanorods can be understood by considering the process of natural oxidation which removes the thin passive layer of ZnO present on the zinc foil substrate. The pace of the growth process can be affected significantly by slowing down the natural oxidation of the zinc foil in an aqueous solution. However, the presence of high percentage of formamide in an aqueous solution can drastically enhance the spontaneous natural oxidation process which could be the reason to produce abundance of Zn^{+2} ions from zinc foil substrate. The coordination among primary amine ($–NH_2$) in formamide with Zn^{+2} ions plays an important role in the formation of zinc–formamide complex (Eq. (1)) [20,21].

$$Zn + n(HCONH_2) + 2H_2O \rightarrow Zn[n(HCONH_2)](OH)_2 + H_2\uparrow \quad (1)$$

The continuous production of the zinc–formamide complex from the zinc foil substrate simultaneously decomposes into ZnO and formamide along with water (Eq. (2)).

$$Zn[n(HCONH_2)](OH)_2 \rightarrow ZnO + [n(HCONH_2)] + H_2O \quad (2)$$

The production and consumption of the OH^- ions in the proposed chemical reactions could give rise to different values of the pH near the zinc foil substrates and in the remaining part of the solution. Although, the nature of the reacting solution has been acidic initially due to low pH value while it has been increased with passage of reaction time and reached at its stable neutral value (~7.8) due to the production of OH^- ions in the reacting solution. The nucleation of the ZnO nanoparticles starts at this stable neutral pH value. Due to the lower activation energy barrier, heterogeneous nucleation is preferential as compared to homogeneous nucleation. Hence, the lower energy between the crystal and the zinc foil substrate interface compared to the energy between the crystal and the solution interface allows the faster nucleation at lower saturation ratios onto the zinc foil substrate than in a homogeneous solution. As a result, single crystalline ZnO nanorods start to grow along a preferred orientation perpendicular to the zinc foil substrate. The production of the Zn^{+2} ions largely depends on the reaction temperature and the concentration of formamide in the solution [21,22]. The presence of the high concentration of formamide (15%) in the chemical reaction readily provides the zinc–formamide complex to supply the Zn^{+2} ions which results in the formation of the ZnO nanorods.

When the reaction time is extended up to 22 h, ZnO nanorods start to break-up into small nanodisk shaped slices along their length as shown in Fig. 1b and this process takes further 2 h for a complete structural transformation of all the ZnO nanorods into nanodisks with the thickness of < 100 nm as shown in Fig. 1c. It is obvious from the image that nanodisks hold their hexagonal shape with high density and a smooth surface of the (0002) crystal plane. The mechanism behind the structural transition of nanorods into nanodisks could be the result of abundantly produced OH^- ions during the chemical reaction shown in Eq. (1). These OH^- ions consequently introduce a high pH value in the surroundings of the zinc foil containing ZnO nanorods and suppress the stability of the nanorods along their length which can accordingly lead to the break-up of the nanorods. The perpendicular orientation of the zinc foil substrate with the bottom of the vial can also play a role in this structural transformation. The growth of nanorods using the proposed chemical reaction is natural but their structural transformation into nanodisks is quite interesting utilizing this single step synthetic approach. Also, the ZnO nanostructures grown using the present technique always have a material with high purity because this approach is based on the natural oxidation of the zinc foil and no additional precursors are involved [20]. Although, few reports on the alteration of ZnO nanostructures by using external precursors can be found in the literature, however,

