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Fabrication of ZnO Nanorods and Nanotubes in Aqueous Solutions

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A novel aqueous solution method has been developed for growing well-aligned crystalline ZnO nanorods (NRs) and nanotubes (NTs) on a variety of substrates including Si wafers, poly(ethylene terephthalate) (PET), and sapphire. Atomic layer deposition (ALD) was first used to grow a uniform ZnO film on the substrate of choice and to serve as templating seed layer for the subsequent growth of NRs and NTs. On this ZnO layer highly oriented two-dimensional NR arrays of ZnO were obtained by solution growth process using zinc nitrate and hexamethylenetetramine in aqueous solution. X-ray diffraction (XRD) analysis confirmed the crystalline nature of the ZnO NRs. The diameter of ZnO NRs obtained varies according to the concentration of reactants, reaction temperature, and solution pH. The length of the ZnO NRs is controlled by growth time as well as by the concentration of reagents in the aqueous solution. ZnO NTs with diameters of 40−60 nm were found to self-assemble on the top faces of ZnO NRs. High-resolution transmission electron microscopy (HRTEM) confirmed the single crystalline nature of the ZnO NTs. Electron energy loss spectroscopy (EELS) analysis indicated the existence of nitrogen at the core of ZnO NTs during their formation, which provides useful information to propose the growth mechanism of ZnO NTs.

1. Introduction

Semiconductor nanorods (NRs) and nanowires have attracted much interest due to their physical properties and potential for diverse electronic and photonic device applications.[1,2] During the past several years, various methods have been developed for the synthesis of one-dimensional nanomaterials that have included template-assisted,[3] vapor−liquid−solid (VLS),[4] colloidal micellar,[5] and electrochemical processes.[6] Because the novel properties of nanomaterials depend on their size and shape, new synthetic strategies and a better understanding of the growth mechanisms by which the size and shape of nanostructures can be easily tailored are key issues in nanomaterials chemistry.

ZnO has a large direct band gap (3.37 eV), excellent chemical and thermal stability, and the electrical properties of a II−VI semiconductor possessing large exciton binding energy (60 meV). ZnO has been recognized as one of the promising nanomaterials in a broad range of high-technology applications, e.g., surface acoustic wave filters,[7] photonic crystals,[8] light-emitting diodes,[9] photodetectors,[10] optical modulator waveguides,[11] varistors,[12] gas sensors,[13] and solar cells.[14] Recent research has demonstrated that the creation of ZnO nanostructures in highly oriented and ordered arrays is of crucial importance for the development of novel devices.[2] Various chemical, electrochemical, and physical deposition techniques have been employed to create *oriented* arrays of ZnO NRs and nanowires. For instance, aqueous thermal decomposition of Zn^{2+} amine complexes,[15] catalytic growth via the vapor−liquid−solid epitaxial (VLSE) mechanisms,[16] metal-organic chemical vapor deposition (MOCVD),[17] pulsed laser deposition,[18] templating with anodic alumina membranes[19] and epitaxial electrodeposition[20] have been successful in creating highly oriented arrays of anisotropic ZnO NRs. Recently, Yang et al.[21] demonstrated

