ELSEVIER



Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation and properties of ZnO nanostructures by electrochemical anodization method

Shuanghu He^a, Maojun Zheng^{a,*}, Lujun Yao^a, Xiaoliang Yuan^a, Mei Li^b, Li Ma^b, Wenzhong Shen^a

^a Laboratory of Condensed Matter Spectroscopy and Opto-Electronic Physics, Department of Physics, Shanghai Jiao Tong University, 1954 Hua Shan Road, Shanghai 200030, China ^b School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

Article history: Received 27 June 2009 Received in revised form 11 October 2009 Accepted 30 October 2009 Available online 14 November 2009

PACS: 81.07.-b 82.45.Aa 78.67.-n 78.55.Et 68.08.Bc

Keywords: Diverse ZnO nanostructures Electrochemical anodization Strong visible emission Electrowettability Near superhydrophobic

1. Introduction

ABSTRACT

ZnO thin films with diverse nanostructures, including nanodot, nanowire and nanoflower, have been fabricated on zinc foils by a simple and rapid electrochemical anodization method. The ZnO thin films reveal very strong visible emission that is ascribed to the transition between V_0Zn_i and valence band. Under the dc or ac electric field, the electroinduced surface wettability conversion from the superhydrophobic to hydrophilic state was observed and the generation of surface defective sites on ZnO films under electric field was used to explain the transition mechanism. This work provides a simple and rapid method for synthesizing different ZnO nanostructures in large scale, and electric field can be used to modulate the wettability of ZnO nanostructures.

© 2009 Elsevier B.V. All rights reserved.

Zinc oxide (ZnO) is a well recognized semiconducting and piezoelectric material. Their wide direct bandgap energy of 3.37 eV with a large excitation binding energy of 60 meV at room temperature [1] is much larger than those of other semiconductor materials. Due to its unique properties such as the excellent thermal and chemical stability, large piezoelectric constant and easy modified electric conductivity, ZnO nanomaterials have been considered to have great potential applications in ultraviolet lasers, solar cells, gas sensors, bio-detectors, UV light-emitting diodes, photo catalysts, field emitter, transparent conductors [2– 9], etc.

The properties of ZnO are strongly dependent on its structures, including the morphology, aspect ratio, and size, orientation, and density of crystal [10–12]. Developments of the controllable synthesis of ZnO nanomaterials in morphology are important to explore their potential applications as smart and functional materials. So far, numerous quasi-one-dimensional nanostruc-

tures of ZnO such as nanowires [13], nanobelts [14] and nanotubes [15] and various self-organized hierarchical ZnO nanostructures in the form of nanorings [16], nanopropellers [17], nanobridges [18], nanonails [19], and nanocombs [20,21] have been successfully synthesized. Various hydrothermal [22–24], thermal evaporation [14,25,26,16], molecular beam epitaxy [27], chemical vapor deposition (CVD) [28], and metal organic chemical vapor deposition (MOCVD) [29] techniques have been reported for fabricating above ZnO nanostructures.

The conventional vapor-phase synthesis methods require expensive systems and rigid environmental conditions, especially the high temperature (\sim 500–1400 °C) and low pressure. Although the solution chemical approach can allow the growth at much lower temperatures (<200 °C) and large-scale production, it requires long reaction time (from a few hours to several days). Recently, electrochemical method attracted much attention due to its short reaction times and low cost. Yang et al. [30] reported the synthesis of highly ordered ZnO ultrathin nanorod and hierarchical nanobelt arrays on zinc substrate with an electrochemical route in the mixed H₂O₂ and NaOH solution.

In this paper, we report an electrochemical anodization method to synthesize different ZnO nanostructures in large scale with less than an hour by using the mixed hydrofluoric acid and methanol

^{*} Corresponding author. Fax: +86 021 54741040. *E-mail address:* mjzheng@sjtu.edu.cn (M. Zheng).

