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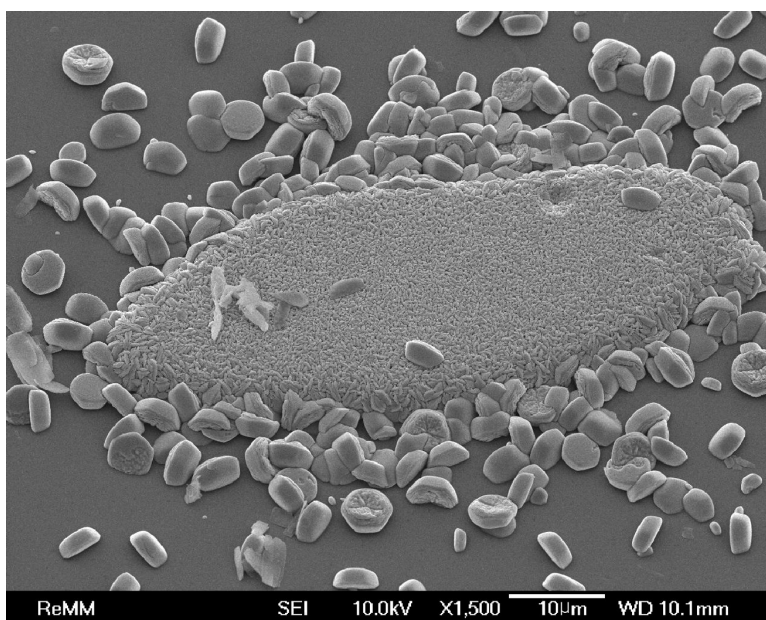
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Controlled Crystal Growth and Crystallite Orientation in ZnO Films/Nanorods Prepared by Chemical Bath Deposition: Effect of Solvent

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ABSTRACT: ZnO films/nanorods have been prepared by chemical bath deposition using a mixed solvent. Precoated ZnO thin seed layers played a key role in the growth of ZnO films/nanorods. The crystallite orientation in the films was successfully controlled by varying the volume ratio of water to ethanol. Films consisting of highly oriented nanorod arrays with the *c*-axis perpendicular to the substrate were fabricated in aqueous solution. The crystals became increasingly tilted as more ethanol was introduced to the solution, resulting in the formation of dense films by the coalescence between adjacent crystals across the whole film surface. The dense films consisting of crystals with a large smooth facet exhibited a markedly enhanced reflectance. The exclusive UV emission in the photoluminescence (PL) spectra indicated a high crystal quality of the prepared ZnO films/nanorods.

1. Introduction

The growth of nanocrystallites with controlled shape and size as well as the organization of them into large 3-dimensional nanostructures has attracted intense attention in nanoscience and nanotechnology in the past decade.^{1,2} More recently, great efforts have been devoted to the synthesis of wide bandgap semiconductor nanorod arrays.^{3–5} Among various wide bandgap semiconductors, ZnO stimulates a wide range of research interests due to its excellent chemical and thermal stability and its specific electrical and optoelectronic property of being a II–VI semiconductor with a large exciton binding energy (~60 meV).⁶ The large exciton binding energy of ZnO enables efficient excitonic lasing at room temperature, which is realized by either optical⁷ or electrical⁸ pumping. Accordingly, it is highly desirable to prepare high-quality ZnO films via a relatively cheap route for various applications.

Chemical bath deposition (CBD), one of the solution growth techniques, has well been developed to fabricate large-area semiconductor thin films in view of its several advantages: it does not require sophisticated instruments; the starting chemicals are commonly available and cheap; the preparation parameters are easily controlled.^{9,10} It is well-known that there are two distinct mechanisms leading to the formation of CBD films: (i) coagulation of colloids formed in solution by homogeneous reaction and then their adsorption on the substrate surface; (ii) ion-by-ion condensation at the surface of the substrate by heterogeneous reaction.¹¹ The former growth mechanism produces porous and poorly adherent films, while the latter one yields dense and adherent films. In general, the epitaxial films grown on a substrate precoated with a seed layer have better film quality than those grown on a bare substrate, which has recently attracted attention for the fabrication of aligned nanorod/