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(1) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Lieber, C. M. *Nature (London)* **2001**, *409*, 66.
(2) Huang, H. M.; Mao, S.; Feick, H.; Yan, H.; Wu, H.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.
(3) Han, Y. J.; Kim, J.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2068.
(4) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435.
(5) Chen, C. C.; Chao, C. Y.; Lang, Z. H. *Chem. Mater.* **2000**, *12*, 1516.
(6) Mohamed, M. B.; Ismail, K. Z.; Link, S.; El-Sayed, M. A. *J. Phys. Chem.* **1998**, *102*, 9370.
(7) Emanetoglu, N. W.; Gorla, C.; Liu, Y.; Liang, S.; Lu, Y. *Mater. Sci. Semicond. Process.* **1999**, *2*, 247.
(8) Chen, Y.; Bagnall, D.; Yao, T. *Mater. Sci. Eng. B* **2000**, *75*, 190.
(9) Saito, N.; Haneda, H.; Sekiguchi, T.; Ohashi, N.; Sakaguchi, I.; Koumoto, K. *Adv. Mater.* **2002**, *14*, 418.
(10) Liang, S.; Sheng, H.; Liu, Y.; Hio, Z.; Lu, Y.; Shen, H. *J. Cryst. Growth* **2001**, *225*, 110.
(11) Lee, J. Y.; Choi, Y. S.; Kim, J. H.; Park, M. O.; Im, S. *Thin Solid Films* **2002**, *403*, 533.
(12) Koch, M. H.; Timbrell, P. Y.; Lamb, R. N. *Semicond. Sci. Technol.* **1995**, *10*, 1523.
(13) Lin, Y.; Zhang, Z.; Tang, Z.; Yuan, F.; Li, J. *Adv. Mater. Opt. Electron.* **1999**, *9*, 205.
(14) Golego, N.; Studenikin, S. A.; Cocivera, M. *J. Electrochem. Soc.* **2000**, *147*, 1592.
(15) Vayssieres, L. *Adv. Mater.* **2003**, *15*, 464.
(16) Huang, H.; Wu, Y.; Feick, H.; Tran, N.; Weber, E.; Yang, P. *Adv. Mater.* **2001**, *13*, 113.
(17) Liu, S.; Wu, J. J. *Mater. Res. Soc. Symp. Proc.* **2002**, *703*, 241.
(18) Choi, J. H.; Tabata, H.; Kawai, T. *J. Cryst. Growth* **2001**, *226*, 493.
(19) Li, Y.; Meng, G. W.; Zhang, L. D.; Phillip, F. *Appl. Phys. Lett.* **2000**, *76*, 2011.
(20) Liu, R.; Vertegel, A. A.; Bohannan, E. W.; Sorenson, T. A.; Switzer, J. A. *Chem. Mater.* **2001**, *13*, 508.

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that a solution synthesis of ZnO nanowires has the potential for scale-up production.

It is known that the gas sensing efficiency and photon-to-electron conversion efficiency are enhanced by increasing surface-to-volume ratios and by quantum confinement effects, respectively. Thus, ZnO NTs which satisfy these properties would be of great interest to investigate. Although a number of researchers have studied ZnO NRs, only a few have obtained ZnO NTs. Vayssieres et al.[22] reported the synthesis of only ZnO microtubes at low temperatures in aqueous solution. Wu et al.[23] and Hu et al.[24] obtained ZnO NTs with diameters of 30 and 400 nm, respectively, but only at high temperatures. We report here a novel seed growth process for fabrication of highly oriented ZnO NRs and NTs in aqueous solution at low temperatures.

2. Experimental Section

To grow well-aligned ZnO NRs, first a substrate is chosen on which a ZnO film is grown by atomic layer deposition (ALD).[25] This ZnO-coated substrate is then used for growing NRs. Virtually any substrate can be used as long as a smooth ZnO film can be grown on its surface. In our experiments Si, poly(ethylene terephthalate) (PET), and sapphire were used as substrates. In this procedure the ZnO film can also be doped during ALD growth to produce a conductive film. For growing the ALD-derived films, diethyl zinc, high-purity water, and trimethyl aluminum were used as sources for zinc, OH^-, and Al, respectively. Typical doped ZnO films contain 1% Al, with a resistivity of $2.6-4.0 \times 10^{-3}$ Ωcm and thickness of 140 nm. Undoped nonconductive ZnO films were also deposited for comparison. After the growth of the thin film on the substrates, ZnO NRs were fabricated on these ZnO thin film surfaces. For comparison studies, ZnO NRs were also grown directly on uncoated substrates.

ZnO NRs were grown in 40 mL of equimolar (0.1 M) aqueous solution of zinc nitrate, $Zn(NO_3)_2 \cdot xH_2O$, and hexamethylenetetramine (HMTA; $C_6H_{12}N_4$) in a conventional reaction flask with a reflux condenser. The reaction temperature was 95 °C. The growth time was 10 h for growth of NRs and 20 h for growth of NTs.

