# **CHAPTER 5**

# Controllable Synthesis of Complex ZnO Nanostructures: Growth and Properties

# W. Z. Shen, D. H. Fan, Y. F. Zhu, G. Q. Ding

Laboratory of Condensed Matter Spectroscopy and Opto-Electronic Physics, Department of Physics, Shanghai Jiao Tong University, Shanghai, 200240, People's Republic of China

## CONTENTS

1.	Introduction		
2.	ZnO and In <sub>2</sub> O <sub>3</sub> Nanodots and Nanopore Arrays by		
	Poro	us Alumina Memoranes	
	2.1.	Controllable Free-Standing Ultrathin Porous	
		Alumina Membranes 207	
	2.2.	ZnO Nanodots and In <sub>2</sub> O <sub>3</sub> "Rods in Nanodots"	
		Arrays 209	
	2.3.	Existence and Functionality of Anion Impurities in	
		Porous Alumina Membranes 212	
	2.4.	ZnO Nanopores and In <sub>2</sub> O <sub>3</sub> "Rods in Nanopores"	
		Arrays	
3.	Integration of ZnO Nanostructures Through Two-Step		
	Ther	mal Evaporation	
	3.1.	ZnO Nanotubes Surrounded by Well-Ordered	
		Nanorods	
	3.2.	Hierarchical ZnO Nanostructures with Controllable	
		Morphology	
	3.3.	Structural and Optical Properties of	
		Hierarchical ZnO Nanostructures	

4.	ZnO Hollow Spheres and ZnO-Based Core/Shell		
	Structures via Chemical Routes		
	4.1.	Template-Free Synthesis of ZnO Hollow Spheres 227	
	4.2.	A General Chemical Conversion Route to	
		Synthesize ZnO-Based Core/Shell Structures 228	
	4.3.	Optical Properties of ZnO Hollow Spheres and	
		ZnO/ZnS Core/Shell Structures	
5.	Summary and Outlook		
	References		

# **1. INTRODUCTION**

Nanostructured materials have unusual physical and chemical properties different from those of bulk materials and are promising for the fabrication of nanodevices [1–3]. Many kinds of basic nanostructural units, such as nanoparticles, nanorods, nanowires, nanobelts, and nanotubes, have been synthesized under various methods. This chapter addresses the design, controllable growth, and optical characterization of five novel zinc and/or indium oxide nanostructures: nanodot arrays, nanopore arrays, hierarchical nanostructures, hollow spheres, and core/shell structures, to improve performances and broaden applications of the metal oxide semiconductor nanostructures.

Nanodot arrays fabricated on semiconductor substrates with high density are of great interest for technological applications due to their unique size dependent properties and easy integration into functional quantum devices [4]. The placement of nanodots on substrates in a controlled manner has been achievable with the advent of e-beam lithography. Current e-beam writing machines can readily write thousands of nanodots with great accuracy and without extraneous efforts. However, the process would take an extraordinary amount of time to write hundreds of millions of nanodots [5]. The developed dip-pen nanolithography has the same shortcomings although highly-ordered nanodot arrays can also be obtained using atomic force microscope (AFM) cantilevers dipped in certain solutions as pens [6, 7].

The assembly or integration of nanostructural units into desired well-ordered architectures is crucial for the realization of functional nanodevices and has been the focus of current nanotechnology [8]. Existing physical and chemical approaches have the ability to assemble nanostructures, but it is still a challenge to arrange basic nanostructures into highly-ordered designed pattern. The physical methods include electric/magnetic field alignment [9], precisely epitaxial growth [10, 11], multi-step vapor-liquid-solid growth mode [12, 13], and nanolithographic technique [14], etc. Generally, the physical approaches are time-consuming and complex although large-scale samples with specific patterns can be obtained. On the other hand, the chemical methods mainly rely on the electrostatic attraction between opposite charges in chemical solution, e.g., polyelectrolytes' adsorption of ions [15], strong coordination interactions of biomolecules with other charged basic nanostructures [16–18], and colloidal aggregation [19, 20]. Most of the chemical approaches are based on suspensions, incurring all the contamination problems of wet processing. Extra steps are needed to integrate the chemically assembled nanostructures onto solid substrates by employing, e.g., the Langmuir-Blodgett [21] and surface chemistry modification [22] techniques.

In addition to the assembly of semiconductor nanopore arrays, integration of onedimensional (1D) semiconductor nanostructures is also a key step to realize multifunctional nanodevices. Hierarchical ZnO nanostructures have received great attention due to their high surface area, integration degree, and structural integrity [23–27]. So far, hierarchical ZnO nanostructures with different symmetries have been prepared by the vapor transport processes [23, 28, 29] and hydrothermal methods [25], where either the synthetic procedures are complicated or the introduction of impurities is inevitable, and in general, it is difficult to realize the controlled integration of nanostructures. The potential application of nanomaterials depends on the shape and size of the assembled nanostructures, and controlled morphology can modulate the properties of nanomaterials. Therefore, realizing an easy and controllable growth of hierarchical nanostructures is strongly urged in order to prompt the application in novel nanodevices.

Furthermore, core/shell structured materials, together with their hollow structures, have attracted much attention in physics, chemistry, and material science communities due to their specific structures and unique properties [30–36]. The core/shell structured materials usually show improved physical and chemical properties for electronics, magnetism, optics, catalysis, mechanics, and electrochemistry [30–34]. And the hollow structures are expected to have potential applications in catalysts, sensors, photonic crystals, artificial cells, nanoscale chemical reactors, energy-storage media, solar cells, and drug-delivery carriers due to the special hollow geometrical shapes and high surface areas [35–42]. Considerable effort has been devoted to prepare ZnO hollow spheres and ZnO-based core/shell structures. Several methods have been demonstrated to successfully realize the synthesis of these novel structures [36–47].

However, the traditional techniques to realize core/shell structures usually face several disadvantages: firstly, most of the previous reports were concentrated on limited compositions of ZnO/CdS, ZnO/ZnS, ZnO/SnO<sub>2</sub>, and ZnO/ZnSe core/shell structures [43–47]. Secondly, the reported synthetic methods are only suitable for a certain specific semiconductor materials [43–46]. Third, the traditional preparation methods usually require special equipment and/or high temperatures, which results in a high-cost and energy-consuming synthesis process [43–46]. Similar shortcomings also found in the traditional methods for preparing ZnO hollow spheres: either requiring special equipment, high temperatures (typically >500°C), and vacuum conditions or demanding spherical templates [36–42]. The template method is usually time-consuming, high-cost and low product yield [48, 49].

In this chapter, we present three simple but effective ways to synthesize novel metaloxide semiconductor nanostructures. We first report the one-step physical approach of fabricating highly-ordered ZnO nanodots and nanopore arrays and assembling  $In_2O_3$ nanocolumns into well-designed "rods in nanodots" and "rods in nanopores" patterns through free-standing ultrathin porous alumina membranes (PAMs). Secondly, we demonstrate the successful integration of hierarchical ZnO nanostructures with controllable morphology by a two-step oxygen-controlled thermal evaporation process at the low temperature of 500°C without any catalysts. Finally, we propose and realize a template-free method to prepare ZnO hollow spheres and a general chemical conversion route to synthesize various high-quality ZnO-based core/shell (such as ZnO/ZnS, ZnO/Ag<sub>2</sub>S, ZnO/CuS, and ZnO/PbS) spheres using inexpensive and commercially available reagents.

# 2. ZnO and In<sub>2</sub>O<sub>3</sub> NANODOTS AND NANOPORE ARRAYS BY POROUS ALUMINA MEMBRANES

#### 2.1. Controllable Free-Standing Ultrathin Porous Alumina Membranes

Self-organized PAMs, fabricated through a typical two-step anodization of Al, is a highlyordered and ideal template for the fabrication of several types of functional nanodot arrays, such as metals of Fe [4], Au [50], Ni [51], and Co [52], and semiconductors of GaAs [53] and Si [51, 54]. One important advantage of the PAM is that the geometrical structure can be controlled easily by the anodizing conditions with pore sizes from 20 to 250 nm, interpore spacing ranging from 50 to 500 nm, and membrane thickness from 0.1 to 200  $\mu$ m [55, 56]. The thickness of the PAMs plays an important role in fabricating nanostructure materials. For example, hardly any growth of GaAs nanodots was observed when the PAM thickness exceeded 500 nm because the Ga atoms could not migrate to the substrate through the deep nanopores [57]. Due to the Van der Waals bonding of the templates with the substrates and deposition limitation of the thicker templates, the template thickness generally should be less than 350 nm for plasma-enhanced chemical vapor deposition [54]. Therefore, the ability to fabricate ultrathin and throughout PAMs and transfer them onto various substrates is the key issue in the fabrication of semiconductor nanodots and nanopores.

The PAMs can be formed through a typical two-step anodization electrochemical procedure [58] with high-purity (99.999%) aluminum foil degreased in acetone as the anode in 0.3-M oxalic acid ( $H_2C_2O_4$ ) electrolyte. The first anodization lasted for 2 h under the constant anodization voltage of 40 V and electrolyte temperature of 10°C. The specimens were then immersed in a mixture of 6.0-wt%  $H_3PO_4$  and 1.8-wt%  $H_2CrO_4$  at 60°C for 4 h to remove the alumina layers. The well-ordered concave patterns on the aluminum foil act as self-assembled masks for the second anodization. The ultrathin PAMs with different thicknesses were realized under different second anodization times and current densities. Figure 1(a) illustrates typical field-emission scanning electron microscope (FE-SEM) morphology of the PAM under anodizing time of 2 min on Si substrate with the barrier layer on the top. Figure 1(b) shows the experimental thickness (filled circles) of the ultrathin PAMs with different anodization times from 4 sec to 10 min from the FE-SEM observation [59].

For thick PAMs (>100  $\mu$ m), the theoretical thickness was suggested to be proportional to the product of the current density (*i*) and anodization time (*t*) [60]. However, for the ultrathin PAMs (<1  $\mu$ m), the theoretical thickness ( $h_{ox}$ ) of the ultrathin PAMs is expected to follow the integrated form of  $h_{ox} = k \int_{0}^{t} i dt$  with *k* a constant. The solid curve in Figure 1(b) is the theoretical thickness on the basis of the measured current–time characteristics and *k* of (5.91 ± 0.02) × 10<sup>-8</sup> cm<sup>-3</sup> mA<sup>-1</sup> s<sup>-1</sup>. It is clear that  $h_{ox}$  can well explain the yielded thickness of the ultrathin PAMs from the FE-SEM images throughout the experimental anodization time. As a result, controllable ultrathin (<1500 nm) PAMs can be fabricated through changing the anodization time. The slightly large theoretical thickness, as compared with the experimental one, ~10 nm, is due to the fact that the dissolution of the alumina in the electrolyte during the second anodization process has not been taken into account in the theoretical estimation.

A nontoxic mixture solution of saturated  $CuSO_4$  and HCl has been demonstrated to remove the Al substrates for free-standing ultrathin PAMs by the aid of a plastic strainer with the height of 1.0 mm, pore diameter of 1.5 mm, and pore distance of 1.0 mm [59]. The PAMs with the unoxided aluminum at the bottom were laid on the plastic strainer, which was fixed in a glass vessel with the surface of the erosive solution just surpassing the upside of the strainer. The aluminum reacted drastically with the erosive solution and the aluminum of 0.2 mm in thickness was removed clearly within 2 min while the PAM was intact. The free-standing ultrathin PAMs were obtained by taking out gently and washing in deionized water. Figure 1(c) presents the reaction time to totally remove the 0.2 mm unoxided aluminum layer in the erosive solution of different CuSO<sub>4</sub>/HCl



**Figure 1.** (a) FE-SEM image of the PAM prepared under 2 min on Si substrate with the barrier layer on the top. (b) Dependence of the PAM thickness on the anodization time under the second anodization conditions of 10°C, 40 V, and 0.3-M  $H_2C_2O_4$ . The filled circles are the experimental data from the FE-SEM observation, and the solid curve is the theoretical result. (c) Dependence of reaction time for 0.2-mm unoxided aluminum removal on HCl content at 0°C. Reprinted with permission from [59], G. Q. Ding et al., *Nanotechnology* 16, 1285 (2005). © 2005, Institute of Physics.

contents at 0°C. The saturated  $\text{CuSO}_4$  solution itself cannot remove the Al completely, and the reaction accelerates when a little HCl is mixed into the saturated  $\text{CuSO}_4$  solution. When the content of HCl increases from 9% to 20%, the total reaction time deceases from 60 to 5 min. The reaction will be so fast that the reaction time is only less than 2 min with the HCl content between 25% and 65%. Further increase of the HCl, however, will slow down the reaction obviously. Generally, pure  $\text{CuSO}_4$  or HCl will produce resultants apt to hydrolyze into Al(OH)<sub>3</sub> which adheres to the Al foil and blocks the reaction. Only proper  $\text{CuSO}_4/\text{HCl}$  contents can restrain the hydrolyzation and speed up the etching process. Furthermore, it is also noted the reaction will produce a lot of heat energy in the surface of unoxided aluminum foils, resulting in the negligible temperature effect, as compared with that of HCl (CuSO<sub>4</sub>) contents.