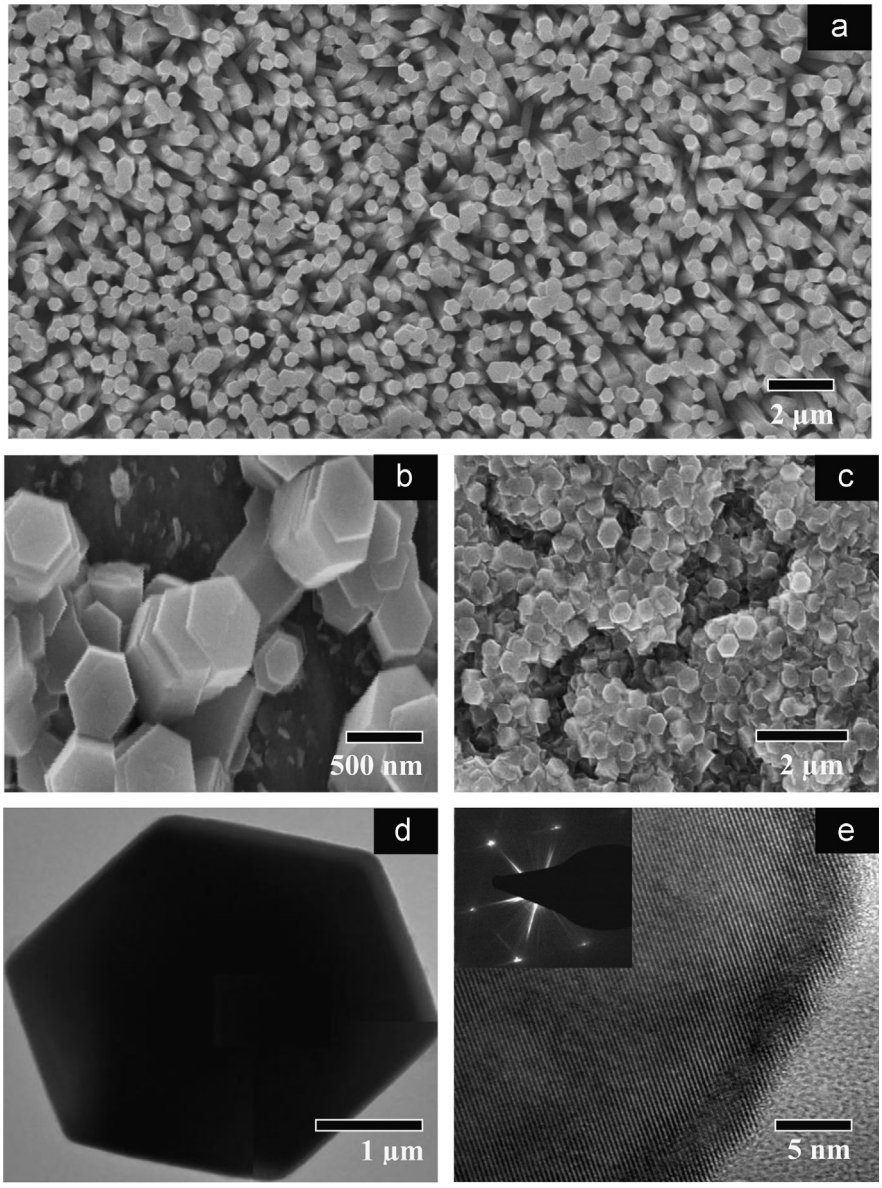

Fig. 1. SEM images of ZnO nanostructures grown on zinc foil at various stages: (a) Hexagonal-shaped ZnO nanorods (18 h). (b) ZnO nanorods (22 h) showing their structural transformation into nanodisks. (c) Large array of hexagonal shaped ZnO nanodisks (24 h). (d) Low-resolution TEM of single nanodisk showing its hexagonal phase. (e) High resolution TEM image of nanodisk showing an impurity free crystal structure. Inset shows the corresponding SAED pattern from the same nanodisk.

such single step, simple structural transformation has not been reported yet. A transmission electron microscope (TEM) is used to study the structural characteristics of the ZnO nanodisks while the sample was prepared by ultrasonic dispersion of product on a copper grid and selected area electron diffraction (SAED) pattern has been recorded to investigate their crystalline growth orientation. Low-resolution TEM image confirms hexagonal shape and thick structure of single nanodisk as shown in Fig. 1d. High resolution TEM image from the edge of the ZnO nanodisk reveals a good crystalline quality of the nanostructure, Fig. 1e. In the inset of Fig. 1e, the SAED pattern recorded from the face of the nanodisk along the [0002] zone axis shows the hexagonal ZnO lattice structure.