The obtained ZnO rods were typically 200−400 nm in diameter and up to about 3 μm long. We believe the following reactions are involved in the formation of ZnO NRs

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \quad (2)$$

$$2OH^- + Zn^{+2} \rightarrow ZnO_{(s)} + H_2O \quad (3)$$

3. Results and Discussion

3.1 Role of ZnO Seed Layer in Nanorod Alignment. Figure 1 shows an SEM image of ZnO NRs fabricated on a Si substrate that was partially covered with an Al-doped ZnO film. It can be seen that alignment of NRs grown on the ZnO-covered substrate (Figure 1, region b) is significantly greater than that for the NRs grown on bare Si region (Figure 1, region a). We suggest that the reason for superior alignment on ZnO film is due to the matching lattice structure and due to the polar nature of the ZnO surface.[26] ZnO surface is either positively charged or negatively charged. In either case the surface will attract ions of opposite charges (OH− or Zn+) to it, and this new surface covered with ions will in turn attract ions with opposite charges to cover the surface next and thereby reacting to form ZnO. Thus, ZnO NRs could grow layer by layer leading to good alignment. In addition, ZnO NRs here are found to grow along (0001) direction; this may be because ZnO has a dipole moment along this direction. This dipole moment will try to align itself with charged ZnO thin film surface to minimize energy. In addition, the ubiquitous surface roughness likely serves as nucleation sites for NR growth. NR alignment and morphology obtained are the same for undoped and Al-doped ZnO films. ZnO NRs grown on bare sapphire substrate have better alignment than NRs grown on bare Si. But compared to bare sapphire, the NR alignment is better on ZnO-coated Si and PET.

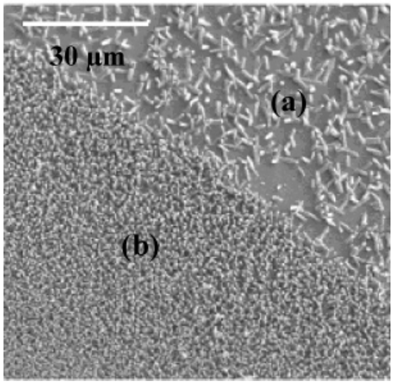

Figure 1. SEM image of ZnO NRs fabricated on a Si wafer which is partially covered with an Al-doped ZnO film: (a) NRs on bare Si have poor alignment, whereas (b) NRs on the ZnO coated part are uniformly aligned (scale bar = 30 μm).

3.2 Surface Effects on Nanorod Diameter Size Distribution. Although well-aligned ZnO NRs could be obtained through the above seed layer growth process, the variation in diameter of ZnO NRs is different when they are grown on different base substrates, e.g., Si vs PET. Figure 2a and b show SEM images of ZnO NRs grown on Si and PET substrates that were covered with conductive ZnO films. The distribution of NR diameters in Figure 2a is significantly more uniform than that in Figure 2b. To understand the reason behind this we should note that the nature of ZnO film *surface* affects the nature of NRs that grow on it For example, size distribution of NRs could be affected by the uniformity of surface roughness because this roughness acts as nucleation sites for NRs. To characterize surface roughness of ZnO film, atomic force microcopy (AFM) was used to image the ZnO films on Si and PET substrates (Figure 3a and b). From the AFM measurements as shown in Figure 3a and b, we can see ZnO film on the Si substrate is composed of small islands (∼100 nm in diameter) which have a uniform size distribution. These small islands (Figure

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(21) Greene, L.; Law, M.; Goldberger, J.; Kim, F.; Johnson, J.; Zhang, Y.; Saykally, R.; Yang, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3031.

(22) Vayssieres, L.; Beermann, N.; Lindquist, S.-E.; Hagfeldt, A. *Chem. Mater.* **2001**, *13* (2), 233.

(23) Wu, J.-J.; Liu, S.-C.; Wu, C.-T.; Chen, K.-H.; Chen, L.-C. *Appl. Phys. Lett.* **2002**, *81*, 1312.

(24) Hu, J. Q.; Bando, Y. *Appl. Phys. Lett.* **2003**, *82*, 1401.

(25) Ott, A. W.; Chang, R. P. H. *Mater. Chem. Phys.* **1999**, *58*, 132.

(26) Wang, Z. L. *Materialstoday* **2004**, *7* (6),26.