The free-standing ultrathin PAMs can be transferred onto various substrates, such as Si, GaAs, glass, and SiO<sub>2</sub>, with the barrier layer on the top [54]. After drying, the specimen was immersed into the 6%  $H_3PO_4$  for 30 to 60 min at 30°C to remove the top barrier layer. After washing several times in deionized water, the specimen was then dried for the nanodot and nanopore array growth. It should be noted that, during the chemical etching and washing process, the PAM mask would not get way from the substrate because of the Van der Waals bonding between the substrate and the membrane.

### 2.2. ZnO Nanodots and In<sub>2</sub>O<sub>3</sub> "Rods in Nanodots" Arrays

The general fabrication process of nanodot arrays by the aid of PAMs is Schemaally shown in Figures 2(a–c). The nanodots are deposited on the substrate through the PAM nanochannels with one nanodot in a singe PAM nanochannel. The nanodot arrays can be realized after the PAM is removed in chemical solution of 1-M NaOH at 20°C for 30 min. Large-scale (>1 cm<sup>2</sup>) highly-ordered ZnO nanodot arrays have been successfully fabricated. Figure 3(a) displays the typical morphology of the ZnO nanodot arrays through a convenient and low-cost technique combining the PAMs with reactive electron-beam evaporation (REBE), without the necessity of catalysts [61]. It is clear that the ZnO nanodot arrays replicate the highly-ordered nanopore pattern of the PAM mask, and retain circular shape and good size uniformity. The average diameter of the ZnO nanodots is 57 nm, and the dots are distributed in a small size range ( $\pm$ 3 nm) with a standard deviation of 5.3%. The ZnO nanodot arrays are found to be ~100 nm in spacing, which is



**Figure 2.** Schema diagrams of (a) one nanodot deposited in a single PAM nanochannel, together with (b) crosssectional and (c) top view of the nanodot arrays after the removal of the PAM. (d) Many nanorods deposited through a single PAM nanochannel, together with (e) cross-sectional and (f) top view of the "rods in nanodots" arrays after the removal of the PAM. Reprinted with permission from [67], G. Q. Ding et al., *Appl. Phys. Lett.* 89, 063113 (2006). © 2006, American Institute of Physics.



**Figure 3.** (a) FE-SEM image of the ZnO nanodots (~57 nm) arrays, together with the HR-TEM image and SAED pattern of a single ZnO nanodot shown in the inset. (b) PL spectra of the highly-ordered ZnO nanodot arrays grown on Si substrates at the temperature between 83 and 308 K under a 325-nm laser excitation. Reprinted with permission from [61], W. L. Xu et al., *Chem. Phys. Lett.* 411, 37 (2005). © 2005, Elsevier.

also in good agreement with the PAM interpore spacing. Hence, the ZnO nanodot size, along with the narrow size distribution, well maintains that of the PAM mask ( $65 \pm 3$  nm) through the lift-off process. The inset of Figure 3(a) shows the high-resolution transmission electron microscopy (HR-TEM) and selected-area electron diffraction (SAED) pattern within a single dot. The clear lattice fringes and bright spots demonstrate good crystallinity of the hexagonal ZnO.

The successful realization of highly-ordered ZnO nanodot arrays was attributed to the ultrathin (~300 nm) PAM templates and the oxygen-full atmosphere in REBE. In the initial stage of the REBE fabrication, ZnO is evaporated by the electron beam and nucleated on Si substrates as well as on the sidewalls of ordered alumina nanoholes. The thicker the PAMs are, the more ZnO adheres to PAM sidewalls, which would result in the clogging of nanopores in PAMs. Therefore, it is necessary for the PAMs to be thin enough to grow smoothly the ZnO nanodot arrays. On the other hand, nanopore size of the PAMs is also a crucial factor to the deposition of ZnO nanodot arrays. In the PAMs with small nanopore size, the nanopores are much more easily to be plugged up by ZnO adhered on the PAM sidewalls, which would prevent ZnO from migrating through the nanoholes. Under this circumstance, the PAMs should be much thinner to fabricate small nanodot arrays.

Figure 3(b) presents the temperature-dependent photoluminescence (PL) spectra of the highly-ordered ZnO nanodot arrays under a 325-nm He-Cd laser excitation. At room temperature, the dominant near-band-edge emission peak at 3.302 eV is observed due to the recombination and emission of free excitons (FE) through an exciton–exciton collision process. This emission energy is almost identical to what is typically observed in high-quality *n*-type ZnO nanowires [62]. The full-width-at-half-maximum (FWHM) of the FE emission is found to be  $\sim$ 0.13 eV, which is comparable to that of well-ordered ZnO nanowires ( $\sim$ 0.12 eV) [63]. There is a secondary broad PL band as a deep level emission centered at ~2.54 eV in the visible green region, which usually presents in ZnO films synthesized by traditional methods and is attributed to the recombination of photogenerated holes with the singly ionized oxygen vacancies [64]. It is clear that the PL band in UV region is much stronger than that in visible region, with an intensity ratio of  $\sim$ 400, while the typical PL intensity ratios for the ZnO films grown by molecular-beam epitaxy (MBE) and metal-oxide chemical vapor deposition (MOCVD) are about 20-40 [65]. The low oxygen vacancies in the current ZnO nanodot arrays can be attributed to the oxygenfull atmosphere under which the REBE is processed. The much larger surface-to-volume ratio in ZnO nanodot arrays than that of ZnO films also greatly decreases the oxygen vacancies in ZnO nanodot arrays by more sufficient interaction of ZnO nanodots with oxygen. As temperature is decreased, additional acceptor-bound exciton (BE) ( $A^0X$ ) emission can be distinguished at  $\sim$ 3.35 eV. The intensity of the BE emission decreases rapidly with increasing temperature and eventually vanishes at temperatures above 108 K, which is lower than that in bulk ZnO of 150 K [66]. It can also be related with the larger surface-to-volume ratio in ZnO nanodots, which increases the interacting surface between ZnO and ambient atmosphere and hence accelerates the decomposition of bound excitons.

It should be noted that the density of the above-yielded nanodot arrays is the same as that of PAM nanopores and limited to  $\sim 10^{11}$  pores cm<sup>-2</sup>. One way to improve the nanodot sheet density is to increase the nanopore density of PAMs, which is restricted by the PAM fabrication. Another way is to deposit multiple nanounits in a single PAM nanochannel. Masuda et al. [50] have demonstrated two or three metal nanoparticles in a single PAM nanochannel through twice-shadowed evaporation of various materials. For quantum device application, it is expected to deposit more nanounits in a single PAM nanochannel for further increase of the sheet density. Controllable indium oxide (In<sub>2</sub>O<sub>3</sub>) nanorods have been deposited within every single nanodot under a magnetron sputtering to form nanodot arrays in conjunction with the PAM technique [67], as shown Schemaally in Figures 2(d–f). The fact that many kinds of nanoscale In<sub>2</sub>O<sub>3</sub> microstructures, such as nanoparticles [68, 69], nanowires [70], nanochains [71], nanofibers [72], nanobelts [73], nanotubes [74], and nanopyramids [75], have been synthesized under different growth methods forms the base for the realization of In<sub>2</sub>O<sub>3</sub> nanostructures with "nanounits in nanodots" by the aid of the PAMs.

Figure 4(a) displays the FE-SEM morphology of the prepared  $In_2O_3$  nanodot arrays using the  $In_2O_3$  sputtering target (90 wt%  $In_2O_3$  and 10 wt%  $SnO_2$ ), demonstrating that every nanodot is composed of ~30 individual nanorods with the average diameter of ~13 nm [67]. This fabricated "rods in nanodots" nanostructure remarkably improves the sheet density to reach over  $10^{12}$  cm<sup>2</sup> in nanomaterials fabricated through the PAM templates. Furthermore, profited from the large-scale fabrication of the PAMs, the area of the synthesized  $In_2O_3$  "rods in dots" nanostructure can be over several square centimeters. The low-magnification FE-SEM image in Figure 4(b) shows an area over 4  $\mu$ m × 5  $\mu$ m with partially unremoved PAM. Figure 4(c)**211** sents the HR-TEM image of two individual  $In_2O_3$  nanorods with average diameter ~13 **211** and height ~50 nm. The lattice fringes in nanorods confirm that every  $In_2O_3$  nanorod is single crystalline. The energy-dispersive



**Figure 4.** FE-SEM images of (a) enlarged  $In_2O_3$  nanodot arrays with ~30 nanorods in every nanodot, and (b) large-area  $In_2O_3$  nanodot arrays after partial PAM was removed. (c, d) HR-TEM images of the  $In_2O_3$  nanorods. Reprinted with permission from [67], G. Q. Ding et al., *Appl. Phys. Lett.* 89, 063113 (2006). © 2006, American Institute of Physics.

X-ray (EDX) spectroscopy during HR-TEM observation confirms that there are three elements in the nanopores: indium, tin, and oxygen, with an approximate atomic indium-totin ratio of ~14:1. Figure 4(d) reveals the 0.506-nm lattice spacing of the cubic  $In_2O_3$  plane (200) and the [100] nanorod growth orientation, and this kind of preferable growth is consistent with the synthesis mechanism of other  $In_2O_3$  nanostructures, such as nanowires [70], nanofibers [72], and nanobelts [73]. The unique benefit is to present a practical and easy handling approach to realize nanounits with one magnitude higher sheet density (over  $10^{12}$  pores cm<sup>-2</sup>) under the PAM templates, and this method further provides a general way to fabricate similar nanostructures of various materials, such as oxides and metals.

It should be noted that PL of  $In_2O_3$  normally originates from the near-band-edge (~3.7 eV) [68, 69] and defect-related (3.27, 2.64, 2.39, and 1.95 eV) emissions [74, 75]. However, it is difficult to detect the weak near-band-edge emissions of pure and good-quality  $In_2O_3$ , since bulk  $In_2O_3$  cannot emit light at room temperature [76]. There are very few papers in the literature [68, 69] reporting the near-band-edge emissions in synthesized  $In_2O_3$  nanoparticles with small sizes, where a mass of such nanoparticles can be used during the PL measurement. In contrast, the present ultrathin (~50 nm) samples have only fixed and limited nanorods. The small amount of the  $In_2O_3$  nanorods leads to the difficulty in observing the weak near-band-edge emissions. Strong defect-related emissions are always related to the amorphous  $In_2O_3$  or oxygen vacancies, and have been widely observed in not-so-good  $In_2O_3$  samples [74, 75]. The experimental fact that there is not any defect-related emission confirms the good quality of the present  $In_2O_3$  nanorods, consistent with the HR-TEM observations.