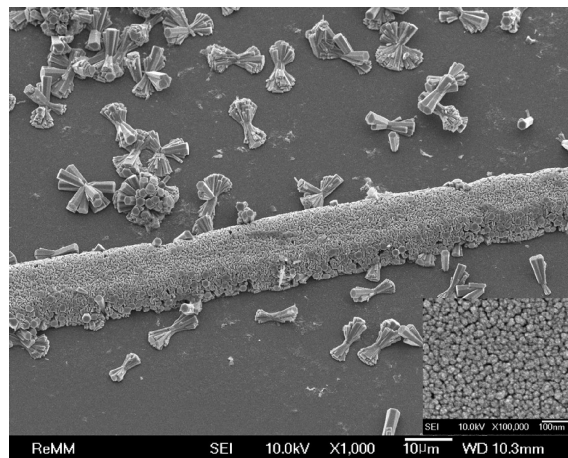


Figure 1. SEM image of ZnO crystals grown on a glass substrate with a precoated seed line in a 25 mM equimolar aqueous solution of zinc acetate and methenamine at 80 °C for 6 h. The inset shows the surface morphology of the sol-gel seed layer.

nanoneedle arrays in aqueous solution.^{5b,6,12} However, little work has been done to prepare dense and adherent ZnO films by CBD.¹³ In addition, although the solvent effect on crystal polymorphism is well-known for organic crystals,¹⁴ this effect on the growth of inorganic crystals has rarely been reported. On the basis of the above discussion, the present study is dedicated to the heterogeneous growth of CBD ZnO thin films on a seeded glass substrate in alcohol–water solutions. We report for the first time the preparation of ZnO thin films with controlled crystallite orientation by varying the volume ratio of water to alcohol.

2. Experimental Section

2.1. Seed Layer Preparation. Corning glass was used as the supporting substrate. Prior to seed layer coating, the substrates were carefully cleaned by distilled water, ethanol, and acetone, sequentially,

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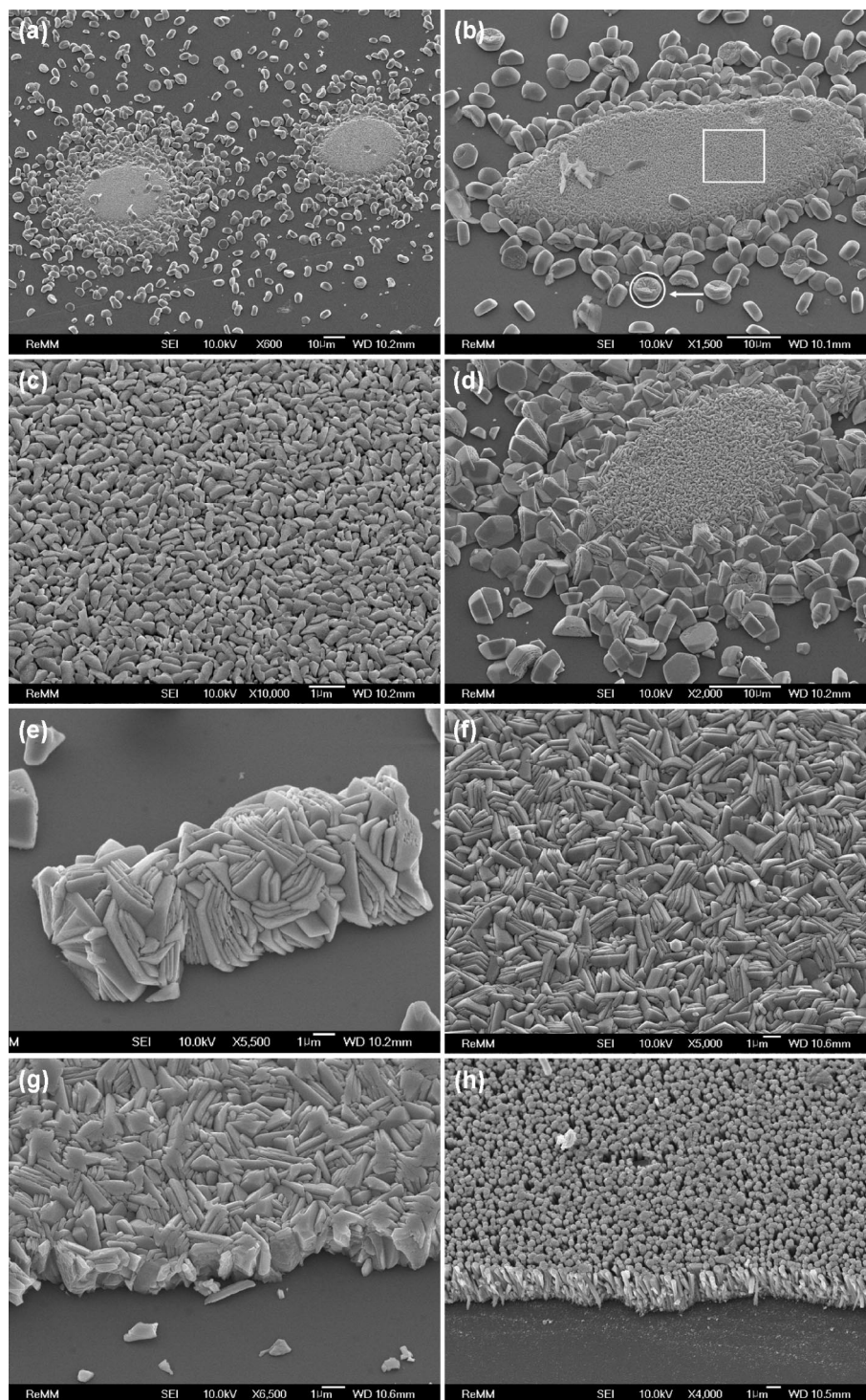