The composition of the presented nanostructures is affirmed by using energy dispersive X-ray spectroscopy (EDS). Fig. 2a illustrates the EDS pattern from ZnO nanodisks which is almost identical to other nanostructures and shows the pure ZnO material without any external impurity. The overall phase purity and crystallinity of ZnO nanorods and nanodisks have been characterized by X-ray diffraction (XRD). All the diffraction peaks are indexed to zinc foil substrate and pure hexagonal wurtzite ZnO structure showing good agreement with the values of the standard card (JCPDS 36-1451), Fig. 2b.

Temperature dependent optical characteristics of the ZnO nanodisks have been analyzed by μ-PL for the temperature range of 20–300 K. The μ-PL of ZnO nanodisks exhibits a strong UV emission and a very weak blue-green emission

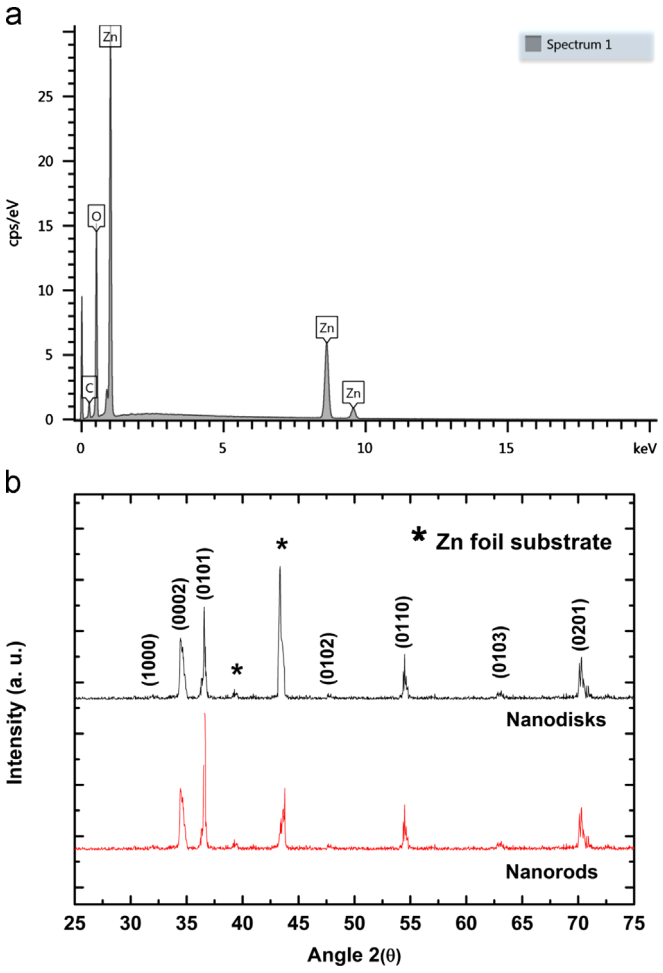

Fig. 2. (a) EDS spectrum of ZnO nanodisks. (b) XRD pattern of ZnO nanorods and nanodisks showing hexagonal phase purity.