## 2.3. Existence and Functionality of Anion Impurities in Porous Alumina Membranes

It is well known that, during the preparation of PAMs, there are oxalic impurities in PAMs due to the competition between the water-splitting reaction  $(3/2H_2O \rightarrow 3H^+ + 3/2O^{2-})$ and dissociation of acids (HC<sub>2</sub>O<sub>4</sub><sup>-</sup>  $\rightarrow$  C<sub>2</sub>O<sub>4</sub><sup>2-</sup> + H<sup>+</sup>) to form conjugate base anions, which can replace  $O^{2-}$  in the oxide as substitution or contamination impurities [77, 78]. Mardilovich et al. [79] have confirmed that oxalic impurities of PAMs during the calcinations could decompose and form other impurities. A limited investigation has demonstrated that the anion impurities play an important role not only in the optoelectronic properties of the PAM itself, but also in the deposition of nanomaterials. Yamamoto et al. [80] proposed, as early as in 1981, that the oxalic impurities incorporated in PAMs can be transformed into luminescent centers, showing a blue PL band around 470 nm. Xu et al. [81] have identified that the blue PL band originates from the coactions of the singly ionized oxygen vacancies and the luminescent centers transformed from oxalic impurities. Choi et al. [82] have observed the relationship between the anion content and the dielectric constant of PAMs: the more anions are incorporated in the alumina, the lower the dielectric constant. Ding et al. [83] have reported that, during the sputtering of ZnO, these localized negative charges will attract  $Zn^{2+}$  ions, resulting in the formation of well-ordered semiconducting ZnO nanopore arrays on top of the PAMs, as discussed in Section 2.4.

An experimental base for the overall understanding the role of the  $C_2O_4^{2-}$  anions has been established [84]. The existence of the  $C_2O_4^{2-}$  anions has been clearly revealed by the structural and optical measurements. The HR-TEM image in Figure 5(a) clearly exhibits the duplex layer structures for the PAM sidewalls, with the dark inner layer and relatively bright outer layer. The different contrast is the result of more anion-contaminated outer layer and the inner layer of high alumina density. Figure 5(b) displays the roomtemperature infrared absorption spectra of the ultrathin PAMs annealed at different temperatures. The infrared vibrational measurements have the ability to reveal the existence of  $C_2O_4^{2-}$  impurity in the PAMs, and the variation of the absorption peak intensity can reflect the corresponding impurity concentration. During the anodization,  $C_2O_4^{2-}$  ions



**Figure 5.** (a) HR-TEM image of the as-deposited PAM. (b) Room-temperature infrared absorption spectra of the as-prepared and annealed PAMs at different temperatures for 3 h. (c) Experimental (filled circles) and calculated (solid curves) transmission spectra of the as-deposited and annealed PAMs in the visible wavelength range. (d) Yielded wavelength-dependent refractive index of the host alumina. Reprinted with permission from [84], D. H. Fan et al., *Micro. Meso. Mater.* 100, 154 (2007). © 2007, Elsevier.

C=O and C-O bonds with the same C atom will average into two equivalent carbon-

oxygen bonds ( $^{-C_{\sim 0}}$ ). The strong coupling between the two equal bonds results in the COO<sup>-</sup> asymmetrical stretching vibration (asym. str.) from 1558 to 1593 cm<sup>-1</sup> and relatively weak COO<sup>-</sup> symmetrical stretching vibration (sym. str.) from 1403 to 1455 cm<sup>-1</sup> [85, 86].

With the increase of annealing temperature, there is gradual decrease of the COOabsorption band intensity, which indicates that annealing can lead to the decrease of the  $C_2O_4^2$  content due to the decomposition of the impurity groups related to  $C_2O_4^2$ . Especially, when the annealing temperature increases from 600 to 800°C, the integrated intensity decreases rapidly, revealing the large decomposition of the  $C_2O_4^{2-}$  impurity groups and therefore sharp decrease of the  $C_2O_4^{2-}$  anion content in the PAMs. The above arguments can also be testified by the shift of the COO<sup>-</sup> sym. str. absorption peak. The COO<sup>-</sup> sym. str. redshifts with increasing annealing temperatures below 800°C, whereas it keeps almost unchanged under annealing at or above 800°C, since stable impurities, such as aluminum-carboxylate complex [80], have gradually been formed in the PAMs due to the decomposition of the impurity groups related to  $C_2O_4^{2-}$ . For the 2342 cm<sup>-1</sup> absorption peak in Figure 5(b), it had been reported that this peak is attributed to the formation of  $CO_2$  inside the PAMs rather than the  $CO_2$  from the air [87]. The increase of the  $CO_2$ absorption peak intensity further confirms that annealing can lead to the decrease of the  $C_2O_4^{2-}$  concentration due to the decomposition of impurity groups related to the  $C_2O_4^{2-}$ in PAMs [81]. However, the CO<sub>2</sub> gasification in PAMs at high annealing temperatures will decrease its intensity.

In addition to the vibrational bands, the change of refractive index of the host alumina also reflects the existence and variety of  $C_2O_4^{2-}$  concentrations in the as-deposited

and annealed PAMs [84]. The wavelength-dependent refractive index of the host alumina in the PAMs below the band gap can be determined from the observed interference fringes in the optical transmission spectra by the aid of the modified four-layer-medium transmission model (i.e., air/PAM/substrate/air) and the fitting procedure described in Chen et al. [88]. The real thickness of the PAMs is measured by SEM, the PAM's porosity is considered since PAMs are composed of alumina and air. Figure 5(c) shows the experimental transmission spectra (filled circles) of the PAMs annealed at different temperatures, together with the corresponding calculated spectra (solid curves). Figure 5(d) presents the yielded wavelength-dependent refractive index of the host alumina in the PAMs annealed at different temperatures. The refractive index in the as-deposited PAMs is  $\sim$ 1.65 at 546 nm, in good agreement with the reported value of  $\sim$ 1.64  $\pm$  0.01 obtained by the optical waveguide method [89]. It can be observed clearly that at a certain wavelength, the refractive index of the host alumina is found to increase with the annealing temperature. Choi et al. [82] have reported that the anion-incorporated alumina had lower dielectric constant compared to that of the pure alumina. The dielectric constant of alumina in the visible and infrared ranges is approximately equivalent to the square of the refractive index due to the low absorption coefficient. Therefore, the decrease of the  $C_2O_4^{2-}$  anion concentration with the increase of annealing temperature results in the observed increase of the refractive index of the host alumina.

#### 2.4. ZnO Nanopores and In<sub>2</sub>O<sub>3</sub> "Rods in Nanopores" Arrays

As we know, the variety of ZnO nanostructures benefits from the facts that ZnO has two polar surfaces (positively charged (0001)-Zn and negatively charged (0001)-O) and three fast growth directions ([0001], [1010], and [2110]) [73, 90]. The basic idea for the realization of large-scale ZnO nanopore arrays comes from the unique properties of both ZnO and PAMs: charged surfaces and controllable sizes in hexagonal morphologies. A number of planes, which are composed of tetrahedrally coordinated  $Zn^{2+}$  and  $O^{2-}$  ions, stack alternately along the *c*-axis to form the hexagonal ZnO grain. As Figure 6(a) shows, the oppositely charged ions produce negatively charged (0001)-O and positively charged (0001)-Zn polar surfaces on either the top or the bottom of the ZnO grain [90]. The width and height of the ZnO grain are determined by the growth along the six equivalent side faces {1010} and the *c*-axis, respectively, and can be well controlled by the growth



**Figure 6.** Schema diagrams of growth mechanism for the ordered ZnO nanopore arrays (a–e) and (f–h)  $In_2O_3$  "rods in nanopores" arrays by the aid of PAMs. Reprinted with permission from [83], G. Q. Ding et al., *Appl. Phys. Lett.* 88, 103106 (2006). © 2006, American Institute of Physics; and from [96], G. Q. Ding et al., *Nanotechnology* 17, 2590 (2006). © 2006, Institute of Physics.

conditions during the magnetron sputtering [91]. On the other hand, as discussed in Section 2.1, PAMs are versatile templates, which have hexagonal nanopore arrays with controllable pore diameter, interpore spacing, and thickness. Each hexagonal nanopore is formed by six hexagonal amorphous alumina nanorods (Fig. 6(b)), where negative charges localize at the intermediate part of the PAM top surfaces [84] due to the inhomogeneous distribution of anion species ( $C_2O_4^{2-}$ ) discussed in Section 2.3.

During the deposition of ZnO grains on PAMs with Si substrates, these localized negative charges will attract  $Zn^{2+}$  ions, resulting in the first ZnO nucleation and growth along the preferable directions at the PAM top surfaces, rather than onto the Si substrates through PAM nanochannels. Under certain growth conditions, the width of the grown ZnO grains on the PAM top surfaces can be very close to the size of the hexagonal amorphous alumina nanorods, and such six grains will form a hexagonal nanopore pattern identical to that of the PAMs, as shown Schemaally in Figure 6(c). Therefore, well-ordered large-scale ZnO nanopore arrays can be fabricated on the top surfaces of the PAMs. With further deposition of ZnO grains, the  $O^{2-}$  ions on the surfaces will play the same role as the localized negative charges in PAMs, leading to the formation of next round of ZnO nanopore array layer, i.e., multilayer growth of ZnO nanopore arrays (Fig. 6(d)). Figure 6(e) shows the cross-sectional view of multilayer ZnO nanopore arrays on top of a PAM on Si (100) substrate.

Figure 7(a) presents the top view FE-SEM image of the realized ZnO nanopore arrays on top of the PAM with the alumina nanorod size of  $\sim$ 30 nm [83]. During the magnetron sputtering deposition, the growth temperature was kept at 200°C to yield suitable ZnO grain width of  $\sim$ 30 nm, i.e., close to the alumina nanorod size. It is clear that the morphology of the ZnO nanopore arrays basically copies the highly-ordered hexagonal pattern of the PAM, with the ZnO pore size, interpore distance and thickness of  $\sim$ 70, 100 and 30 nm, respectively. HR-TEM at the interface between the ZnO nanopore arrays and PAMs (Fig. 7(b)) shows clean and perfect microstructure of the crystalline ZnO at the top surface of amorphous alumina with a very thin ZnO transitional layer (3-4 nm in thickness), confirming that high-quality ZnO nanopore arrays can be grown by the present technique. Both the lattice distance of 0.52 nm and the SAED pattern shown in the inset demonstrate that the growth orientations of ZnO grains perpendicular and parallel to the top surfaces of PAMs are [0002] and [1010], respectively. This kind of growth mechanism for the ZnO nanopore arrays agrees with the fast growth directions of ZnO. The evidence for the synthesis of the ZnO nanopore arrays can also be observed in the EDX spectra (Fig. 7(c)) taken on different layers of the specimen in Figure 7(a). The EDX spectrum for the bottom PAM layer shows three peaks: i.e., the strong Si peak from the Si substrate, and the Al and O peaks due to the porous alumina layer. The absence of a Zn peak indicates that there is no ZnO deposited on either the sidewalls of the PAM or the Si substrate through the PAM nanochannels, consistent with the clean PAM nanochannels and Si substrate in the FE-SEM images. In contrast, the EDX spectrum for the top porous arrays does exhibit the Zn peak, verifying the formation of ZnO nanopores on the top surface of PAM. The EDX compositional line profile in the inset of Figure 7(c) further supports the above arguments.

Micro-Raman and PL (Fig. 7(d)) measurements have been carried out to characterize the optical properties of the ordered ZnO nanopore arrays. Under the backscattering geometry of  $Z(X, -)\overline{Z}$ , the Raman spectra display one of the fundamental optical modes in wurtzite ZnO [92]: A<sub>1</sub>(LO) (LO = longitudinal optical) at ~570 cm<sup>-1</sup>, which redshifts with the increase of temperature. The absence of E<sub>2</sub> mode is associated with the oxygen deficiency [93]. In the PL spectra, as temperature is increased, the exciton emission in UV region decreases in intensity, shifts to low energy, and increases in the FWHM. The absence of oxygen-vacancy-related green (~500 nm) luminescence band confirms again the high quality of the fabricated ZnO nanopore arrays. The low-magnification image displayed in Figure 7(e) indicates the growth of large-scale (>8  $\mu$ m × 12  $\mu$ m) ordered ZnO nanopore arrays.