Figure 2. SEM images of ZnO crystals grown on a glass substrate with a seed spot in a 25 mM equimolar solution (90% ethanol) of zinc acetate and methenamine at 80 °C for 6 h (a and b) and 24 h (d and e). (c) Close observation of the selected area in part b. (f) 30° tilted view of ZnO film grown on a glass substrate with a fully covered seed layer at the same condition of parts d and e. (g) 30° tilted cross-sectional image of part f. (h) 30° tilted view of ZnO nanorods grown on a seeded substrate in a 25 mM equimolar aqueous solution of zinc acetate and methenamine at 80 °C for 24 h.

followed by distilled water rinsing and drying by a N_2 gas gun. A thin sol layer was coated on glass substrate by a dip-coating method from a 0.1 M sol. Preparation of the sol is described in detail elsewhere.¹⁵ ZnO films of ca. 10 nm in thickness were then produced after annealing at 400 °C for 10 min. For the preparation of the seed line, a thin line of ca. 10 μ m in diameter was dipped in the sol. Then, the sol line was transferred onto the substrate, which was followed by annealing to crystallize the seed line.

2.2. Preparation of ZnO Films/Nanorods. ZnO films/nanorods were prepared by a simple CBD method. A mixed solvent of water and alcohol including ethanol, methanol, and 2-propanol at various

volume ratios was used in this work. The seeded substrates were placed in 50 mL of a 25–100 mM equimolar solution of zinc acetate ($Zn(Ac)_2 \cdot 2H_2O$, extra pure) and methenamine ($C_6H_{12}N_4$, extra pure) in a 250-mL conical flask with a reflux condenser. The solution temperature was maintained at 80 °C using a thermostatically controlled oil bath. Finally, the prepared films/nanorods were thoroughly washed by deionized water and allowed to dry at room temperature before characterization.

2.3. Characterization. Film structure was monitored by X-ray diffraction (XRD) θ – 2θ scan via Philips X'Pert PW-3710 with Cu