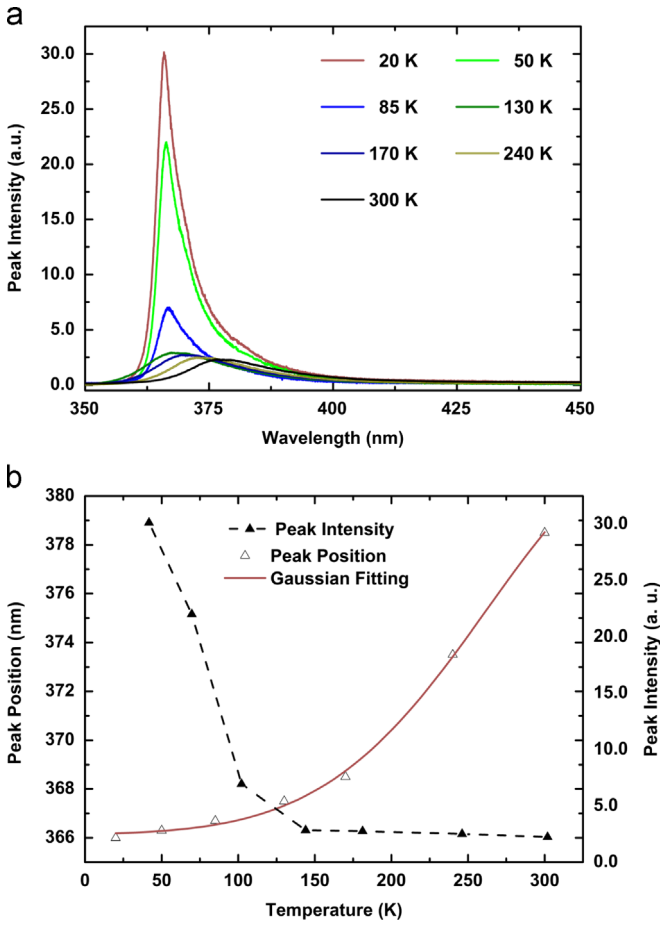

Fig. 3. (a) Temperature dependent μ-PL spectra of ZnO nanodisks ranging from 20 to 300 K. (b) Effect of increase in temperature on the intensity and peak position of UV emission peak.

peak. In ZnO, the UV emission peak is generally considered as a band gap-related emission and the visible emission is imputed to deep level defects related emission. The strength of UV emission peak from ZnO nanodisks compared to the visible emission is attributed to high crystalline quality of ZnO nanodisks which indeed confirms our discussion on the better crystal quality achieved by the presented synthetic technique. Micro-PL spectra show a red-shift in the UV exciton related emission with the gradual increase in the temperature value, shown in Fig. 3a. Red-shift in the UV emission peak has been related to the band gap shrinkage of ZnO nanodisks which is consistent with the well-known Varshni relation [23] and earlier published work [24,25]. The temperature dependence of the μ-PL peak intensity and position is clearly shown in Fig. 3b. The high UV emission intensity at 20 K is a strong evidence of a high optical quality of ZnO nanodisks. However, the slight increase in the intensity of the deep levels emission is observed with the increase of temperature.

4. Conclusions

The presented synthetic strategy has full potential for the large scale production of nanostructures but also has the capability to govern the time dependent morphological evolution for ZnO nanorods and their structural transformation into nanodisks. The abundantly produced OH^- ions from the metallic zinc foil substrate and orientation of the substrate have been suggested as a key behind the transformation of ZnO nanorods into nanodisks slices. The strong intensity of the UV peak in μ-PL emission indicates a high crystalline quality of the ZnO nanodisks. Temperature dependent μ-PL shows an energy red-shift and intensity decrease of the UV emission peak with increasing temperature. The synthesis of the ZnO nanostructures may offer promising applications for optical and sensing devices due to their high surface area to volume ratio.

References

[1] A.P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, Science 271 (1996) 933.
[2] M. Law, L.E. Greene, A. Radenovic, T. Kuykendall, J. Liphardt, P.J. Yang, ZnO–Al_2O_3 and ZnO–TiO_2 core–shell nanowire dye-sensitized solar cell, Journal of Physical Chemistry B 110 (2006) 22652.
[3] X.D. Bai, E.G. Wang, P.X. Gao, Z.L. Wang, Measuring the work function at a nanobelt tip and at a nanoparticle surface, Nano Letters 3 (2003) 1147.