It should be noted that, during the formation of a ZnO nanopore array layer, the growth along side faces ( $\langle 10\overline{1}0 \rangle$  directions) is restrained by the adjacent ZnO grains,



**Figure 7.** (a) Top-view FE-SEM image of the ordered ZnO nanopore arrays on top of PAM, (b) HR-TEM image of the interface between the PAM and ZnO, with the SAED pattern of the top ZnO layer shown in the inset, (c) EDX spectra of the bottom PAM layer and the top ZnO layer in (a). The inset is the EDX compositional line profile along the arrow in (e) cross the interface (position 0  $\mu$ m). (d) Micro-Raman and PL spectra of the highly-ordered ZnO nanopore arrays at the temperatures between 83 and 293 K under a 325-nm laser excitation. (e) Low-magnification FE-SEM image of the ZnO nanopore arrays on top of PAM. (f) FE-SEM image of four ZnO nanopore array layers with the same morphology and height. Reprinted with permission from [83], G. Q. Ding et al., *Appl. Phys. Lett.* 88, 103106 (2006). © 2006, American Institute of Physics.

limiting the growth along the  $\langle 0001 \rangle$  orientation with the height of the ZnO grains along the *c*-axis to a certain value (~30 nm from Fig. 7). With the further continuous deposition of ZnO, the O<sup>2-</sup> ions on the surface of the ZnO nanopore array layer will attract the Zn<sup>2+</sup> ions (i.e., play the same role as the localized negative charges in PAMs), leading to the next round of ZnO nucleation and preferable direction growth. It is therefore expected a multilayer growth of ZnO nanopore arrays (Fig. 6(d)) with the polar (0001)-Zn surface at the bottom to minimize the energy due to the polar surfaces and charges. Figure 7(f) displays the realized four ZnO nanopore array layers with the same morphology and height (every layer ~30 nm), which clearly demonstrate the above expectation. The multilayer growth in nanostructures may be related to the orientation dependent growth energy.

The variety of  $C_2O_4^{2-}$  anion impurity concentration in the PAMs also affects the deposition and crystallization of nanomaterials. Figures 8(a–c) display the FE-SEM images of the fabricated ZnO nanopore arrays on both the as-deposited and annealed PAMs to demonstrate the role of the  $C_2O_4^{2^-}$  anion concentration [84]. It is clear that ordered ZnO nanopore arrays have been formed on the top surface of the as-deposited PAMs (Fig. 8(a)) with the pattern identical to that of PAMs, and every hexagonal ZnO nanopore is composed of six ZnO grains. When the PAMs were annealed below 400°C, the morphology of the sputtered ZnO nanopores was basically unchanged. With the annealing temperature increased to 600°C, the yielded ZnO nanopores were no more circular and the cells of ZnO nanopores were not hexagonal any more, as shown in Figure 8(b). Many ZnO grains (much more than six) were irregularly deposited on the surface of a single PAM cell, and the regularity of the ZnO nanopore arrays decreases obviously. Especially, under the PAMs annealed at 900°C, the regularity of ZnO nanopore arrays becomes very poor and even parts of nanopores are jammed by ZnO particles (Fig. 8(c)).

X-ray diffraction (XRD) measurements can further testify to the effect of the anion impurity in PAMs on the crystallization of these ZnO nanopore arrays. Figure 8(d) shows the XRD spectra of the ZnO nanopore arrays deposited on top of the PAMs annealed at different temperatures. The XRD spectrum of the ZnO nanopore arrays deposited on the as-prepared PAM exhibits a strong (002) orientation peak and two weak (100) and (101) peaks [94] without any other diffraction peaks. As we know, the higher the relative intensity of the strongest (002) diffraction peak is, the better the ZnO crystal quality is. It is found that the ZnO (002) peak intensity gradually decreases with the increase of the annealing temperature, which clearly indicates that lower anion impurity concentration leads to lower crystal quality. In the PAMs annealed at 900°C, besides the weak ZnO diffraction peaks, two  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> diffraction peaks appear at  $2\theta = 45.92^{\circ}$  and 67.06° [95], confirming that high-temperature annealing can lead to the crystallization of the PAMs [81].



Figure 8. FE-SEM images of the ZnO nanopore arrays deposited on top of (a) as-deposited PAM, and PAMs annealed at (b) 600°C and (c) 900°C. (d) XRD spectra of the ZnO nanopore arrays deposited on top of as-deposited and annealed PAMs at different temperatures. Reprinted with permission from [84], D. H. Fan et al., *Micro. Meso. Mater.* 100, 154 (2007). © 2007, Elsevier.

The above strategy for the realization of large-scale ZnO nanopore arrays can be extend to integrate indium oxide single-crystalline nanocolumns into highly-ordered twodimensional (2D) nanopores patterns through magnetron sputtering by the aid of PAMs. As shown in Figures 6(f and g),  $In_2O_3$  thin films with nanocolumn microstructure can be grown on different substrates, and during the deposition of sputtered  $In_2O_3$  on PAMs with, e.g., Si substrates, the localized negative charges in PAMs will attract ions, resulting in the  $In_2O_3$  nucleation and growth along the preferable directions at the PAM top surfaces. Due to the easily well-shaped arrangement of columns,  $In_2O_3$  nanocolumns will be assembled to form a hexagonal cell pattern identical to that of the PAMs. It is therefore expected that well-ordered and large-scale  $In_2O_3$  "rods in nanopores" arrays (Fig. 6(h)) can be fabricated on the top surfaces of the PAMs.

Figure 9(a) displays the top-view FE-SEM morphology of the yielded  $In_2O_3$  "rods in nanopores" arrays [96]. The highly-ordered hexagonal pattern with the pore size of ~50 nm and interpore spacing of ~100 nm, confirms that the 2D  $In_2O_3$  nanopores basically copy the PAM surface morphology. The enlarged image in Figure 9(b) demonstrates that the sputtered  $In_2O_3$  has many nanopores surrounded by nanoscale grains with the size of ~15 nm on the surface. The cross-section of  $In_2O_3$  nanopores on top of PAM reveals that these grains have nanocolumn microstructure with height of ~50 nm. The nanocolumn nature of  $In_2O_3$  grains can be further confirmed by the HR-TEM images of both the top surface (Fig. 9(c)) and side view (Fig. 9(d)), where well arrangement of the nanocolumns and interfaces of the  $In_2O_3$  grains can be obviously observed, and the size, shape, and arrangement of these sputtered  $In_2O_3$  nanocolumns are consistent with the FE-SEM observations.

It is interesting to note that the top surface of a single  $In_2O_3$  nanocolumn displays a pyramid-like morphology with the height of triangular facets ~5 nm (Figs. 9(b and d)). The small facets can be indexed to the  $In_2O_3$  (222) planes with clear interplanar spacing of 0.290 nm through the HR-TEM image of Figure 9(e). The formation of triangular facets is due to the fact that, during the crystal growth of  $In_2O_3$ , the (222) plane with slower growth rate tends to appear as the facets over the fast growing plane, which has been demonstrated in the synthesis of  $In_2O_3$  nanopyramids [97]. The atomic-resolution HR-TEM image (Fig. 9(f)) of a single nanocolumn's side surface clearly reveals both the lattice distances of 0.506 nm of plane (200) and 0.253 nm of plane (400). These HR-TEM results confirm that every  $In_2O_3$  nanocolumn is single-crystalline, and that the growth orientations perpendicular and parallel to the top surfaces of PAMs are [100] and [010], respectively, while the top surface of the nanocolumns is indexed to (222) planes. The growth along [100] direction is much faster than that along [222] direction, resulting in the columnar microstructure with pyramid-like top morphology.

The microstructure of the obtained 2D nanopores can be characterized by XRD and EDX. The two diffraction peaks in Figure 9(g) can be attributed to (222) and (400) planes of the cubic  $In_2O_3$  structure of  $Mn_2O_3$  (I) type with a cell constant of 1.012 nm [98]. It is noted that the strongest diffraction peak of the  $In_2O_3$  nanopores is (400), while in the bulk  $In_2O_3$  the strongest peak is (222) with the relative intensity of the (400) plane of 35 (JCPDF No. 44-1087). The XRD results coincide well with the above-demonstrated (222) facets and preferable [100] growth orientation of  $In_2O_3$  nanocolumns through HR-TEM images. The EDX analysis during HR-TEM observation (Fig. 9(h)) reveals that there are three elements in the nanopores, i.e., indium, tin, and oxygen, with an approximate atomic ratio of indium to tin equal to 12:1. Both the XRD and EDX results confirm that the obtained nanopores are really composed of tin-doped  $In_2O_3$ . The resistivity of the  $In_2O_3$  nanopores is only  $\sim 4 \times 10^{-4} \Omega$  cm, which is beneficial to the application of the highly-ordered 2D  $In_2O_3$  nanopores in nanoelectronic devices.

The successful assembly of large-scale and highly-ordered 2D  $In_2O_3$  "rods in nanopores" arrays is due to the electronic attraction between the localized charges in PAMs and the sputtered well-arranged  $In_2O_3$  nanocolumns. Ding et al. [96] have further demonstrated that the morphology of the assembled  $In_2O_3$  nanopore arrays is controllable by adjusting either the PAM configurations (pore diameter and interpore spacing) or



**Figure 9.** (a) FE-SEM image of the  $In_2O_3$  nanopores; inset is the FE-SEM image of the free-standing  $In_2O_3$  nanopore arrays directly transferred onto a Si substrate. (b) Top-view FE-SEM images of  $In_2O_3$  "rods in nanopores" arrays on top of PAM with the cross-sectional view shown in the inset. (c) HR-TEM image of a single  $In_2O_3$  nanopore. (d) HR-TEM image shows several well-arranged  $In_2O_3$  nanocolumns. (e) Top-surface HR-TEM image from the box in (c) reveals that the (222) fringes are separated by 0.290 nm. (f) Side-surface HR-TEM image from the box in (d) demonstrates the growth orientation along the nanocolumns of Ref. [100]. (g) XRD and (h) EDX spectra of the  $In_2O_3$  nanopore arrays. Reprinted with permission from [96], G. Q. Ding et al., *Nanotechnology* 17, 2590 (2006). © 2006, Institute of Physics.

sputtering conditions (substrate temperature and argon pressure), revealing that the presented method provides the possibility of a general approach for nanounit integration. Finally, it should be noted that apart from the anion concentration, the thickness of PAMs and growth conditions also play important roles in the yielded nanostructures. The ultrathin PAMs generally lead to the formation of nanodot arrays, and the proper growth conditions in combination with relatively thick PAMs are helpful to improve the order degree of the nanopore arrays.

# 3. INTEGRATION OF ZnO NANOSTRUCTURES THROUGH TWO-STEP THERMAL EVAPORATION

#### 3.1. ZnO Nanotubes Surrounded by Well-Ordered Nanorods

The performance of semiconductor nanodevices depends significantly on the shape and size of the nanostructures. Realizing the integration of ZnO nanostructures with monotonic morphology is a key step to broadening the application of the functional nanomaterials. A simple two-step thermal evaporation process has been demonstrated to be an effective approach to the successful realization of hierarchical ZnO nanotubes surrounded by well-ordered nanorods (ZNSWN) [99]. The basic idea comes from the controllable oxidation rate of Zn at different substrate temperatures below and above the melting point of Zn (419.5°C), alone with the consideration of polar surfaces and fast growth directions of hexagonal ZnO.

Figure 10(a) shows the Schema diagram of the designed two-step preparation technique. At step one, *n*-type Si wafer was used as the substrate and placed at position A along the carrier gas. The hexagonal-shaped Zn nanowires with little oxidation had been synthesized at a low substrate temperature of  $\sim 200^{\circ}$ C by evaporating Zn powder. At step two, the step-one-deposited samples were employed as the substrates and placed at position B. The integration of monotonic nanostructures can be realized by heating the step-one samples and Zn powder at high temperature of 500°C. Figure 10(b) displays Schemaally the formation processes of the controllable hierarchical ZnO nanostructures. Little oxidized Zn nanowires were prepared in the first step (Schema (b)), and the ZnO nanostructures with controlled morphologies (Schemas (c)–(f)) can be realized by adjusting the oxygen flow rate at the second step.