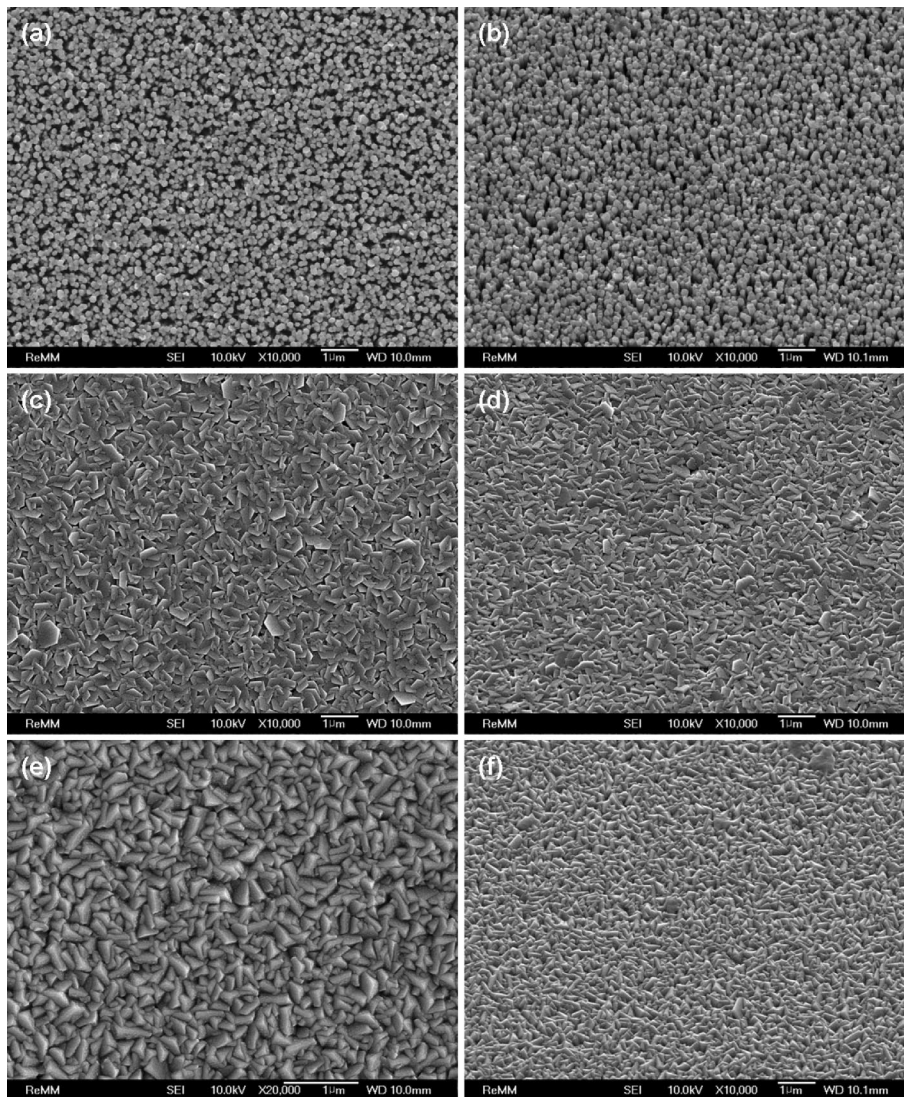


Figure 3. SEM images of ZnO thin films grown in a 25 mM equimolar solution of zinc acetate and methenamine at 80 °C for 3 h with various ethanol contents: (a and b) 0%; (c and d) 25%; (e and f) 50%. Parts a, c, and e are plane view; b, d, and f are a 30°-tilted view.

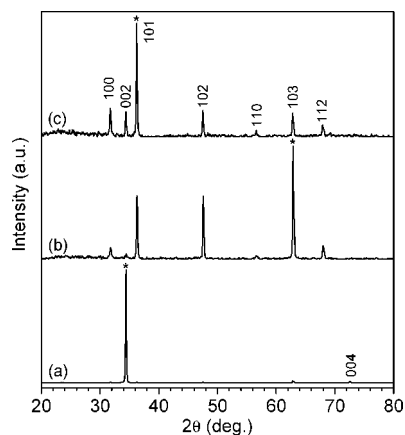


Figure 4. XRD θ - 2θ scan of ZnO thin films grown in a 25 mM equimolar solution of zinc acetate and methenamine at 80 °C for 3 h with various ethanol contents: (a) 0%; (b) 25%; (c) 50%. The asterisk (*) indicates the strongest reflection in the spectra.

K α radiation. Sample morphology was examined by field emission scanning electron microscopy (FESEM) (JEOL, JSM-6500F) operating at an accelerating voltage of 10 kV. Optical reflectance and transmittance were recorded on a UV-vis spectrophotometer (HP 8453). Photoluminescence (PL) measurements were performed by

employing a SPEX 750 M PL spectrometer. Samples were excited by a 325 nm He-Cd laser with an output of 4 mW power at room temperature.

3. Results and Discussion

3.1. Effect of Seed Layer. Precoating with a ZnO seed layer is crucial for the solution growth of highly oriented ZnO nanorod arrays.^{16–20} Various techniques including radio frequency (RF) sputtering,¹⁶ pulsed laser deposition,¹⁷ electron beam evaporation,¹⁸ dip-coating using colloidal solution¹⁹ or transparent sol²⁰ have been employed for the seed layer deposition. In this work, the seed layer was prepared by the sol-gel method. The inset in Figure 1 shows the surface morphology of the sol-gel seed layer. The smooth seed layer consisted of uniform nanoparticles with a size of about 20–30 nm. To clearly understand the effect of the seed layer, seed lines were coated on the bare glass substrate which was used for crystal growth in a 25 mM equimolar aqueous solution of zinc acetate and methenamine at 80 °C for 6 h. Figure 1 illustrates the SEM image of ZnO crystals grown on a glass substrate with the precoated seed line. As seen in Figure 1, densely aligned ZnO microrods were grown on the seed line. On the contrary, discrete and randomly oriented microrod clusters were formed on the bare part of the substrate. Accordingly, the seed layer plays a key role in the formation