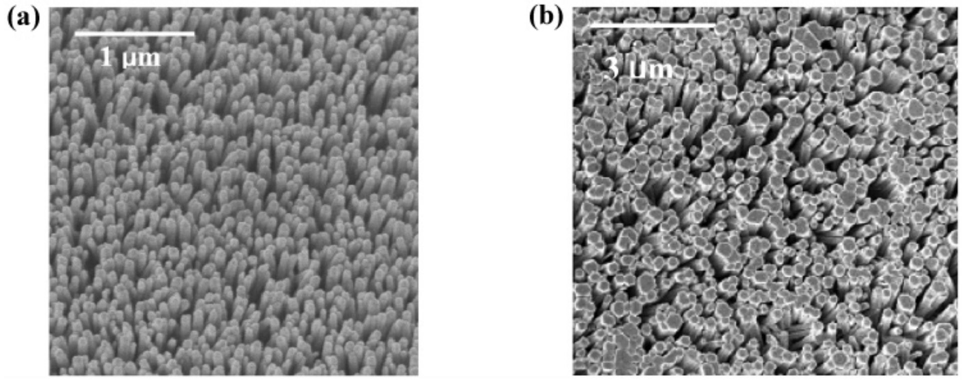

Figure 2. Images of well-aligned ZnO NRs fabricated on Al-doped ZnO film on (a) a single-crystal Si wafer and (b) a PET substrate.

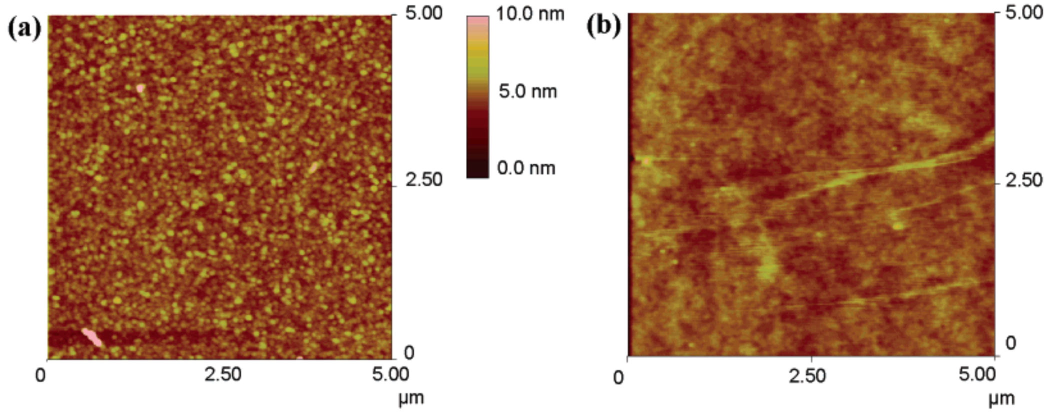

Figure 3. AFM images of Al-doped ZnO film on (a) a Si wafer and (b) a PET substrate. The islands observed are due to surface roughness. Note that island size distribution is much more uniform for Si in (a) than for PET in (b). Since these islands act as nucleation sites for NRs, their size distributions determine the size (diameter) distribution of NRs.

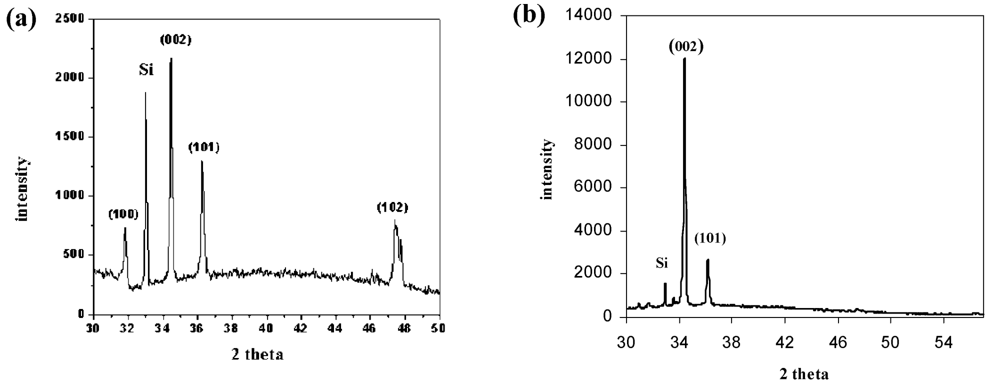

Figure 4. X-ray diffraction pattern of ZnO NRs on (a) a bare Si substrate and (b) a ZnO-coated Si substrate. The peaks indicate the crystalline nature of NRs; in (a) the relative intensities of peaks show only partial orientation of NRs, while in (b) the relative intensities indicate superior alignment.

3a) on Si substrate logically serve as nuclei for growth of ZnO NRs (Figure 2a). In Figure 3b we see the PET surface does not have uniform island size distribution compared to that of Si substrate. This in turn leads to larger distribution of NR diameters on PET substrates.