^{0169-4332/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.apsusc.2009.10.104

electrolyte. It reveals that kinds of nanostructures such as ZnO nanodots, nanowires and nanoflowers can be obtained by controlling the concentration of the electrolyte and reacting times. The photoluminescence (PL) further shows that the ZnO nanostructures have a strong visible emission, which originates from the transition between V_0Zn_i and valence band. The droplet stability and electrowetting behavior of ZnO nanostructure films were also explored under a dc (ac) voltage by measuring the contact angles (CAs).

2. Experimental details

The electrochemical anodization of the Zn foil was performed in a tailor-made holder exposed to the electrolyte. Round Zn foil (99.99% purity, 0.25 mm thickness) with a radius of 1 cm was degreased in acetone and ethanol for 2 min of ultrasonic cleaning, washed with deionized water. Prior to the electrochemical treatment, the Zn foil was electropolished under constant condition at the room temperature. The electrolyte composition was a 1:2 volume mixture of phosphoric acid and ethanol. The voltage was 4.5 V and the stable electropolishing current density was ~10 mA cm⁻². The electropolishing process lasts for about 20 min and a satisfactory mirror finished Zn was obtained.

The cathode was a graphite plate (or Zn foil) and the polishing Zn foil used as the anode with the distance of them was 50 mm. The

anodization was conducted in mixed electrolyte of water, hydrofluoric acid (48%) and methanol (99.9%). The HF concentration is 1 wt.% and the methanol volume fraction is 30% or 50%. The reaction time ranges from 30 s to 30 min and the applied voltage is from 9.7 V to 16.7 V. Finally, the white ZnO thin films were deposited on the Zn foils, thoroughly washed with deionized water to eliminate remainder, and dried in air at room temperature.

The morphologies of ZnO films were characterized by scanning electron microscopy (SEM) (Philips XL30FEG). The Raman spectra and PL were measured by Jobin-Yvon LabRAM HR 800UV micro-Raman system with a 325 nm, an Andor DU420 classic CCD detector and Linkam THMS600 temperature stage and the hydrophobicity of the ZnO films was examined with an OCA 20 CA system (Data Physics Instrument GmbH, Germany).

3. Results and discussion

3.1. Structure and morphology

Fig. 1(a)–(f) shows the corresponding SEM images of samples A–F prepared under the same voltage of 9.7 V but with different reaction times in the electrolyte including 50 vol.% methanol. ZnO nanodots with average diameter of about 62 nm and 115 nm can be clearly observed at the wall of the Zn trench in Fig. 1(a) and (b), respectively. It can be seen that the sidewall of the trench in the

Fig. 1. SEM images of ZnO nanostructures grown on the Zn foil with different reaction times in a mixed solution of methanol and water (50 vol.% methanol, 1 mass% HF): (a) sample A, 30 s; (b) sample B, 1 min; (c) sample C, 5 min; (d) sample D, 10 min; (e) sample E, 15 min; (f) sample F, 30 min. The length of inserted scale bars is 500 nm.

sample B is shorter than that in the sample A. With increasing reaction time, the nanowire structure appears as shown in Fig. 1(c) and the sidewall of the trenchs in Zn substrate nearly disappears. Sample D exhibits a flower-like morphology after electrochemical anodization of the Zn foil for 10 min, seen in Fig. 1(d), each flower has a size of 1 μ m and is composed of hundreds of sheet-like nanopetals. The thickness of the nanopetal is about 30 nm on average. The nanoflowers disappear and the nanowires and nanodots can be seen again when the reaction time is 15 min and 30 min as shown in Fig. 1(e) and (f).

Fig. 2(a) shows the SEM images of the ZnO naonostructured thin films synthesized in 30 vol.% methanol under the voltage of 9.7 V with the reaction time for 15 min. It exhibits a large-scale flowerlike nanostructure with the average size of the nanoflowers about 500 nm. In order to explore the effect of applied voltage to the morphology, we increase the voltage to 16.7 V without changing other conditions compared with that of sample D. However, the morphology of sample H still is flower-like as shown in Fig. 2(b).