Table 1. Inclination Angle between the (001) Plane and Other Planes in the Hexagonal ZnO Lattice Calculated Based on JCPDS No. 36-1451²⁸ ($a = 3.24982$ Å, $c = 5.20661$ Å)

plane	100	002	101	102	110	103	200	112	201	004
inclination angle (deg)	90	0	61.61	42.77	90	31.66	90	58.03	74.88	0

of oriented structure or uniform films on the substrate. The merit of the seed layer mainly arises from the fact that introducing the seed layer can effectively lower the interface energy between the crystal nuclei and the substrate and hence decrease the nucleation barrier.¹⁸

3.2. Effect of Solvent. The solvent effect on ZnO crystal growth was investigated by employing a mixed solvent of water and ethanol. Figure 2a–g depicts the ZnO crystals and films grown in a 25 mM equimolar (volume percentage of ethanol: 90%) solution of zinc acetate and methenamine. As seen in Figure 2a, fat plate crystals are developed at an ethanol content of 90%, which is quite different in shape from the microrod clusters formed in aqueous solution (Figure 1). It is more clearly seen in Figure 2b that the (00 $\bar{1}$) base face of the hexagonal crystals is faceted and that the (001) face of the plates possesses a rough hole as indicated by the arrow. On the other hand, dense films are formed on the seeded area of the substrate. The dense films consist of uniform crystals with an irregular shape (Figure 2c). One can see on the brim of the film in Figure 2b that the crystal fragments in the film are caused by the aggregated plate growth on the seed layer, which retards the development of single plates in the films. Extending the growth time to 24 h leads to a slight increase in plate thickness, while the diameter of the crystals remains unchanged (Figure 2d). Note that the rough hole in the (001) face of the plates is filled and a multilayered structure is developed on the (001) face of most crystals. We believe that the crystal growth herein may involve the oriented attachment of $\text{Zn}(\text{OH})_4^{2-}$ along the [001] direction (c -axis) by a dehydration process. If a seed layer preexists, these crystals are aggregated together and build up the dense film (Figure 2d). Figure 2e illustrates how these crystals are aggregated on the seed layer. It is seen that the crystals penetrate each other, indicating the intergrowth between crystals. When the substrate is fully covered with the seed layer, this intergrowth is observed on the whole film surface (Figure 2f and g). In the case of an aqueous solution, highly oriented ZnO nanorod arrays are prepared (Figure 2h), as previously reported in the literature.

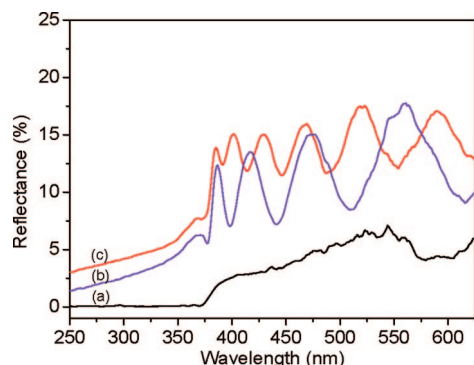
Solvent effects on the evolution of crystal morphology are well-known in organic chemistry. They are generally interpreted in terms of solvent–surface interactions such as hydrogen-bonding, electrostatic, and van der Waals interactions.^{14,21} The interactions at specific crystal faces would inhibit the growth of the corresponding faces as the solute molecules are hampered

in reaching the surface. However, little is known with regard to the solvent effect on inorganic crystal growth.^{22,23} The above experimental results (Figures 1 and 2) show that the crystal growth along the c -axis is retarded. Instead, the lateral growth is developed on the addition of ethanol. In addition, the aspect ratio of the crystals is found to decrease gradually with increasing ethanol content in the solution (see the Supporting Information, Figure S1). Therefore, the solvent effect can be effectively employed like a tailor-made additive to control the ZnO crystal morphology,²⁴ although it is not clear whether selective adsorption of ethanol molecules on the (001) plane or solvent–surface interaction takes place or not.

3.3. Controlled Crystallite Orientation. As discussed above, uniform and dense films can be grown from the solution by employing a mixed solvent and seeded substrate. A systematic investigation of the solvent effect on the film structure was further carried out.