Figure 11 (a) displays Schemaally the hexagonally shaped Zn nanowires with little oxidation prepared at low substrate temperature of  $\sim$ 200°C. Figure 11(b) shows the FE-SEM image of the step-one-prepared sample. It exhibits hexagonally shaped nanowires with widths of 300–600 nm and lengths of up to several tens of micrometers. The EDX



**Figure 10.** (a) Experimental apparatus for the two-step thermal vapor deposition process. (b) Schema diagram of the growth process for the hierarchical pure ZnO nanostructures with controllable morphology. a:  $ZnO_x$  molecules or clusters, b: Zn nanowires with little oxidation, c: ZnO nanotubes, d: ZnO nanotubes surrounded by well-ordered nanorods, e: ZnO nanowires surrounded by well-ordered nanorods, and f: ZnO nanowires surrounded by nanorods. Reprinted with permission from [110], D. H. Fan et al., *J. Nanosci. Nanotechnol.* 8, 6325 (2008). © 2008, American Scientific Publishers.



**Figure 11.** (a) Schema diagrams of Zn nanowire with little oxide prepared in the step-one thermal evaporation. (b) Low- and (c) high-magnification FE-SEM images of the one-step-prepared hexagonally shaped Zn nanowires with little oxide. The inset in (b) shows the EDX spectrum. Reprinted with permission from [99], D. H. Fan et al., *J. Phys. Chem. C* 111, 9116 (2007). © 2007, American Chemical Society.

spectrum in the inset of Figure 11(b) shows that apart from the Zn and O element, no other elements are observed, which confirms that there is no existence of other metal clusters in the Zn/Zn suboxide nanowires, and also excludes the possibility that the nanowires are realized by the catalysis-assisted growth. The relatively large atomic ratio of Zn and O (~19:1) indicates that little Zn is oxidized into Zn suboxide at the first step, i.e., the nanowire is dominated by Zn with little oxidation. High-magnification image of Figure 11(c) displays flat and smooth terrace- and step-like structures on the hexagonal-shaped ends, clearly revealing a layer-by-layer growth mode. This is consistent with the previous report on the ZnO nanorods prepared by MOCVD [100]. There are no nanoparticles at the end of nanowires, suggesting that the growth mechanism is not vapor–liquid–solid (VLS) process because a typical characteristic of VLS is the existence of nanoclusters capping at the end of a 1D nanostructure [101].

The hexagonal mound-like morphology in Figure 11(c) indicates the existence of an Ehrlich–Schwoebel barrier (ESB) during the formation of Zn nanowires with little oxidation [102, 103]. During the formation process of 1D nanostructures, if the adspecies on the nucleated island experience an ESB when diffuse across the island's edge, the next atomic layer may nucleate before the previous layer completes, thereby leading to the multilayer growth and the eventual appearance of the mound structure. Baxter et al. [104] have shown that the ESB plays an essential role in the formation of ZnO hexagonal pyramids. However, the ESB decreases with the increase of heating time in the evaporation, resulting in the relatively smoother surface. Similar observation has been reported by Liu et al. [102] in nanoprisms, where the next atomic layer would not nucleate until the previous one has completed due to the very small ESB in the layer-by-layer growth mode.

On the basis of EDX spectra and FE-SEM observation, one can deduce the growth process as follows. During the course of heating Zn powder, the formed Zn and  $ZnO_x$  ( $x \le 1$ ) molecules or clusters are transported to the low-temperature region by the carrier gas absorbing on the surface of Si substrates. Since Zn belongs to the hexagonal crystal system with the six-fold symmetry, Zn and  $ZnO_x$  molecules or clusters on the substrate could migrate to form the steady hexagonal nanoclusters, and then the nanowires can grow by the layer-by-layer mode. During the growth process of nanowires, the surface of nanowires, however, could not completely be oxidized into ZnO due to the low growth temperature.

Novel hierarchical 1D ZnO nanostructures can be realized by evaporating the Zn powder at 500°C and heating the step-one samples simultaneously at the same temperature, as shown Schemaally for the formed ZNSWN nanostructures in Figure 12(a). Figure 12(b) displays the high-magnification FE-SEM image of the yielded single ZNSWN nanostructure after the second step. The high-magnification image of a single nanorod in Figure 12(c) reveals a columniform structure with a conic tip, which is quite different from the hexagonal structure formed at the first step in Figure 11(c), indicating that the



**Figure 12.** (a) Schema diagrams of the ZNSWN nanostructures. High-magnification FE-SEM images of a single (b) ZNSWN nanostructure and (c) nanorod on the nanotube sidewall. (d) EDX spectrum of the two-stepprepared sample. (d) FE-SEM image of the prepared ZnO nanotube without Zn source in the second step. (f) TEM image of a single ZNSWN nanostructure. (g) TEM image of nanorods on the surface of a single nanotube. The inset shows HR-TEM image of a nanotip indicated by the ellipse in (g). SAED patterns of the (h) nanorods and (i) tube wall conjoint with nanorods. Reprinted with permission from [99], D. H. Fan et al., *J. Phys. Chem. C* 111, 9116 (2007). © 2007, American Chemical Society.

ZnO nanorods are not synthesized through the layer-by-layer growth mechanism [99]. By comparing the EDX results of the one-step samples (Fig. 11(b), inset) and two-step ones (Fig. 12(d)), although no other new elements have been introduced except Zn and O, the atomic ratio of Zn and O decreases to 1.05:1, which demonstrates that Zn has almost been oxidized at the second stage.

The origins of the nanorods can be further investigated by designed experiments. Figure 12(e) shows the FE-SEM image of two-step samples synthesized without the Zn source, which demonstrates clearly the absence of nanorods on the surface of the nanotubes. It is clear that the existence of Zn source is responsible for the formation of nanorods in ZNSWN nanostructures, while the sublimed Zn is not. In addition, compared with the sidewall thickness of nanotubes in Figure 12(e), there is an increasing size in Figure 12(b), which reveals the diameter increase of the nanotubes prepared in the case of heating Zn source. As there is a thin layer of ZnO on the surface of the nanowires (step one), the surface of nanowires will not be sublimed due to the high melting point of ZnO (1975°C). It also indicates that before the growth of the nanorods on the sidewall in the beginning of the second step, Zn and Zn suboxide gas will first nucleate and form the ZnO layer on the surface of nanowires, resulting in the increase of the physical diameter during the transformation of nanowires to nanotubes structure. Furthermore, it should be clarified for the motivation of introducing appropriate amount of oxygen in argon gas flow in step one, which is helpful for the realization of ZNSWN nanostructures. On the one hand, it will help to form a thin ZnO film on the sidewall of the Zn nanowires, which is the base for the later growing of ZnO nanorods. On the other hand, if pure argon is used in the experiment, one will see the forming of pure Zn nanowires, but when it comes to the next deposition stage, the surface of the pure Zn nanowires will be oxidized and sublimed simultaneously, so the surface oxidation will be uneven, which is detrimental for the realization of high-quality ZNSWN nanostructures.

Further morphological and structural analysis of individual ZNSWN nanostructures can be characterized by the HR-TEM and SAED. Figure 12(f) shows the TEM morphology

of the ZNSWN nanostructures, which consists of the nanotube with the light inner part and relatively dark outer one, together with the nanorods on the surface of the outer wall. The result further confirms that the prepared nanostructures belong to the hierarchical ZNSWN nanostructures. The high-magnification image of the sidewall in Figure 12(g) reveals that the lengths of the nanorods are around 250 nm and the widths 30–100 nm, and no nanocluster or tiny nanocrystal is formed at the growth front. The lattice fringes of ZnO nanorods in the inset of Figure 12(g) and the corresponding SAED pattern in Figure 12(h) indicate that the nanorod is single-crystalline, and it grows along [1120] direction with a uniform structure without noticeable defects such as stacking faults. The lattice spacing of 0.26 nm corresponds to the spacing of [0002] crystal planes of wurtzite ZnO. Figure 12(i) shows the SAED pattern of the tube wall which is conjoint with nanorods, indicating that the nanotube is also single-crystalline with growth direction along [0001]. In the idealized ZnO crystal growth, 1D ZnO nanostructures generally grow along [0001] direction due to the high growth rate along this orientation [105]. However, considering the fact that the side face on the ZnO nanotube is along the [1120] direction, one can expect the [1120] growth of the nanorods due to the restriction of the epitaxial relationship; i.e., the growth direction of the nanorod is determined by that of the nanotube wall. Similar experimental observation has been previously reported by Fan et al. [106].

Generally speaking, the oxidation rate varies with the crystal surfaces. In comparison with other surfaces, the Zn {0001} one has the lowest energy, which trends to be the most stable to resist oxidation [107]. When the Zn nanowires with little oxidation are heated at  $\sim$ 500°C, the sidewall of hexagonal nanowires is oxidized into ZnO shells since the {1120} surface has the relatively higher energy compared with the {0001} one. At the same time, the remaining Zn inside the nanowires can be sublimed through the open ends at the {0001} surface due to the low melting point of Zn (419.5°C), leading to the formation of hexagonal ZnO nanotubes.

Apart from the VLS mechanism, the screw dislocation mechanism is also well acknowledged to explain the growth dynamics of 1D nanomaterials [100]. From Figures 12(c and f), it is clear that no additional metal particles or tiny nanocrystals appear on the top of the nanorods, ruling out the possibility of the catalytic process during the growth of well-aligned ZnO nanorods [100, 108]. On the other hand, the growth rate along the dislocation line in the screw dislocation model is much higher than that along the radius direction, resulting in the crystal 1D structure morphology [100, 109]. The conic tip with spiral morphology at the end of 1D structured materials is the evidence that screw dislocation mechanism manifests itself. The FE-SEM and TEM observation of non-hexagonally shaped nanorods in Figure 12 agrees well with the characteristics of smooth facets and rough tips in the screw dislocation growth model.

The formation process of the ZNSWN nanostructures can therefore be deduced as follows. Zn and Zn suboxide gases yielded by heating Zn powder are transported to the substrate, and nucleate at the Zn/Zn suboxide nanowires. During the second step of the growing process, the yielded Zn and Zn suboxide gases first nucleate on the surface of the nanowires and form the ZnO layer. With continuous supplementation of Zn and Zn suboxide gases, the ZnO nanorods are epitaxially grown on the surface of the nanowires through the screw dislocation growth mechanism. And at the same time, the hexagonal ZnO nanotubes are gradually formed since the sublimation of the remaining Zn inside the nanowires. With the further increase of the evaporation time, the ZNSWN nanostructure is then realized. In addition, the different nucleation dimensions on the nanotube side facet may result in the observed nonuniform width (30–100 nm) of the nanorods.

#### 3.2. Hierarchical ZnO Nanostructures with Controllable Morphology

The two-step thermal evaporation process can be used to not only prepare the ZNSWN nanostructure, but also realize morphology-controllable hierarchical ZnO nanostructures by changing the growth condition [110]. Figures 13(a) and (a') show the above-mentioned ZNSWN nanostructures prepared under Ar flow rate of 260 sccm and  $O_2$  flow rate of 60 sccm, where the average diameter and length of nanorods on the sidewall are ~70 nm



**Figure 13.** FE-SEM images of the hierarchical ZnO nanostructures by heating the step-one sample and Zn powder for 80 min with: (a) and (a')  $Ar:O_2 = 260:60$ , (b) and (b')  $Ar:O_2 = 260:90$ , (c) and (c')  $Ar:O_2 = 260:120$ . FE-SEM images of ZNSWN samples prepared at  $Ar:O_2 = 260:60$  under different heating times: (d) 20 min, (e) 50 min, and (f) 80 min. The inset in (b') is a single nanorod on the nanowire sidewall. Reprinted with permission from [99], D. H. Fan et al., *J. Phys. Chem. C* 111, 9116 (2007). © 2007, American Chemical Society; and from [110], D. H. Fan et al., *J. Nanosci. Nanotechnol.* 8, 6325 (2008). © 2008, American Scientific Publishers.

and 250 nm, respectively. When the oxygen flow rate increases to 90 sccm, the morphology of ZnO nanostructures has obviously change, as shown in Figures 13(b) and (b'). They are composed of central axial nanowires surrounded by well-ordered nanorods with six-fold structural symmetry, which is different from the ZNSWN nanostructures in Section 3.1, indicating that the oxygen flow rate can effectively control the formation of ZnO hierarchical nanostructures. Compared with the hierarchical nanostructure in Figure 13(a), not only the morphology of nanostructures has an obvious change, but also the average diameter and length of the nanorods become large up to about 100 nm and 600 nm, respectively. The inset in Figure 13(b') reveals that in the nanostructures of nanowires surrounded by well-ordered nanorods, the nanorod also has columniform structure with a conic tip similar to the image of nanorods in the ZNSWN nanostructures, implying the same growth mechanism of nanorods in these two kinds of nanostructures.