[4] M.Q. Israr, J.R. Sadaf, M.H. Asif, O. Nur, M. Willander, B. Danielsson, Potentiometric cholesterol biosensor based on ZnO nanorods chemically grown on Ag wire, Thin Solid Films 519 (2010) 1106.
[5] Y. Xi, J. Song, S. Xu, R. Yang, Z. Gao, C. Hu, Z.L. Wang, Growth of ZnO nanotube arrays and nanotube based piezoelectric nanogenerators, Journal of Materials Chemistry 19 (2009) 9260.
[6] Q. Wan, C.L. Lin, X.B. Yu, T.H. Wang, Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors, Applied Physics Letters 84 (2004) 124.
[7] J.R. Sadaf, M.Q. Israr, S. Kishwar, O. Nur, M. Willander, White electroluminescence using ZnO nanotubes/GaN heterostructure light-emitting diode, Nanoscale Research Letters 5 (2010) 957.
[8] M.Q. Israr, J.R. Sadaf, L.L. Yang, O. Nur, M. Willander, J. Palisaitis, P.O.Å. Persson, Trimming of aqueous chemically grown ZnO nanorods into ZnO nanotubes and their comparative optical properties, Applied Physics Letters 95 (2009) 073114.
[9] Z. Jing, J. Zhan, Fabrication and gas-sensing properties of porous ZnO nanoplates, Advanced Materials 20 (2008) 4547.
[10] C.X. Xu, X.W. Sun, Z.L. Dong, M.B. Yu, Zinc oxide nanodisks, Applied Physics Letters 85 (2004) 3878.
[11] P. Gao, Y. Chen, Y. Wang, Q. Zhang, X. Li, M. Hu, A simple recycling and reuse hydrothermal route to ZnO nanorod arrays, nanoribbon bundles, nanosheets, nanocubes and nanoparticles, Chemical Communications 2 (2009) 2762.
[12] C.Y. Tsay, K.S. Fan, S.H. Chen, C.H. Tsai, Preparation and characterization of ZnO transparent semiconductor thin films by sol–gel method, Journal of Alloys and Compounds 495 (2010) 126.
[13] Z. Zhang, H. Yuan, Y. Gao, J. Wang, D. Liu, J. Shen, L. Liu, W. Zhou, S. Xie, X. Wang, X. Zhu, Y. Zhaoand, L. Sun, Large-scale synthesis and optical behaviors of ZnO tetrapods, Applied Physics Letters 90 (2007) 153116.
[14] C.C. Wu, D.S. Wuu, T.N. Chen, T.E. Yu, P.R. Lin, R.H. Horng, H.Y. Lai, Growth and characterization of epitaxial ZnO nanowall networks using metal organic chemical vapor deposition, Japanese Journal of Applied Physics 47 (2008) 746.
[15] A. Umar, Y.B. Hahn, ZnO nanosheet networks and hexagonal nanodiscs grown on silicon substrate: growth mechanism and structural and optical properties, Nanotechnology 17 (2006) 2174.
[16] C. Xu, D. Kim, J. Chun, K. Rho, B. Chon, S. Hong, T. Joo, Temperature-controlled growth of ZnO nanowires and nanoplates in the temperature range 250–300 °C, Journal of Physical Chemistry B 110 (2006) 21741.
[17] H. Yu, Z. Zhang, M. Han, X. Hao, F. Zhu, A general low-temperature route for large-scale fabrication of highly oriented ZnO nanorod/nanotube arrays, Journal of the American Chemical Society 127 (2005) 2378.
[18] Z.R. Tian, J.A. Voigt, J. Liu, B. Mckenzie, M.J. Mcdermott, M.A. Rodriguez, H. Konishi, H. Xu, Complex and oriented ZnO nanostructures, Nature Materials 2 (2003) 821.
[19] H.K. Sun, M. Luo, W.J. Weng, K. Cheng, P.Y. Du, G. Shen, G.R. Han, Position and density control in hydrothermal growth of ZnO nanorod arrays through pre-formed micro/nanodots, Nanotechnology 19 (2008) 125603.
[20] Z. Zhang, H. Yu, Y. Wang, M. Yong Han, Aggregation-driven growth of well-oriented ZnO nanorod arrays, Nanotechnology 17 (2006) 2994.
[21] N. Boukos, C. Chandrinou, K. Giannakopoulos, G. Pistolis, A. Travlos, Growth of ZnO nanorods by a simple chemical method, Applied Physics A 88 (2007) 35.
[22] Z. Zhang, H. Yu, X. Shao, M. Han, Near-room-temperature production of diameter-tunable ZnO nanorod arrays through natural oxidation of zinc metal, Chemistry: A European Journal 11 (2005) 3149.
[23] P. Varshni, Temperature dependence of the energy gap in semiconductors, Physica (Amsterdam) 34 (1967) 149.
[24] B.Q. Cao, W. Cai, H. Zeng, Temperature-dependent shifts of three emission bands for ZnO nanoneedle arrays, Applied Physics Letters 88 (2006) 161101.
[25] K.J. Hong, T.S. Jeong, Growth and optical absorption spectra of ZnO films grown by pulsed laser deposition, Journal of Crystal Growth 280 (2005) 545.