In order to prepare transparent thin films on the glass substrate from the solution, the substrate was fully covered with the sol–gel seed layer and the deposition time was reduced to 3 h. Indeed, all prepared samples were highly transparent in the visible range with a transmittance of about 80% (see the Supporting Information, Figure S2). Figure 3 shows the SEM images of ZnO thin films grown at various ethanol contents. As was expected, the ZnO film comprising highly oriented nanorod arrays with the uniform diameter of ca. 200 nm was fabricated in aqueous solution (Figure 3a and b). Generally, the crystal size depends largely on the preparing conditions including solute concentration, growth temperature, and deposition time. Our experimental results reveal that the diameter of the rod ranges from 100 nm to 3 μm depending on the growing conditions (see the Supporting Information, Figure S3). In the case of the films deposited in the 25% ethanol solution, the nanorods in the film became fat. Also, these crystals were tilted resulting in the coalescence between crystals across the whole film surface (Figure 3c and d). A further increase in ethanol content to 50% led to the survival of only one crystal corner for each hexagonal rod on the film surface (Figure 3e and f).

The film morphologies in Figure 3 can be better understood by analyzing the film structure. Figure 4 illustrates the XRD spectra of the prepared ZnO thin films. For the film grown in aqueous solution, the (002) peak predominated the spectra (Figure 4a), indicating that the oriented nanorods grew perpendicular to the substrate. For the film grown in the 25% ethanol solution, the (003) peak became the strongest reflection; diffractions from the (102) and (101) planes were also strengthened (Figure 4b). The (101) peak was further enhanced on the addition of more ethanol (50%) (Figure 4c). For the films under the symmetrical XRD θ – 2θ scan, the strongest diffraction peak generated in the spectra should arise from the lattice plane almost parallel to the substrate. Therefore, Figure 4 reveals that the (002), (103), and (101) planes are closely parallel to the substrate for films grown in solutions with an ethanol content of 0, 25, and 50%, respectively. As seen in Table 1, the inclination angles between (002) and (103) and (002) and (101) were 31.66° and 61.61°, respectively. As the ethanol content increased, the crystals formed in the films were gradually tilted, which led to the (002), (103), and (101) planes lying parallel to the substrate surface in sequence. Accordingly, we have

**Figure 5.** Reflectance spectra of ZnO thin films grown in a 25 mM equimolar solution of zinc acetate and methenamine at 80 °C for 3 h with various ethanol contents: (a) 0%; (b) 25%; (c) 50%.

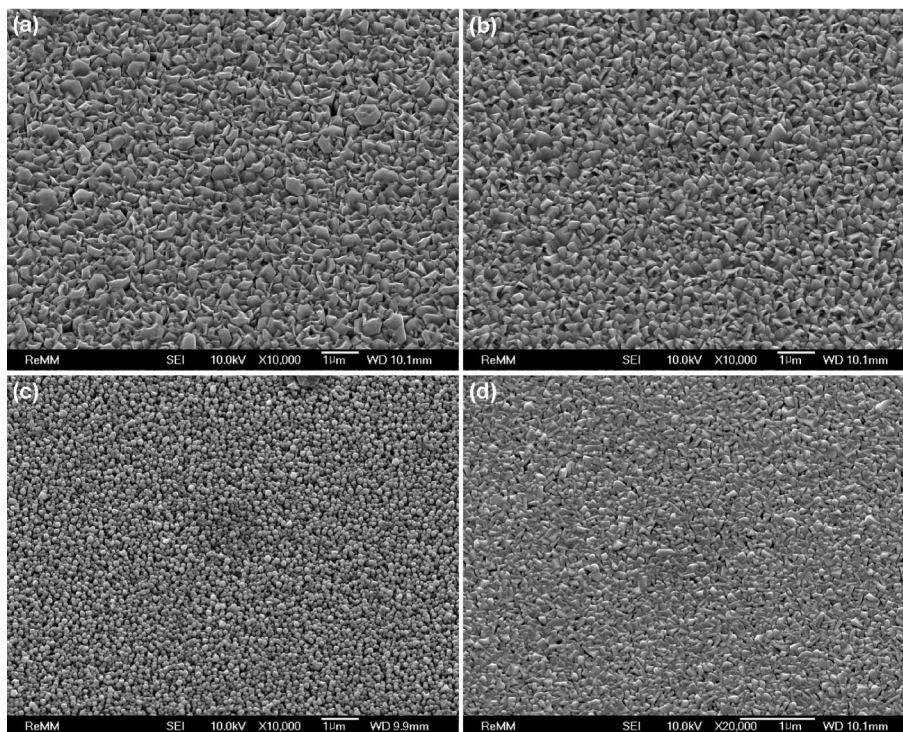


Figure 6. SEM 30°-tilted view images of ZnO thin films grown in a 25 mM equimolar solution of zinc acetate and methenamine at 80 °C for 3 h using a mixed solvent of water and alcohol with methanol content of (a) 25% and (b) 50% and 2-propanol content of (c) 25% and (d) 50%.