3.3 Crystal Structure and Chemical Composition of Nanorods. According to the XRD pattern (Figure 4) for NRs grown on bare Si, zincite ZnO (wurtzite structure) is the only crystallographic phase detectable in the well-aligned crystalline hexagonal ZnO rods. Figure 4 also illustrates the texture effect of the anisotropic morphology and orientation on the relative intensities of the diffraction peaks (normalized to (101) reflection which is usually the most intense feature in the ZnO zincite diffraction pattern).

As expected, the (002) diffraction peak in Figure 4b exhibits a substantially greater intensity, further confirming that NRs are much better aligned on a ZnO-coated substrate and also that NRs grow along (0001) direction. The crystalline structure of the ZnO NRs obtained is quite similar to that of ZnO microrods reported in the literature.[27] From energy-dispersive X-ray spectroscopy (EDS) it was found that ZnO NRs were nearly stoichiometric with little excess of Zn.

3.4 Effect of Reaction Temperature, pH, and Concentration on Nanorod Morphology. To learn more about the growth mechanism of NRs, we performed a series of

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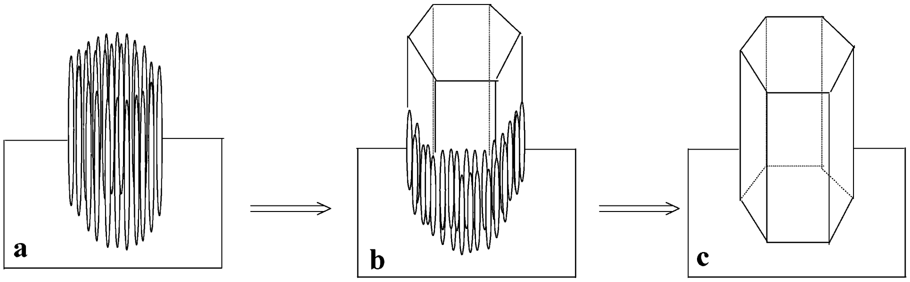
(27) Vayssieres, L.; Keis, K.; Lindquist, S.-E.; Hagfeldt, A. *J. Phys. Chem. B* **2001**, *105*, 3350.

Scheme 1. Growth Mechanism of ZnO Rods: (a) NRs grow as a bundle but are independent, (b) NRs begin to coalesce, and (c) a single NR results.



experiments by changing the reaction temperature. We found that the diameter of the NRs increased from 100−300 nm to 500−700 nm as the solution temperature was decreased from 98 to 92 °C. We noticed that when the temperature increased from 92 to 98 °C, the pH value of solution decreased from 5.60 to 5.35. Since high temperatures may cause more evaporation of ammonia, they thus decrease the base concentration. Therefore, after some time there might not be enough base left in the solution to react with zinc nitrate. This would restrict the growth of NRs' diameter and length. Even though Vayssieres et al.[22] did a similar reaction with same concentration (0.1 M) of reactants as we did, they used a stoppered flask which would limit the evaporation or loss of ammonia, and thus the high concentration of base would result in formation of microrods of ZnO. Their latest results indicate that diameters of rods and tubes could be brought into the nanometer range by lowering the concentration of reactants.[15] The average diameter of NRs increases with concentration of zinc nitrate and HMTA in the solution. Also, in our experimental work we found that the diameter of NRs decreased exponentially with the pH of solution.

3.5 Physical Mechanism for Nanorod Growth. Pacholski et al.[28] and Penn and Banfield[29−31] have observed phenomenon where smaller nanostructures such as nanoparticles undergo attachment or coalescence to form larger dimension nanostructures. In our case we observed some NRs (see Figure 5) that are formed out of bundling of smaller diameter NRs. We believe thin diameter NRs grow as a bundle individually initially and eventually coalesce to form large-diameter rods. The reason for this could be lowering of surface energy. Since the reaction temperature was low (88 °C) for the experiment corresponding to Figure 5, high concentration of base (due to lower evaporation at lower temperature) might have resulted in ZnO rods with large diameters of the order of ∼1.5 μm. According to our experimental results and the literature,[28] the proposed growth mechanism of crystalline hexagonal rods of ZnO is shown in Scheme 1. Step (a) is the growth process of fine ZnO rods which bundle together. Steps (b) and (c) are the growth steps of hexagonal rods of ZnO via the coalescence mode.