The overall reactions for the anodization of Zn can be represented as follows:

$$\mathrm{HF} \to \mathrm{H}^+ + \mathrm{F}^- \tag{1}$$

$$H_2 O \rightarrow H^+ + O H^- \tag{2}$$

The H^+ ion moves to the cathode, meanwhile the F^- and OH^- ions move to the anode under the influence of the electric field. The reaction happens in the experiment process:

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \to \mathrm{H}_{2} \uparrow \tag{3}$$

$$Zn \to Zn^{2+} + 2e^{-} \tag{4}$$

Therefore, that the gas escapes on the cathode was found. The Zn foil has been etched to a series of parallel trenches at the beginning of the anodication. The Zn^{2+} and OH^- concentrations in the electrolyte are getting larger and larger along with the increasing of anodization time. The ion OH^- preferentially loses the electron because of OH^- low electrode potential compared with F^- . The reaction is

$$40H^{-} \rightarrow 2H_{2}O + 2O + 4e^{-} \tag{5}$$

The combination of the oxygen and the Zn produces the ZnO nanodots at the wall of the trench because of its low surface energy:

$$Zn + 0 \rightarrow ZnO$$
 (6)

With the reaction time increasing, the Zn on the trench sidewalls dissolves due to the reaction (4) under the electric field. The trench sidewalls become thinner and shorter but the number of the nanodots increases and the average diameter gets larger as shown in Fig. 1(a)–(c). Then ZnO nanodot connects with the other

nanodots and the nanaowire forms presented in Fig. 1(c). After the reaction of 10 min, the nanowires change into the nanoflowers. Finally, the OH⁻ concentration in the electrolyte becomes lower after the reaction time exceeding 10 min and also the concentration of oxygen atoms in the electrolyte reduces, so the ZnO nanoflower dissolves. The nanowires and nanodots appear again when the reaction time increases to 15 min and 30 min, respectively. The mechanism that how does the nanowires transform to the nanoflowers is still under discussion. We will study this research deeply on the subsequent work.

3.2. Optical properties

The optical properties of hierarchical ZnO nanostructure have been studied by room-temperature Raman and PL measurements. ZnO has a wurtzite structure with $C_{6\nu}$ (P6₃mc) point-group symmetry. Group theory predicts that the optical phonon modes at the point of the Brillouin zone (BZ) belong to the following irreducible representation: $\Gamma_{opt} = 1A_1 + 2B_1 + 1E_1 + 2E_2$. Both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active. The two nonpolar E_2 modes (E_2 low, E_2 high) are Raman active only. The B_1 modes are infrared and Raman inactive (silent modes). The frequencies of the fundamental optical modes in ZnO are as follows [31]: E_2 (low) = 101 cm⁻¹, E_2 (high) = 437 cm⁻¹, A_1 (TO) = 380 cm⁻¹, A_1 (LO) = 574 cm⁻¹, E_1 (TO) = 407 cm⁻¹, and E_1 (LO) = 581 cm⁻¹. The E_2 (low) is associated with the vibration of the heavy Zn sublattice, while E_2 (high) mode corresponds to band characteristic of wurtzite phase [31]. The feature at about 573 cm⁻¹ is contrary to the change of the A_1 (LO) phonon and is induced by the defect, which is one of the very outstanding characteristics of ZnO phonon Raman spectra. Under the backscattering geometry of $Z(X, -)Z^{-}$, only E_1 (LO) and E_2 (high) modes can be observed since other modes are forbidden according to the Raman selection rules [32].

Fig. 3 displays Raman spectra of ZnO nanostructured thin films under different reaction times and different applied voltages and they show a similar pattern for all. There is only one apparent ZnO photon mode appearing at 578 cm⁻¹, which has been assigned to the E_1 (LO) mode. It is generally accepted that E_1 (LO) mode is associated with the oxygen vacancies, zinc interstitial defect states and free carries [33]. The high intensity of E_1 (LO) indicates that the samples prepared by electrochemical anodization have many oxygen vacancies or zinc interstitial defect states and the samples have poor crystal quality. In order to explore which kinds of defect cause this E_1 (LO) mode, the composition of the ZnO nanostructures is investigated using energy dispersive X-ray spectroscopy (EDX). Fig. 4 shows the EDX spectrum of samples D and H. The pattern indicates that the ZnO nanostructures are composed of only Zn and O. Quantitative analysis shows that the mean atomic



Fig. 2. SEM images of ZnO nanostructures grown on the Zn foil with reaction time 15 min in different electrolytes and anodic voltages: (a) sample G (30 vol.% methanol, 1 mass% HF and applied voltage is 9.7 V) and (b) sample H (50 vol.% methanol, 1 mass% HF and the applied voltage is 16.7 V). The length of inserted scale bars is 500 nm.