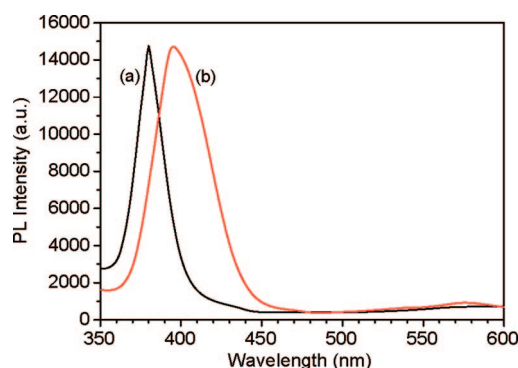


Figure 7. Typical PL spectra of ZnO films/nanorods with crystal sizes of hundreds of nanometers (a) (sample illustrated in Figure 3) and several micrometers (b) (sample illustrated in Figure S3a).

demonstrated the solution growth of ZnO thin films with controlled crystallite orientation by employing the solvent effect.

Figure 5 shows the reflectance spectra of ZnO thin films grown at various ethanol contents. The reflectance below 375 nm was rather weak due to the band gap light absorption. However, an abrupt increase in reflectance above 375 nm was observed for all samples. The film grown in the aqueous solution had a lower reflectance due to the less densely oriented nanorods. On the other hand, the reflectance was markedly enhanced as the films became denser, especially for the films grown in the 25% ethanol solution, owing to the large smooth facet of the crystals presented on the film surface.

The solvent effect on the film growth was also investigated for alcohols other than ethanol. As shown in Figure 6, a gradual titling of the crystals in the films was observed with increasing methanol and 2-propanol contents, although the film morphology depended slightly on the type of alcohol.

3.4. PL Properties. PL measurements are an effective way to evaluate the crystal quality of ZnO nanostructures. Figure 7 shows the room-temperature PL spectra of ZnO films under the

excitation of a 325 nm He–Cd laser. Typically, for the film with the rod or crystal size of hundreds of nanometers, a sharp UV peak with the fwhm of 188 meV appeared at 380 nm (3.27 eV). On the contrary, a much broader UV peak with the fwhm of 318 meV appeared at 395 nm (3.15 eV) for the film consisting of microrods 3 μ m in diameter (Supporting Information, Figure S3a). A shift of the UV peak may be ascribed to a difference in crystal size. Nevertheless, the visible emission above 450 nm was rather weak and negligible in both cases. The UV emission comes from the recombination of free excitons,²⁵ while the visible emission such as green and yellow emissions is related to the structural defects of oxygen vacancies and oxygen interstitials,^{26,27} respectively. As a result, the PL data presented here indicate that the prepared films are of high crystal quality and possess few structural defects.

4. Conclusions

We have systematically investigated the solvent effect on the ZnO crystal growth and film structure in the CBD process. The aspect ratio of ZnO crystals formed was gradually decreased with increasing ethanol content, leading to the transformation of rods into discs. In addition, the crystallite orientation in ZnO films was easily controlled: the nanorods in the films were found to become increasingly tilted as the ethanol content increased. Other alcohols such as methanol and 2-propanol exhibited a similar result. The prepared ZnO films/nanorods were of high crystal quality, as indicated by the exclusive UV peak in the PL spectra.

Acknowledgment. This work was supported by the 2007 Research Fund of the University of Ulsan.