3.6 Growth of ZnO Nanowires and Nanotubes. *3.6.1 ZnO Nanotubes.* Interestingly, some very small (∼40−60 nm) diameter NRs (we would like to call them nanowires as they are very thin in diameter) were observed in another set of experiments where growth time was 10 h or longer. Figure 6a is an SEM image of a sample in the experiment set after 10-hour reaction. These nanowires (NWs) were very short making us believe they had just begun to grow. Thus, to make sure these NWs were not artifacts, we increased the growth time to 20 h to see if we could still obtain them and if they grow longer with time. More ZnO nanowires with lengths of the order of a few micrometers were observed in the SEM images (Figure 6b), confirming that these NWs were not simply artifacts. The length of NWs can be experimentally tailored by adjusting the growth time. However, as they grow longer and longer they do not just stand up but become like "spaghetti" and get intertwined as can be seen in Figure 6b. When TEM was performed on these NWs we found that some of them were actually hollow and thus they were nanotubes (NTs) rather than solid NWs.

3.6.2 Crystal Structure of NWs and NTs. To learn more about these ZnO NWs, TEM (Hitachi HF-2000) and selected area electron diffraction (SAED, Hitachi HF-2000) were used to characterize the ZnO NW structures. TEM samples were prepared by gently dragging the holey (400 mesh Cu, SPI supplies) carbon grids along the surface of the samples.

We noticed not only nanowires, but also nanotubes (NTs), of ZnO in TEM images (Figure 7). Structures having diameters less than 40 nm were solid in nature and were thus NWs (Figure 7a); however, structures having diameters larger than 40 nm were fully or partially hollow in nature and were thus NTs (Figure 7b and c). Figure 7d shows a

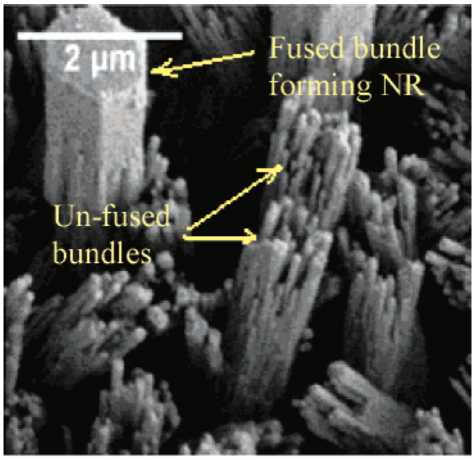


Figure 5. SEM image of ZnO rods obtained after reaction at 88 °C for 10 h. Here bundles of NRs are clearly visible. Note that in the upper left corner a bundle has fused together to form a single rod.

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(28) Pacholski, C.; Kornowski, A.; Weller, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1188.

(29) Banfield, J. F.; Welch, S. A.; Zhang, H.; Ebert, T. T.; Penn, R. L. *Science* **2000**, *289*, 751.

(30) Penn, R. L.; Banfield, J. F. *Science* **1998**, *281*, 969.

(31) Penn, R. L.; Banfield, J. F. *Geochim. Cosmochim. Acta* **1999**, *63*, 1549.

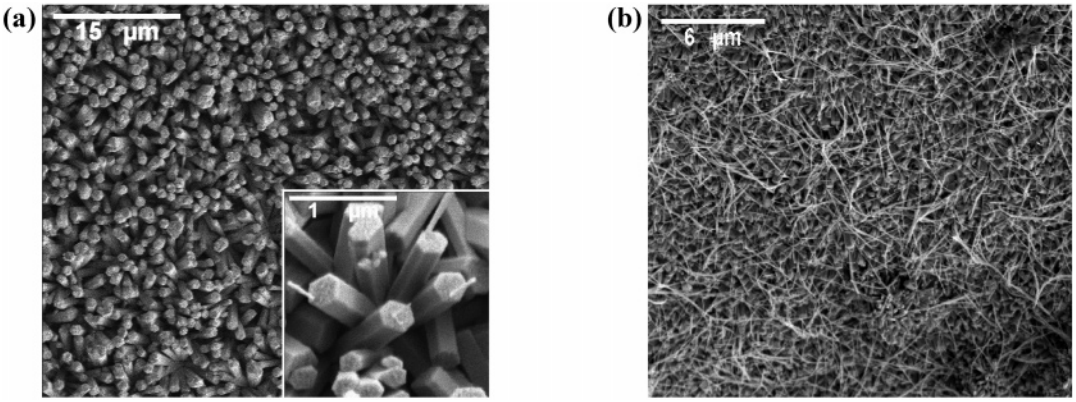

Figure 6. (a) ZnO NTs (see inset) beginning to grow on top faces of NRs after 10 h of growth time; (b) NTs grow longer when growth time is 20 hours.