Fig. 3. The Raman spectra of samples B, D, E and H.

ratio of Zn/O of the ZnO nanostructrures is about 1.3:1 and 1.1:1, respectively for samples D and H. From the above data it is obvious that the number of Zn atoms is more. We can infer that E_1 (LO) mode is associated with zinc interstitial defect. Comparing the Raman spectrum of samples D and H, the intensity of E_1 (LO) mode of sample D is higher than that of sample H. In other words, the sample H has better crystal quality than the sample D. This phenomenon proves that the higher voltage applied, the more oxygen atoms produced in the unit time and the more chance the Zn atoms and oxygen atoms collide, the better quality of ZnO nanostructures synthesized.

The photoluminescence spectrum of the various ZnO nanostructured thin films was shown in Fig. 5. For the samples B, D and E, there is a near absence ultraviolet (UV) peak at \sim 380 nm and a very strong green emission at \sim 576.2 nm. It is generally accepted that, for ZnO film, the UV emission called as the near band edge emission (NBE) which originates from the recombination of the free excitons through an exciton–exciton collision process, and the green emission in visible region generally nominated as deep level



Fig. 4. The EDX spectra of the samples D and H.



Fig. 5. Room-temperature photoluminescence spectra of samples B, D, E and H.

emission (DLE) is probably related to the variation of the intrinsic defects in ZnO films, such as zinc vacancy (V_{Zn}), oxygen vacancy (V_O), interstitial zinc (Zn_i), interstitial oxygen (O_i), and antisite oxygen (O_{Zn}) [34,35]. In the visible region, different peaks originate from different transitions. The peak on 525 nm relates to the transition between V_OZn_i (complex of V_O and Zn_i) and valence band, and the peak on 574 nm relates to the transition between V₀Zn_i and valence band or between exciton level and antisite oxygen (O_{Zn}) . It can be deduced that a very strong green emission band near 576 nm observed in the PL spectra of samples B, D and E should originate from the transition between V₀Zn_i and valence band in the ZnO nanostrutures. These results can agree with the results from the Raman spectrum. In addition, the strong green peak also indicates that high surface-to-volume ratio is an important factor to affect the intensity of green emission. The abundant surface/interface in ZnO nanostructure can introduce a high density of defects at the surface and interface to form defect energy bands, which can trap free carriers from the bulk, resulting in the stronger visible emission. Yao et al. [36] also reported that the surface-to-volume ratio can influence significantly the PL emission efficiency. It can be seen a strong peak at the 373 nm considered as the UV emission peak and a weak peak at 573 nm considered as the visible emission peak from the PL spectrum of sample H. Comparing the PL spectrum of the samples D and H, the intensity of UV emission of sample H is larger than that of sample D. Meanwhile the intensity of visible emission of sample H is smaller than that of sample D. It indicates that the sample H has better quality than the sample D, which also has been obtained from experimental result from the EDX spectrum and the Raman spectrum. This work reveals that the strong visible emission from ZnO nanostructure can be realized by controlling the growth conditions in electrochemical anodization method.

3.3. Electrowetting behavior

The wettability and capillary transport of water have attracted much attention due to the fundamental interest for several applications in nanofluidic and separation technologies [37]. For water to wet the membranes, work has to be done to overcome the energy barrier to realize the transition from the hydrophobic to hydrophilic state. Some theoretical models [38,39] have been built to explore the electrowetting behaviors. Now, surface wettability conversion on carbon nanotube membranes and silicon nanowire thin films has been realized by electrical methods [40–43]. As to



Fig. 6. Photographs of water droplet shape on the sample D: (a) no voltage applied; (b) +50 V bias applied; (c) -50 V bias applied and (d) 50 V ac bias applied.