With the further increase of oxygen flow rate, new hierarchical ZnO nanostructures can be achieved. Figure 13(c) presents the FE-SEM image of the sample synthesized at Ar flow rate of 260 sccm and  $O_2$  flow rate of 120 sccm. The high-magnification FE-SEM of a single nanostructure in Figure 13(c'), which is quite different from the two kinds of ZnO nanostructures reported above, further reveals the change of structure and morphology. The non-ordered ZnO nanorods grow randomly from the sidewall of the central axial nanowire. The average diameter of nanorods increases to ~200 nm and the length reduces to ~300 nm. In addition, the nanorods in the sidewall display the hexagon-shaped top, suggesting the preferential growth of ZnO nanorods along [0001] orientation.

In general, the nucleation rate and availability of  $ZnO_x$  vapor have the great influence on the morphology of crystal. At low flow rate of oxygen gas, the relatively low supply of  $ZnO_x$  vapor and the decrease of nucleate rate may lead to an epitaxial growth of columniform nanorods with a conic tip from the surface of nanowires due to the thermodynamical equilibrium process of long time. At high flow rate of oxygen gas, however, the growth of ZnO nanorods might be kinetically controlled, since the growth rate of [0001] direction depends on the oxygen partial pressure to a different extent [111]. As a result, the hexagon-shaped nanorods grow preferentially along [0001] orientation. In addition, the variety of the oxygen supply has a great effect on the width and length of ZnO nanorods growing on nanowires or nanotubes. The increasing oxygen flow rate leads to the enhancement of  $ZnO_x$  concentration, which can promote the increase of nanorod width and length. Nevertheless, when the oxygen flow rate is too high, the high oxygen supplementation quickly oxidizes the surface of Zn powder into ZnO, preventing the further evaporation of Zn, and consequently, the prepared sample at high oxygen supply shows the shortest length of nanorods.

The above observations suggest the following formation mechanism of the oxygencontrolled hierarchical ZnO nanostructures. When Zn nanowires with little oxidation were evaporated at 500°C without Zn source, the hexagonal ZnO nanotubes will be formed because of the sublimation of the remaining Zn inside the nanowires, as shown in the Schema (c) of Figure 10(b) and FE-SEM image in Figure 12(e). At low oxygen concentration, the yielded Zn and ZnO<sub>x</sub> ( $x \le 1$ ) molecules or nanoclusters by heating Zn source are transported to the substrate by the carrier gas, forming  $ZnO_{x}$  nucleation on the nanowire's surface. With a continuous supply of  $ZnO_x$ , ZnO nanorods epitaxially grow from the nanowire surface. In the meantime, Zn inside the nanowires sublimates and forms hexagonal ZnO nanotubes. Consequently, the ZNSWN nanostructure of the Schema (d) of Figure 10(b) and FE-SEM image in Figure 12(b) can be expected. With the further increase of the oxygen flow rate, the increasing oxygen concentration in the quartz tube will quickly oxidize the surface of nanowires into ZnO and prevent the formation of nanotubes, resulting in the nanostructure of nanowires surrounded by well-ordered nanorods as shown in the Schema (e) of Figure 10(b) and FE-SEM image in Figure 13(b'). At high flow rate of oxygen gas, the high concentration  $ZnO_{r}$  can lead to the formation of non-ordered hexagonal nucleation at the initial stage. With continuous supplementation of  $ZnO_x$  gases, the non-ordered ZnO nanorods with a regular hexagon cross-section grow along the preferential [0001] direction from the surface of nanowires to form the nanostructure of the Schema f of Figure 10(b) and FE-SEM image in Figure 13(c').

The morphology of the hierarchical ZnO nanostructures can also be modulated by changing the evaporation time. Figures 13(d–f) show the FE-SEM images of the ZNSWN samples experienced 20, 50, and 80 min in the step-two stage, respectively. It is clear that, with the increase of reaction time, the length of nanorods increases from  $\sim$ 50 to 250 nm, demonstrating the nucleation, absorption, and growth process, which as a whole increases the length of the nanorods. The variation of nanorods in Figures 13(d–f) suggests that the length of nanorods can be controlled by adjusting the reaction time (growth rate of  $\sim$ 3 nm min<sup>-1</sup>), with the nanotube hexagonal cross sections remaining unchanged.

#### 3.3. Structural and Optical Properties of Hierarchical ZnO Nanostructures

XRD, PL, and Raman measurements could provide different perspectives to gain more insight into the structural information and optical properties of the fabricated hierarchical ZnO nanostructures with controllable morphology. Figure 14(a) shows the XRD spectra of the hierarchical ZnO samples under different flow rate ratios of argon and oxygen gases (Curves (a): 260:60, (b): 260:90, and (c): 260:120) and heating times (Curves (d): 20 min, (e): 50 min, and (f): 80 min). The observed wurtzite ZnO diffraction peaks indicate that the step-one samples as the substrates are oxidized into ZnO at the second step due to the relatively high substrate temperature (~500°C). However, it is found that the sample synthesized at the heating time of 20 min (Curve (d)) exhibits not only strong ZnO diffraction peaks but also weak Zn ones, suggesting that little heating time cannot



**Figure 14.** (a) XRD, (b) PL, and (c) Raman spectra of the prepared hierarchical ZnO nanostructures at step two under the heating time of 80 min with different ratios of argon flow rate and oxygen one, a:  $Ar:O_2 = 260:60$ , b:  $Ar:O_2 = 260:90$ , and c:  $Ar:O_2 = 260:120$ ; ZNSWN nanostructures prepared at  $Ar:O_2 = 260:60$  by different heating times of d: 20 min, e: 50 min, and f: 80 min. Reprinted with permission from [99], D. H. Fan et al., *J. Phys. Chem.* C 111, 9116 (2007). © 2007, American Chemical Society; and from [110], D. H. Fan et al., *J. Nanosci. Nanotech.* 8, 6325 (2008). © 2008, American Scientific Publishers.

make it complete oxidization. Furthermore, the intensity of ZnO (002) peak increases gradually with the oxygen flow ratio and heating time, revealing that the increase of oxygen supply and evaporating time can improve the crystal quality of the synthesized ZnO nanostructures [95].

Figure 14(b) displays the room-temperature PL spectra of these hierarchical ZnO nanostructures. Curves (a), (b), and (c) represent the PL spectra of the samples prepared at different oxygen flow rates. All spectra consist of UV peak (~388 nm) and green emission ( $\sim$ 510 nm). It is well-known that the UV peak originates from the recombination of FE and the visible emission is associated with structural defects [95]. The abundant surface/interface in ZnO nanostructures 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 [112]. With the increase of oxygen supplementation, the increasing nanorod size can lead to a small surface-to-volume ratio, which is expected to decrease the visible emission intensity. The improvement of crystal quality may also be a reason for the variation of peak intensity. The increase of intensity ratio of UV emission to visible peak with oxygen supplementation reveals that the optical properties can be modulated by the controllable morphology of ZnO nanostructures. The PL spectra of the prepared ZnO nanostructures under different heating times (Curves (d), (e), and (f)) also exhibit the similar results. With the increase of evaporation time, the decreasing intensity ratio of UV to visible emission indicates that the morphology of nanostructures will have a great effect on the optical properties.

Figure 14(c) shows Raman scattering results of these hierarchical ZnO nanostructures. All Raman spectra present two apparent ZnO phonon modes at 437 and 581 cm<sup>-1</sup>, which has been assigned to the  $E_2(high)$  and  $E_1(LO)$ , respectively [113]. With the increase of oxygen gas or heating time, the increase of  $E_2(high)$  intensity implies the better crystal quality [114]. This argument is consistent with the XRD and PL observation. It is generally accepted that  $E_1(LO)$  mode is associated with the oxygen vacancies [115]. The appearance of  $E_1(LO)$  mode reveals the existence of defects in the prepared samples. With increasing oxygen flow rate, the decrease of  $E_1(LO)$  intensity (Curves (a), (b), and (c)) indicates that high oxygen supply can decrease oxygen vacancies in the nanostructure, which leads to the increase of PL intensity ratio of the UV peak to the visible one in Figure 14(b). A similar conclusion can also be drawn from the variety of  $E_1(LO)$  intensity at the samples prepared under the different heating times (Curves (d), (e), and (f)). These experimental results clearly demonstrate that the change of oxygen flow rate and evaporating time can not only realize the controllable hierarchical ZnO nanostructures, but also modulate their optical properties for nanoscale electronic and optoelectronic device applications.

# 4. ZnO HOLLOW SPHERES AND ZnO-BASED CORE/SHELL STRUCTURES VIA CHEMICAL ROUTES

## 4.1. Template-Free Synthesis of ZnO Hollow Spheres

As discussed in Section 2.4, ZnO has three fast growth directions ([0001], [1010], and [2110]). As a result of different growth rates in various directions, spherical ZnO structure is not easily fabricated without the help of a spherical template. Fortunately, encapsulation of crystallization additives in solution has been shown to be able to control the nucleation and growth rate of crystals [116]. Tian et al. [117] have reported that a very small quantity of citrate ions slows crystal growth along the  $\langle 001 \rangle$  orientation, providing us a simple approach to control the aspect ratio (length-to-width) of the ZnO nanorods. On the basis of this concept, a template-free hydrothermal method has been demonstrated to synthesize large-scale ZnO hollow spheres [118]. The key points for the successful realization are that a high concentration of trisodium citrate is employed to control the nucleation and growth rate of ZnO crystal forming solid spheres with core/shell structures, and proper pH of an alkaline solution to remove the cores generating ZnO hollow spheres.

Figures 15(a–d) illustrate the whole processes, and the following reactions may be involved during these processes if one uses  $Zn(NO_3)_2$  and  $C_6H_{12}N_4$  as the  $Zn^{2+}$  and  $OH^-$  sources:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \tag{1}$$

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

$$Zn^{2+} + 2OH^{-} \leftrightarrow Zn(OH)_{2}$$
(3)

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O$$
 (4)

$$Zn(OH)_2 + 4NH_3 = (Zn(NH_3)_4)^{2+} + 2OH^{-}$$
(5)



**Figure 15.** Schema diagrams of the formation process of ZnO hollow spheres and ZnO-based core/shell structures. (a) Synthesis of  $Zn(OH)_2$  solid spheres. (b) Formation of  $Zn(OH)_2/ZnO$  spheres with core/shell structure. (c) Partial dissolution of the  $Zn(OH)_2$  cores in alkaline solution. (d) Formation of ZnO hollow spheres. Synthesis of (e) ZnO solid spheres, (f) ZnO/ZnS, (g) ZnO/Ag<sub>2</sub>S, (h) ZnO/CuS, and (i) ZnO/PbS core/shell spheres. Reprinted with permission from [118], Y. F. Zhu et al., *J. Phys. Chem. C* 111, 18629 (2007). © 2007, American Chemical Society.

Since a high concentration of trisodium citrate is used to control the nucleation and growth rate,  $Zn(OH)_2$  solid spheres are expected to be yielded (Fig. 15(a)) (Eqs. (1–3)). With the increase of reaction time, ZnO nanowires begin to form on the surface of  $Zn(OH)_2$  solid spheres via a process that involves dissolution of  $Zn(OH)_2$  and formation of ZnO by precipitation from solution (Eq. (4)) [119]. These ZnO nanowires bend and connect with each other on the surface of  $Zn(OH)_2$  cores forming ZnO shells, leading to the formation of solid spheres with a core/shell structure (Fig. 15(b)). If one transfers the solid spheres with core/shell structures into a solution contain a proper amount of ammonia. These Zn(OH)<sub>2</sub> cores in the spheres can be dissolved (Eq. (5)) (Figs. 15(c–d)).