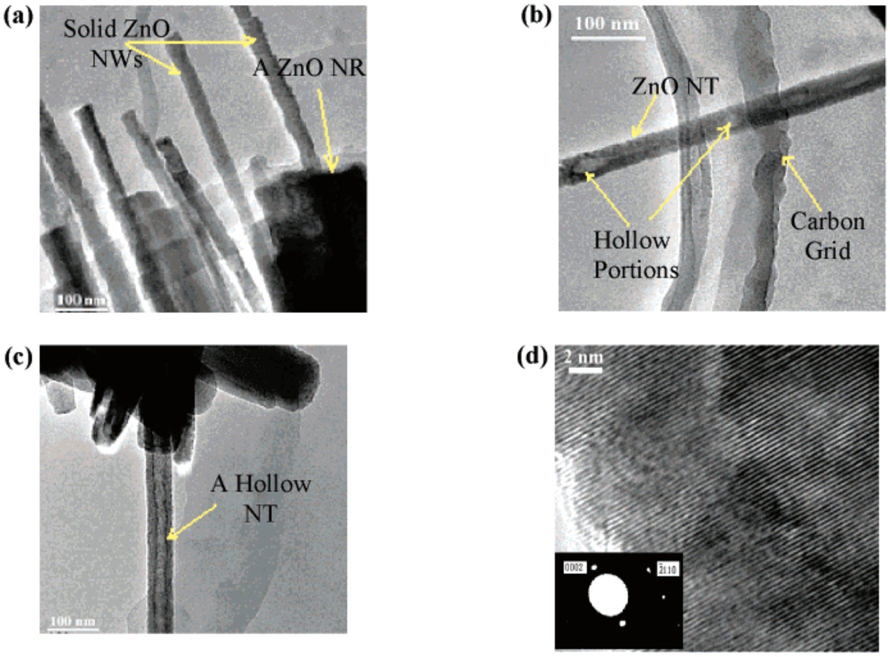

Figure 7. (a) TEM image of ZnO nanowires. (b) TEM image of a ZnO partially hollow NT. (c) TEM image of ZnO NT. (d) High-resolution TEM image and SAED from a ZnO NT.

high-resolution TEM image and a selected area electron diffraction pattern taken from a ZnO NT. The spacing between adjacent lattice planes is about 0.26 nm, which corresponds to the distance between two (0002) planes in ZnO crystal.[32] The electron diffraction pattern can be assigned to hexagonal ZnO single crystals in the $(01\bar{1}0)$ beam direction. The high-resolution TEM and SAED results suggest that (0001) is the preferred growth direction for ZnO nanowires or NTs.

3.6.3 Proposed Growth Mechanism for Nanotubes. To understand the growth mechanism of these secondary ZnO NWs (diameter <40 nm) and NTs (diameter >40 nm) electron energy loss spectroscopy (EELS) was used to characterize them. EELS analysis indicated that nitrogen exists in the ZnO NWs, but not in the NTs. Thus, we believe the solid nanorods have a nitrogen-containing compound which is at the core during initial growth steps but subsequently dissolves into the solution leading to hollow NT structure, because hollow NTs did not show any nitrogen signal in EELS. We suggest that NTs are hollow as compared to NWs because it is easier for solution to enter a larger opening and etch away the organics. Further studies on this subject would be carried out.

Figure 7b shows a partially hollow NT; because it is not perfectly hollow, we did see a nitrogen signal in EELS because of the leftovers of the nitrogen-containing compound. As mentioned in the literature[33−35] there are two possible coordination complexes $[Zn(H_2O)_2(HMTA)_2](NO_3)_2$ and $[Zn(H_2O)_4(HMTA)_2](NO_3)_2$ (see eqs 4 and 5) that can form in our reaction solution. These are organic in nature and the detected nitrogen signal in EELS might come from these organic complexes.

$$Zn(NO_3)_2 + 2H_2O + 2HMTA \rightleftarrows [Zn(H_2O)_2(HMTA)_2](NO_3)_2 \quad (4)$$

$$Zn(NO_3)_2 + 4H_2O + 2HMTA \rightleftarrows [Zn(H_2O)_4(HMTA)_2](NO_3)_2 \quad (5)$$

These organometallic complexes might act as nuclei and form NRs of these organic compounds followed by formation of an overlying ZnO shell, or the shell and core may just

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[32] Schulz, H.; Thiemann, K. H. *Solid State Commun.* **1979**, *32*, 783.