ZnO, much investigations focus on CA change with UV illumination [44]. Our objective here is to study the effect of the application of external potential on the droplet stability and electrowetting behavior of ZnO nanostructure films.

Fig. 6(a) shows that the CA of a water droplet on the sample D film is about 132°, which is larger than that of relatively flat ZnO films (CA = 109°) [45]. Above results indicate that the as-prepared ZnO films have hydrophobic property. For a given material, the surface free energy and the surface roughness are two main factors governing the surface wettability. Most often micro–nano-binary structures are required to achieve very high CAs. In the present case, the ZnO films have special surfaces is greatly enhanced by the networks with the combination of the different scales. It is believed that the near superhydrophobic feature of ZnO films could be ascribed to the surface with network structures to trap air in the interspaces [46].

A Pt wire was inserted into the water droplet to establish electrical contact. The droplet shape and CA is found to remain unchanged in 2 min when an applied voltage to sample D is low, which we think that lower voltage cannot break through the energy barrier. As seen in Fig. 6(b), the CAs change from 132° to 119° when a bias of +50 V (Pt wire as the cathode, the substrate as the anode) is applied to the droplet of sample D for 2 min. Meanwhile, the CA reduces to 76° with a -50 V bias applied as shown in Fig. 6(c). Then an ac voltage of 50 V with a frequency of 50 Hz was also applied to the two electrodes. After 2 min the CA change of electrically driven wetting of the sample D is 43°, which means that it turns into hydrophilic surface, as shown in Fig. 6(d). For samples B and H, they also reveal similar electrowetting behavior. We suggest the obvious electrowetting behavior could result from the generation of surface defective sites on ZnO films under the effect of electric field. Water molecules may very easily coordinate into the surface defective sites, leading to the increase of the water adsorption [45]. The water dropped on the ZnO film surface dissociates into H₃O⁺ and OH⁻, because of high electrostatic fields at the interface between the ZnO film and the Pt wire [47]. Charge transport occurs by the movement of a proton from a H_3O^+ ion to an adjacent water molecule, and so on. Then the protonic conduction is set up in the water droplet. For the interface between the ZnO film and Zn, the work function for ZnO and Zn is 5.3 eV and 4.3 eV, respectively. In this situation the electrons in ZnO transform to the Zn, and the electrons in water transform to the ZnO if a bias of +50 V is applied to the Zn and Pt wire. The lattice oxygen loses the electrons and leads to the formation of surface oxygen vacancies on the surface between the ZnO film and Zn. The formation process of defective sites is represented as follows [45]:

$$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^- + \Box \quad (oxygen \ vacancy)$$
 (7)

As shown in Fig. 6, the bubbles can be clearly seen in the experiment process. The water molecules coordinate into the oxygen vacancy sites (\Box), which leads to dissociative adsorption of the water molecules on the surface. This process gives rise to increased water adsorption and leads to the decrease in CA. Meanwhile, some of electrons from the water droplet react with the lattice metal ions (Zn^{2+}) to form Zn^+ defective sites (surface trapped electrons) (Eq. (8)).

$$Zn^{2+} + e^- \rightarrow Zn_s^+ \tag{8}$$

In ambient condition, the Zn_s^+ tends to react immediately with oxygen molecules absorbed on the surface between the water droplet and the ZnO film (Eq. (9)).

$$Zn_s^+ + O_2 \rightarrow Zn^{2+} + O_2^-$$
 (9)

The water and oxygen compete to dissociatively adsorb on the surface defective sites, which leads to desorption of water molecules on the surface. Thus the CA increases. Therefore it can be deduced that the water absorption could dominate in the whole process based on the fact of the CA decrease. If a -50 V bias applied to the Zn and Pt wire, the potential barrier with the Zn and

ZnO film decreases and the more electrons in the Zn transport to the ZnO film comparing with a +50 V bias applied. The process (Eq. (7)) happens on the surface between the water droplet and the ZnO film, while the processes (Eqs. (8) and (9)) happen on the surface between the ZnO film and the Zn. However, the CA change of that a positive voltage applied is 13° , less than the CA change (56°) of that a negative voltage applied. We suggest that the more surface oxygen vacancies produce in the unit time with a negative voltage applied. When applying an ac bias voltage, we obtained the changed CA value between the positive and the negative voltage that applied, in other words, the influence of ac bias voltage is the cooperative interaction of them, which demonstrates that the CA value can be controlled by changing the polarity of the applied bias.