The hydrothermal reaction solution for the synthesis of  $Zn(OH)_2/ZnO$  core/shell was prepared from aqueous solution containing 25-mM  $Zn(NO_3)_2 \cdot 6H_2O$ , 25-mM  $C_6H_{12}N_4$ , and 6.8-mM  $C_6H_5Na_3O_7 \cdot 2H_2O$ . After the clear solution was removed into a Pyrex glass bottle (the total volume of the reaction mixture was 40 mL), silicon substrates were put into the solution. After being sealed, the bottle was heated at 85°C for about 60 min in a conventional laboratory oven. In the second step, the silicon substrates with product on them were transferred into a Pyrex glass bottle containing 10-mM  $Zn(NO_3)_2 \cdot 6H_2O$ , 10-mM  $C_6H_{12}N_4$ , and 2.7-mM  $C_6H_5Na_3O_7 \cdot 2H_2O$ . The pH of the solution was adjusted to about 8 by adding drops of ammonia. After being sealed, the bottle was heated at 85°C again for another 15 to 60 min. The final product on the Si substrates was washed with deionized water repeatedly to remove any residual chemical salts and then dried under air atmosphere for characterization.

Figures 16(a and b) present the FE-SEM images of the as-prepared Zn(OH)<sub>2</sub>/ZnO core/shell spheres. From Figure 16(a), it is obvious that large-scale spheres can be obtained. The broken sphere in Figure 16(b) indicates that the as-prepared sphere has a core in it forming the core/shell structure. The hollow spheres are obtained subsequently by removing the cores without affecting the spherical structure of the shells. The strategy is to transfer the as-prepared sample into a bottle containing a solution at pH = 8 with the other reactants almost unchanged. Figure 16(c) displays the morphology of the sample treated in the alkaline solution for 15 min, from which we can see that some of the shells have a partially opened mouth on them. These broken spheres clearly indicate that the cores in the spheres have been partially dissolved. When the reaction time is increased to 60 min, all the cores in the spheres were removed, as shown in Figure 16(d). The hollow nature of the spheres is clearly depicted via the partially opened spheres. Although some of the spheres are still "closed," further evidence for the hollow structure can be found from the TEM image. As demonstrated in Figure 16(e), there is a strong contrast difference in all of the spheres with light inner center and relative dark edge, confirming that the obtained spheres are hollow. The inset of Figure 16(e) displays the SAED pattern of a hollow sphere, which reveals that they are in an amorphous state. During the TEM measurements, EDX analysis has also been performed. The result in Figure 16(f) indicates that the hollow spheres are mostly composed of Zn and O elements. The signal of Cu originates from the copper grid, while the C peak should come from carbon film on the Cu grid and impurity groups in the as-prepared spheres [118].

# 4.2. A General Chemical Conversion Route to Synthesize ZnO-Based Core/Shell Structures

The above concept for the realization of ZnO hollow spheres can be further employed to the synthesis of various semiconductor core/shell structures via chemical conversion on spherical templates. One can anneal the Zn(OH)<sub>2</sub>/ZnO solid spheres to form ZnO solid spheres, and use the ZnO solid spheres to react with thioacetamide (TAA) for the synthesis of ZnO/ZnS core/shell structures. Compared with the solubility product constant ( $K_{sp}$ ) of other metal sulfides, the  $K_{sp}$  of ZnS is relatively higher ( $K_{sp}$  of ZnS is 2.93 × 10<sup>-25</sup>, while  $K_{sp}$  of Ag<sub>2</sub>S is 6.69 × 10<sup>-50</sup>,  $K_{sp}$  of CuS is 1.27 × 10<sup>-36</sup>, and  $K_{sp}$  of PbS is 9.04 × 10<sup>-29</sup>) [120]. Therefore, the obtained ZnO/ZnS core/shell structures can be used as templates to realize other ZnO-based core/shell structures. A general chemical



**Figure 16.** FE-SEM images of (a, b)  $Zn(OH)_2/ZnO$  core/shell spheres, (c)  $Zn(OH)_2/ZnO$  core/shell structures with the  $Zn(OH)_2$  cores partially dissolved in alkaline solution, and (d) ZnO hollow spheres. (e) TEM image of ZnO hollow spheres, with the SAED pattern shown in the inset. (f) EDX spectrum of the ZnO hollow spheres. Reprinted with permission from [118], Y. F. Zhu et al., *J. Phys. Chem. C* 111, 18629 (2007). © 2007, American Chemical Society.

conversion route to synthesize various ZnO-based core/shell structures has been realized [121], with the whole processes shown schematically in Figures 15(b, e–i).

Two different solutions were used to synthesize spherical structures with different sizes. One solution was prepared from aqueous solution containing 5-mM  $Zn(NO_3)_2$ .  $6H_2O_1$ , 5-mM  $C_6H_{12}N_4$ , and 1.36-mM  $C_6H_5Na_3O_7 \cdot 2H_2O_2$ . The other solution was prepared using the same reactant but with higher concentration; i.e., 25-mM  $Zn(NO_3)_2 \cdot 6H_2O$ , 25-mM  $C_6H_{12}N_4$ , and 6.8-mM  $C_6H_5Na_3O_7 \cdot 2H_2O$ . With the same procedures as in Section 4.1, the  $Zn(OH)_2/ZnO$  solid spheres were obtained by heating the solutions at 90°C for about 50 min. Pure ZnO solid spheres were prepared by further annealing the yielded Zn(OH)<sub>2</sub>/ZnO products at 400°C under an air atmosphere for 120 min before they were used for the next step chemical reaction. Figures 17(a and b) display the FE-SEM images of the prepared ZnO solid spheres with different sizes. The sizes of the spheres could be controlled by changing the concentration of precursor solution during the fabrication process. The EDX spectrum shown in Figure 17(d) indicates that the obtained spheres are composed of Zn and O elements. This controllable synthesis of ZnO spheres provides the possibility of preparing ZnO-based core/shell structures with different sizes, and in the following the ZnO solid spheres with large sizes (Fig. 17(b)) is employed to realize various ZnO-based core/shell structures.

The key attempt is to synthesize ZnO/ZnS core/shell structures for the further realization of other ZnO-based core/shell spheres. The obtained ZnO solid spheres are



**Figure 17.** FE-SEM images of (a, b) ZnO solid spheres with different sizes, and (c) ZnO/ZnS core/shell structured spheres. EDX spectra of (d) ZnO solid spheres and (e) ZnO/ZnS core/shell spheres. (f) XRD patterns of ZnO solid spheres (Curve (a)) and ZnO/ZnS core/shell spheres (Curve (b)).

transferred into a solution containing 0.2-M TAA to make the conversion of ZnO solid spheres into ZnO/ZnS core/shell spheres. The TAA solution provides sulfide ions to react with zinc ions dissolved from the ZnO spheres for forming ZnS. During the reaction process, the solution temperature was kept constant at 90°C. Figure 17(c) displays the FE-SEM image of the ZnO/ZnS core/shell structured spheres. Although no significant changes were observed in comparison with the morphology of the prepared ZnO solid spheres in Figure 17(b), the compositional information of the EDX spectrum in Figure 17(e) exhibits the presence of Zn, O, and S elements, providing powerful evidence for the successful incorporation of S element into the ZnO spheres. XRD characterization can clearly demonstrate the crystal structure and transformation process of these spheres. Curves (a) and (b) in Figure 17(f) represent the diffraction patterns of ZnO (shown in Fig. 17(b)) and ZnO/ZnS (Fig. 17(c)) spheres, respectively. From Curve (a), it can be clearly observed that only the peaks corresponding to the hexagonal ZnO [JCPDF No. 36-1451] are detected, confirming that the spheres before reacting with TAA solution consist of pure polycrystalline ZnO. The diffraction peaks of cubic ZnS [JCPDF No. 05-0566] appear after the ZnO solid spheres treated in the TAA solution (Curve (b)), indicating the formation of a thin layer of ZnS on the ZnO spheres.

The present chemical conversion method suggests that spherical or other suitably shaped objects composed of reactive material can act as both reactants and templates to synthesize core/shell structures, i.e., this chemical approach can be extended to the synthesis of other ZnO-based core/shell spheres. ZnO/Ag<sub>2</sub>S, ZnO/CuS, and ZnO/PbS core/shell spheres have been successfully synthesized along with the above proposal by transferring the prepared ZnO/ZnS core/shell structured sphere templates into aqueous solutions containing Ag<sup>+</sup>, Cu<sup>2+</sup>, and Pb<sup>2+</sup>, respectively [121]. Figures 18(a–c) show the

FE-SEM images of the as-prepared ZnO/Ag<sub>2</sub>S, ZnO/CuS, and ZnO/PbS core/shell spheres. It is noted that the morphology of the starting material (Fig. 17(c)) is preserved during the reaction process. The temperature of the aqueous solutions used in this procedure was also kept at around 90°C to accelerate the reaction process. A color change of ZnO/ZnS spheres has been observed right after immersing them into the above-mentioned solutions, indicating the formation of new products. After the chemical reaction is finished, XRD measurements have also been performed to identify the microstructural modifications. Figure 18(d) presents the diffraction patterns of the yielded core/shell spheres, together with that of the pure ZnO solid spheres for comparison. It is obvious that in addition to the hexagonal ZnO structure [[CPDF No. 36-1451], diffraction peaks originating from monoclinic Ag<sub>2</sub>S [JCPDF No. 14-0072], hexagonal CuS [JCPDF No. 06-0464], and cubic PbS [JCPDF No. 05-0592] also clearly appear, confirming that the reaction products are ZnO/Ag<sub>2</sub>S, ZnO/CuS, and ZnO/PbS core/shell spheres, respectively.

### 4.3. Optical Properties of ZnO Hollow Spheres and ZnO/ZnS Core/Shell Structures

During the preparation of ZnO hollow spheres, a high concentration of trisodium citrate was employed to control the nucleation and growth rate of ZnO crystal for producing spherical structures. Therefore, the citric acid ions may form impurity groups in the as-prepared spheres. Fourier transform infrared absorption measurement has been carried out to gain more information about the composition of the as-prepared ZnO hollow spheres. Figure 19(a) displays the room-temperature infrared absorption spectrum of the as-prepared ZnO hollow spheres. Such a spectrum can be used to identify the functional

-CH2-C groups presented in the prepared samples. In the citrate groups,

(d)

C-CH-

PbS ٠ CuS ¥ Ag,S



Figure 18. FE-SEM images of (a) ZnO/Ag<sub>2</sub>S, (b) ZnO/CuS, and (c) ZnO/PbS core/shell spheres. (d) XRD patterns of a: ZnO solid spheres, b: ZnO/Ag<sub>2</sub>S, c: ZnO/CuS, and d: ZnO/PbS core/shell spheres.



**Figure 19.** Room-temperature (a) infrared absorption spectra of the as-prepared and annealed ZnO hollow spheres, (b) Raman and (c) PL spectra of the annealed ZnO hollow spheres, (d) PL spectra of the ZnO solid spheres and ZnO/ZnS core/shell spheres. Reprinted with permission from [118], Y. F. Zhu et al., *J. Phys. Chem. C* 111, 18629 (2007). © 2007, American Chemical Society.

C=O and C-O bonds with the same C atom will average into two equivalent carbon-

oxygen bonds  $({}^{-C} {}^{-C} {}^{-C})$ . As discussed in Section 2.3, the strong coupling between the two equal bonds results in the COO<sup>-</sup> asym. str. vibration from 1558 to 1593 cm<sup>-1</sup> and relatively weak COO<sup>-</sup> sym. str. vibration from 1403 to 1455 cm<sup>-1</sup> [85, 86]. Therefore, the absorption bands at ~1570 and ~1420 cm<sup>-1</sup> in the as-prepared sample can easily be attributed to the COO<sup>-</sup> asym. and sym. str. vibration modes, respectively. In addition, the band at 1240 cm<sup>-1</sup> is due to C–O str. vibration, while another band appearing at 1300 cm<sup>-1</sup> can be ascribed to the twisting (twi.) mode of the methylene groups [122]. The infrared absorption spectrum indicates that the as-prepared ZnO hollow spheres do contain citrate impurities.