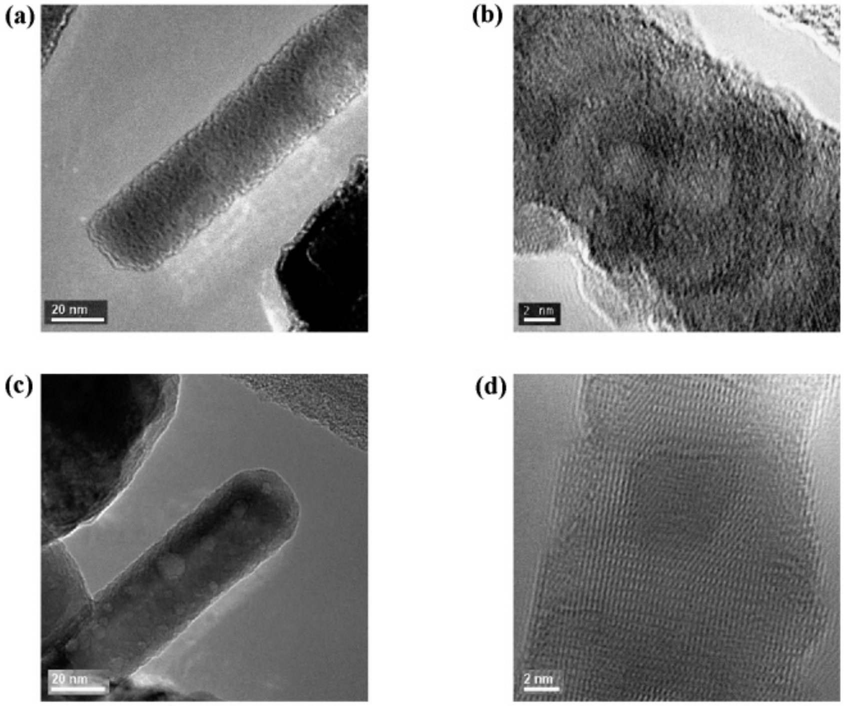

Figure 8. (a) TEM image of a ZnO nanowire before annealing at 500 °C; (b) High-resolution TEM image before annealing at 500 °C; (c) TEM image of a ZnO NW after annealing at 500 °C; (d) high-resolution TEM image after annealing at 500 °C. It can be clearly seen from (b) and (d) that crystallinity of NWs improves with annealing.

grow side by side. Afterward, these organic complexes forming the core dissolve, leaving the ZnO shell behind.

To further verify the existence of organics in NWs one sample was calcined in an oven at 500 °C with airflow for 30 min. Before calcination, the ZnO nanowire surface was rough, and no hollow structure was observed from TEM image (Figure 8a). High-resolution TEM indicated that the crystalline structure of ZnO nanowires was poor (Figure 8b). After calcination at 500 °C with flow air for 30 min, TEM analysis shows a hollow and high-crystalline structure of ZnO (Figure 8c and d). High-temperature annealing could have burned off all the organics in the wires, resulting in a hollow structure.

4 Summary and Conclusion

In summary, highly oriented, well-aligned, ZnO NRs were grown on various substrates coated with ZnO film, which was formed by ALD. The strength of this method is that any substrate can be used to grow well-aligned and uniform ZnO NRs so long as a uniform ZnO film can be grown on it. ZnO NTs were obtained when growth times were increased, and the growth mechanisms of ZnO NRs and NTs in aqueous solution at low temperature were investigated. NRs (100−500 nm) were grown in the first 10 h, and in the second 10 h NTs (40−60 nm) were self-assembled on the top of the NRs. This novel discovery of combined growth of ZnO NRs and NTs gives us more options and flexibility in designing 1-D nanostructures.

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(33) Chou, K. S.; Chen, W. H.; Huang, C. S. *J. Chin. Inst. Chem. Eng.* **1990**, *21*, 327.
(34) Grodzicki, Z.; Szlky, E. *Polish J. Chem.* **1984**, *58*, 999.
(35) Grodzicki, Z.; Szlky, E. *Polish J. Chem.* **1984**, *58*, 1009.