4. Conclusion

ZnO thin films with different nanostructures in the form of nanodot, nanowire and nanoflower were prepared by a simple and rapid electrochemical anodization method. The PL property can be controllable by changing growth conditions. Past studies paid more attention to the fabrication of ZnO nanostructure with highquality UV emission. Here a very strong visible emission and narrow full-width of half-maximum (FWHM) (30-40 nm) have been observed in the ZnO nanostructures with abundant surface/ interface and high density of defects. This ZnO films may have potential applications in visible optoelectronic devices, photoanodes of dye-sensitized solar cells and sensors. On the other hand, much researches focused on CA change with UV illumination and we demonstrate that the surface wettability can also be governed by the application of external potential on the ZnO nanostructure films, which is ascribed to the generation of surface defective sites on ZnO films under effect of electric field.

Acknowledgments

This work was supported by the Natural Science Foundation of China (grant no. 10874115), Shanghai Key Basic Research Project of 08JC1411000, Shanghai Nanotechnology Research Project 0952nm01900, and National Major Basic Research Project of 2006CB921507. We thank Instrumental Analysis Center of SJTU for SEM analysis.

References

- [1] Y.F. Chen, D.M. Bagnall, H.J. Koh, K.T. Park, K. Hiraga, Z.Q. Zhu, T. Yao, J. Appl. Phys. 84 (1998) 3912.
- [2] M.S. Arnold, P. Avouris, Z.W. Pan, Z.L. Wang, J. Phys. Chem. B 107 (2003) 659.