Supporting Information Available: SEM images of the ZnO crystals grown on bare glass substrate in the solution with various ethanol contents (Figure S1); transmittance spectra of ZnO thin films grown in the solution with various ethanol contents (Figure S2); and SEM images of ZnO rod arrays grown at various experimental

conditions (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Kim, F.; Kwan, S.; Akana, J.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 4360.
- (2) Love, J. C.; Urbach, A. R.; Prentiss, M. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 12696.
- (3) Kim, H.-M.; Kim, D. S.; Park, Y. S.; Kim, D. Y.; Kang, T. W.; Chung, K. S. *Adv. Mater.* **2002**, *14*, 991.
- (4) Yang, J.; Liu, T.-W.; Hsu, C.-W.; Chen, L.-C.; Chen, K.-H.; Chen, C.-C. *Nanotechnology* **2006**, *17*, S321.
- (5) (a) Huang, M.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897. (b) Greene, L. E.; Law, M.; Goldberger, J.; Kim, F.; Johnson, J. C.; Zhang, Y.; Saykally, R. J.; Yang, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3031.
- (6) Vayssieres, L. *Adv. Mater.* **2003**, *15*, 464.
- (7) Yu, S. F.; Yuen, C.; Lau, S. P.; Lee, H. W. *Appl. Phys. Lett.* **2004**, *84*, 3244.
- (8) Leong, E. S. P.; Yu, S. F. *Adv. Mater.* **2006**, *18*, 1685.
- (9) Kostoglou, M.; Andritsos, N.; Karabelas, A. J. *Ind. Eng. Chem. Res.* **2000**, *39*, 3272.
- (10) Hoffmann, R. C.; Jeurgens, L. P. H.; Wildhack, S.; Bill, J.; Aldinger, F. *Chem. Mater.* **2004**, *16*, 4199.
- (11) Xu, H. Y.; Xu, S. L.; Li, X. D.; Wang, H.; Yan, H. *Appl. Surf. Sci.* **2006**, *252*, 4091.
- (12) Chang, Y. C.; Chen, L. J. *J. Phys. Chem. C* **2007**, *111*, 1268.
- (13) Izaki, M. *Chem. Commun.* **2002**, 476.
- (14) Weissbuch, I.; Torbeev, V. Y.; Leiserowitz, L.; Lahav, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3226.
- (15) Wang, M.; Kim, E. J.; Chung, J. S.; Shin, E. W.; Hahn, S. H.; Lee, K. E.; Park, C. *Phys. Stat. Sol. A* **2006**, *203*, 2418.
- (16) Yu, H.; Zhang, Z.; Han, M.; Hao, X.; Zhu, F. *J. Am. Chem. Soc.* **2005**, *127*, 2378.
- (17) Sun, Y.; Fuge, G. M.; Fox, N. A.; Riley, D. J.; Ashfold, M. N. R. *Adv. Mater.* **2005**, *17*, 2477.
- (18) Tong, Y.; Liu, Y.; Dong, L.; Zhao, D.; Zhang, J.; Lu, Y.; Shen, D.; Fan, X. *J. Phys. Chem. B* **2006**, *110*, 20263.
- (19) Choy, J.-H.; Jang, E.-S.; Won, J.-H.; Chung, J.-H.; Jang, D.-J.; Kim, Y.-W. *Adv. Mater.* **2003**, *15*, 1911.
- (20) Li, S.; Zhou, S.; Liu, H.; Hang, Y.; Xia, C.; Xu, J.; Gu, S.; Zhang, R. *Mater. Lett.* **2007**, *61*, 30.
- (21) Stoica, C.; Verwer, P.; Meekes, H.; van Hoof, P. J. C. M.; Kaspersen, F. M.; Vlieg, E. *Cryst. Growth Des.* **2004**, *4*, 765.
- (22) Peiró, A. M.; Ayllón, J. A.; Peral, J.; Domènech, X.; Domingo, C. *J. Cryst. Growth* **2005**, *285*, 6.
- (23) Wang, W.; Gu, B.; Liang, L.; Hamilton, W. A.; Wesolowski, D. J. *J. Phys. Chem. B* **2004**, *108*, 14789.
- (24) Cao, B.; Cai, W.; Li, Y.; Sun, F.; Zhang, L. *Nanotechnology* **2005**, *16*, 1734.
- (25) Yao, B. D.; Shi, H. Z.; Bi, H. J.; Zhang, L. D. *J. Phys.: Condens. Mater.* **2000**, *12*, 6265.
- (26) Vanheusden, K.; Warren, W. L.; Seager, C. H.; Tallant, D. R.; Voigt, J. A.; Gnade, B. E. *J. Appl. Phys.* **1996**, *79*, 7983.
- (27) Wu, X. L.; Siu, G. G.; Fu, C. L.; Ong, H. C. *Appl. Phys. Lett.* **2001**, *78*, 2285.
- (28) McMurdie, H. F.; Morris, M. C.; Evans, E. H.; Paretzkin, B.; Wong-Ng, W.; Ettlinger, L.; Hubbard, C. R. *Powder Diffr.* **1986**, *1*, 76.

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