- [3] W.I. Park, J.S. Kim, G.C. Yi, M.H. Bae, H.J. Lee, Appl. Phys. Lett. 85 (2004) 5052.
- [4] G.S.T. Rao, D.T. Rao, Sens. Actuators B 55 (1999) 166.
- [5] X.D. Wang, C.J. Summers, Z.L. Wang, Nano Lett. 4 (2004) 423.
- [6] Q.H. Li, Q. Wan, Y.J. Chen, T.H. Wang, H.B. Jia, D.P. Yu, Appl. Phys. Lett. 85 (2004) 636.
- [7] C.X. Xu, X.W. Sun, B.J. Chen, Appl. Phys. Lett. 84 (2004) 1540.
- [8] K. Tominaga, N. Umezu, I. Mori, T. Ushiro, T. Moriga, I. Nakabayashi, Thin Solid Films 334 (1998) 35.
- [9] T. Minami, S. Ida, T. Miyata, Y. Minamino, Thin Solid Films 445 (2003) 268.
- [10] Z.L. Wang, J. Phys. Condens. Matter 16 (2004) R829.
- 11] J. Zhang, L.D. Sun, J.L. Yin, H.L. Su, C.S. Liao, C.H. Yan, Chem. Mater. 14 (2002) 4172. [12] Q. Zhao, H.Z. Zhang, Y.W. Zhu, S.Q. Feng, X.C. Sun, J. Xu, D.P. Yu, Appl. Phys. Lett. 86 (2005) 203115.
- [13] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang,
- Science 292 (2001) 1897.
- [14] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science 291 (2001) 1947.
- [15] H.D. Yu, Z.P. Zhang, M.Y. Han, X.T. Hao, F.R. Zhu, J. Am. Chem. Soc. 127 (2005) 2378. [16] X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang, Science 303 (2004) 1348.
- [17] P.X. Gao, Z.L. Wang, J. Phys. Chem. B 106 (2002) 12653.
- [18] J.Y. Lao, J.Y. Huang, D.Z. Wang, Z.F. Ren, Nano Lett. 3 (2003) 235.
- [19] H.Q. Yan, R.R. He, J. Johnson, M. Law, R.J. Saykally, P.D. Yang, J. Am. Chem. Soc. 125 (2003) 4728.
- [20] Z.L. Wang, X.Y. Kong, J.M. Zuo, Phys. Rev. Lett. 91 (2003) 185502.
- [21] C.X. Xu, X.W. Sun, Z.L. Dong, M.B. Yu, J. Cryst. Growth 270 (2004) 498
- [22] L.E. Greene, M. Law, J. Goldberger, F. Kim, J.C. Johnson, Y.F. Zhang, R.J. Saykally, P. Yang, Angew. Chem. Int. Ed. 42 (2003) 3031.
- [23] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P. Yang, Nat. Mater. 4 (2005) 455.
- [24] M.S. Tokumoto, S.H. Pulcinelli, C.V. Santilli, V. Briois, Phys. Chem. B 107 (2003) 568
- [25] W.L. Hughes, Z.L. Wang, Appl. Phys. Lett. 82 (2003) 2886.
- [26] X.Y. Kong, Z.L. Wang, Nano Lett. 3 (2004) 1625.
- [27] A.S. Shaporev, V.K. Ivanov, A.E. Baranchikov, Y.D. Tret'yakov, Inorg. Mater. 43 (2007) 35.
- [28] Y.B. Li, F.D. Valle, M. Simonnet, I. Yamada, J.J. Delaunay, Nanotechnology 20 (2009) 045501.
- [29] J.B. Baxter, E.S. Aydil, Appl. Phys. Lett. 86 (2005) 053114.
- [30] J.H. Yang, G.M. Liu, L. Jun, Y.F. Qiu, S.H. Yang, Appl. Phys. Lett. 90 (2007) 103109.
- Ì31Ì T.C. Damen, S.P.S. Porto, B. Tell, Phys. Rev. 142 (1966) 570.
- [32] S.K. Sharma, G.J. Exarhos, Solid State Phenom. 55 (1997) 32.
- [33] Z.C. Zhang, B.B. Huang, Y.Q. Yu, D.L. Cui, Mater. Sci. Eng. B 86 (2001) 109.
- [34] D.H. Fan, Z.Y. Ning, M.F. Jiang, Appl. Surf. Sci. 245 (2005) 414.
- [35] H.Q. Li, Z.Y. Ning, S.H. Cheng, M.F. Jiang, Acta Phys. Sin. 53 (2004) 867. [36] B.D. Yao, Y.F. Chan, N. Wang, Appl. Phys. Lett. 81 (2002) 757.
- [37] M.H. Jin, X.J. Feng, L. Feng, T.L. Sun, J. Zhai, T.J. Li, L. Jiang, Adv. Mater. 17 (2005)
- 1977. [38] K.H. Kang, Langmuir 18 (2002) 10318.
- [39] V. Bahadur, S.V. Garimella, Langmuir 23 (2007) 4918.
- [40] Z.K. Wang, L.J. Ci, L. Chen, S. Nayak, P.M. Ajayan, N. Koratkar, Nano Lett. 7 (2007) 697.
- [41] J.Y. Chen, A. Kutana, C.P. Collier, K.P. Giapis, Science 310 (2005) 1480.
- [42] N. Verplanck, E. Galopin, J.C. Camart, V. Thomy, Nano Lett. 7 (2007) 813.
- [43] L.B. Zhu, J.W. Xu, Y.H. Xiu, Y.Y. Sun, D.W. Hess, C.P. Wong, J. Phys. Chem. B 110 (2006) 15945
- [44] X.J. Feng, L. Feng, M.H. Jin, J. Zhai, L. Jiang, D.B. Zhu, J. Am. Chem. Soc. 126 (2004) 62
- [45] R.D. Sun, A. Nakajima, A. Fujishima, T. Watanabe, K. Hashimoto, J. Phys. Chem. B 105 (2001) 1984.
- [46] A.B.D. Cassie, S. Baxter, Trans. Faraday Soc. 40 (1944) 546.
- [47] G.V. Kunte, S.A. Shivashankar, A.M. Umarji, Bull. Mater. Sci. 31 (2008) 835.