Generally speaking, annealing can decompose impurity groups in the sample and improve the crystal quality. Thermal treatment of the as-prepared ZnO hollow spheres was performed at 400°C under an air atmosphere for 120 min. Figure 19(a) also shows the room-temperature infrared absorption spectrum of the annealed ZnO hollow spheres. Except for the absorption peak at around 1100 cm<sup>-1</sup> due to the str. vibrations of Si–O–Si in the oxidized Si substrates [123], all the absorption bands corresponding to the citrate impurities disappear, clearly demonstrating that the impurities have been removed after the annealing process. The room-temperature Raman spectrum in Figure 19(b) exhibits the remarkable nonpolar optical phonon  $E_2$ (high) mode of ZnO at 437 cm<sup>-1</sup>, which is a typical Raman active branch of wurtzite ZnO. In addition to the 520 cm<sup>-1</sup> structure from the Si substrate, the other two very weak peaks at 332 and 581 cm<sup>-1</sup> correspond well to the ZnO multiple-phonon (Mp) scattering process and  $E_1$ (LO) mode, respectively [124, 125]. The appearance of the characteristic Raman peaks demonstrates that the annealed ZnO hollow spheres are of good crystalline wurtzite structure.

PL is a powerful tool to investigate the optical properties of the yielded novel semiconductor structures. Figure 19(c) presents the room-temperature PL spectrum of the annealed ZnO hollow spheres, which has a strong UV peak at 376 nm and a negligible green band. As discussed in Section 2.2, the UV emission originates from the recombination of free excitons in the near-band-edge of the wide bandgap ZnO. Although the origin of the broad visible luminescence is still under controversy due to its complexity, it is generally believed that the green emission comes from the recombination of a photogenerated hole with the singly ionized oxygen vacancy [64]. The strong narrow UV peak and the negligible green band in the PL spectrum also indicate the high optical quality of the annealed ZnO hollow spheres.

As mentioned in the introduction section, the core/shell structured materials usually show improved physical and chemical properties. Figure 19(d) shows the roomtemperature PL of the ZnO solid spheres and ZnO/ZnS core/shell spheres to show the improved optical properties of the prepared ZnO/ZnS core/shell spheres over their single components. The PL spectrum of ZnO solid spheres shows a strong UV emission peak at 377 nm and a negligible green band. The ZnO/ZnS core/shell spheres basically exhibit the PL behavior of the ZnO cores with a small redshift (~10 nm) in the UV region and a distinct enhancement in luminescence intensity. The redshift in the PL spectrum can be attributed to the strain caused by the lattice mismatch between ZnO and ZnS. Theoretical work has already predicted that the strain in the ZnO/ZnS interface is strong enough to reduce the total system bandgap [126]. In addition, a wider bandgap semiconductor material (ZnS) coated on the ZnO passivates the surface electronic states of the ZnO cores, resulting in an obvious enhancement in the PL intensity of UV emission. Such an enhancement in the emission has also been observed in the coaxial CdS/ZnS nanowires [127].

Finally, it should be noted that the previous reports reveal that the ZnO hollow and core/shell spheres prepared through the conventional methods contain a large number of oxygen vacancies resulting in a weak UV emission and a strong broad green emission [40–42, 47]. The PL observation in Figure 19(c) demonstrates that the ZnO hollow spheres obtained through the present method possess high optical quality with low oxygen vacancies. After coating a thin layer of ZnS on ZnO solid spheres, the intensity of UV emission enhances obviously in Figure 19(d). Therefore, these ZnO hollow and ZnO/ZnS core/shell spheres are more applicable for the fabrication of optoelectronic devices, such as UV light-emitting diodes and diode lasers.

#### 5. SUMMARY AND OUTLOOK

In this chapter, we have reviewed our recent development in the fabrication and characterization of ZnO and/or  $In_2O_3$  semiconductor nanostructures, mainly nanodot arrays, nanopore arrays, hierarchical nanostructures, and hollow spheres as well as core/shell structures. We have attempted to present a broad overview on the design, controllable synthesis, structural, and optical properties of a wide variety of such metal oxide nanostructures.

- (1) With simple tuning the PAM nanopore size and height through the change in anodization conditions, an effective approach has been demonstrated for fabricating ZnO nanodot arrays with controllable dot sizes and special In<sub>2</sub>O<sub>3</sub> "rods in nanodots" arrays with improved sheet density of In<sub>2</sub>O<sub>3</sub> nanorods over 10<sup>12</sup> cm<sup>-2</sup>. High-quality ZnO nanopore arrays with ordered hexagonal pattern have been proposed and realized by the aid of unique properties of ZnO (hexagonal structure, polar surfaces, and preferred growth directions) and PAMs (controllable hexagonal nanopores and localized negative charges). The versatile PAMs allow us to easily assemble the single-crystalline In<sub>2</sub>O<sub>3</sub> nanocolumns by the electrostatic attraction of the localized charges into well-designed In<sub>2</sub>O<sub>3</sub>"rods in nanopores" arrays.
- (2) Taking advantages of the controllable oxidation rate of Zn at different substrate temperatures below and above the Zn melting point, we have prepared the hierarchical pure ZnO nanostructures with controllable morphology by the two-step oxygen-controlled thermal evaporation method at low temperature without any catalysts. The Zn nanowires with little oxidation were firstly deposited on the Si substrate located at the low-temperature area at step one, the hierarchical ZnO

nanostructures were then synthesized at step two by evaporating the pure Zn powder and simultaneously heating the one-step-prepared samples. It is shown that the morphology of the hierarchical ZnO nanostructures can be well-controlled by changing the oxygen flow rate and evaporation time. PL results indicate that the optical properties can be modulated through controlling the morphology of the ZnO nanostructures, which indicates that the prepared hierarchical pure ZnO nanostructures can be potentially applied in nanoscale electronic and optoelectronic devices.

(3) A simple, low-temperature, efficient, environmentally benign, template-free hydrothermal method has been developed to realize the large-scale ZnO hollow spheres. The successful realization lies in the facts that we use high concentration of trisodium citrate to control the nucleation and growth rate of ZnO crystal for producing  $Zn(OH)_2/ZnO$  solid spheres with core/shell structure, and then remove subsequently the  $Zn(OH)_2$  cores by dissolving in a solution with pH = 8. The concept for the realization of ZnO hollow spheres has been further employed to the synthesis of various semiconductor core/shell structures via chemical conversion on spherical templates. ZnO solid spheres obtained through annealing the Zn(OH)<sub>2</sub>/ZnO solid spheres react with TAA for the synthesis of ZnO/ZnS core/shell structures, which can be used as templates to realize other high-quality ZnO-based core/shell structures, such as ZnO/Ag<sub>2</sub>S, ZnO/CuS, and ZnO/PbS. PL measurements have demonstrated that the annealed ZnO hollow spheres are of good crystalline wurtzite structure with high optical quality. Compared with the uncoated ZnO solid spheres, the UV emission of ZnO/ZnS core/shell spheres is dramatically enhanced, showing potential application in UV optoelectronic devices.

For the prospects of these three methods, it should be noted that the as-synthesized large-scale regular ZnO and  $In_2O_3$  nanodots and nanopore arrays by the aid of the PAM templates are yielded at a significant percentage (near 100%) without any other formation of ZnO and  $In_2O_3$ . These ZnO and  $In_2O_3$  nanostructures make them possible for the application of filters and sensors due to the large surface areas with polar charges. The ZnO and  $In_2O_3$  nanopore array layers can also be taken away intactly from the PAM surfaces to produce ZnO and  $In_2O_3$  templates. The crystalline semiconducting nanopores templates have great advantages over the amorphous PAMs, especially in the conductive and optical properties. Through epitaxial growth on the lattice planes, high-quality heterojunction nanostructures can even be fabricated using ZnO and  $In_2O_3$  templates. This approach provides a general way to fabricate similar nanostructures of various other semiconductor oxides and nitrides with polar surfaces. Therefore, the present PAM-aided technique might be of great importance for future metal oxide nanodevice applications with the advantages of technological simplicity, industrialization, robustness, as well as without the necessity of catalysts.

Furthermore, the idea of employing the controllable oxidation rate of metal at temperatures below and above the metal melting point in the simple two-step thermal evaporation approach can not only integrate single ZnO nanostructures into controlled hierarchical ones, but also realize the assembly of other semiconductor nanostructures. It is also possible to fabricate hetero-nanostructures by assembling materials such as  $In_2O_3$  or CdO nanorods on ZnO nanotubes by evaporating In or Cd powder under suitable temperature at the second stage. The successful preparation of those complicated metal-oxide nanostructures would greatly broaden the potential applications of nanostructures in novel nanodevices.

Finally, it is reasonable to assume that more ZnO-based core/shell structures can be realized through transferring the ZnO/ZnS core/shell structured sphere templates into aqueous solutions containing other metal cations under the condition that those yielded metal sulfides have lower  $K_{sp}$  than that of ZnS. Since core/shell structures usually show improved physical and chemical properties compared with their individual materials, these ZnO-based core/shell structures may find broader application in optoelectronic, photocatalytic, and photovoltaic devices than those of pure ZnO structures. We can

also expect that the concept of chemical conversion can be employed to prepare other semiconductor core/shell structures with various geometrical shapes. For example, FeS has even larger  $K_{sp}$  (1.59 × 10<sup>-19</sup>) compared with ZnS, synthesis of various FeS-based core/shell structures (including FeS/ZnS, FeS/Ag<sub>2</sub>S, FeS/CuS, etc.) may be possible by using different FeS nanostructures (e.g., nanowires, nanorods, nanospheres, etc.) as templates. Therefore, the present chemical conversion process is a general, facile, and economic way to synthesize semiconductor core/shell structures with various compositions and geometries for novel and unique properties.

# ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China under contracts 10734020 and 10674094, National Major Basic Research Project of 2006CB921507, National Minister of Education Program of IRT0524, and Shanghai Municipal Key Project of 08XD14022.

### REFERENCES

- 1. S. Kara, M. R. Pafall, W. H. Rippard, T. J. Silva, S. E. Russek, and J. A. Katine, Nature 437, 389 (2005).
- 2. M. Law, D. J. Sirbuly, J. C. Johnson, J. Goldberger, R. J. Saykally, and P. D. Yang, Science 305, 1269 (2004).
- 3. Z. H. Zhong, D. L. Wang, Y. Cui, M. W. Bockrath, and C. M. Lieber, *Science* 302, 1377 (2003).
- 4. K. Liu, J. Nogués, C. Leighton, H. Masuda, K. Nishio, I. V. Roshchin, and I. K. Schuller, *Appl. Phys. Lett.* 81, 4434 (2002).
- 5. Y. W. Su, C. S. Wu, C. C. Chen, and C. D. Chen, Adv. Mater. 15, 49 (2003).
- 6. P. E. Sheehan, L. J. Whitman, W. P. King, and B. A. Nelson, Appl. Phys. Lett. 85, 1589 (2004).
- 7. R. D. Piner, J. Zhu, F. Xu, S. H. Hong, and C. A. Mirkin, Science 283, 661 (1999).
- 8. R. S. Friedman, M. C. McAlpine, D. S. Ricketts, D. Ham, and C. M. Lieber, Nature 434, 1085 (2005).
- J. Hone, M. C. Liaguno, N. M. Nemes, A. T. Johnson, J. E. Fischer, D. A. Walters, M. J. Casavant, J. Schmidt, and R. E. Smalley, *Appl. Phys. Lett.* 77, 666 (2000).
- 10. J. Goldberger, R. He, Y. F. Zhang, S. Lee, H. Q. Yan, H. J. Choi, and P. D. Yang, Nature 422, 599 (2003).
- 11. X. D. Wang, C. J. Summers, and Z. L. Wang, Nano Lett. 4, 423 (2004).
- K. A. Dick, K. Deppert, M. W. Larsson, T. Martensson, W. Seifert, L. R. Wallenberg, and L. Samuelson, Nat. Mater. 3, 380 (2004).
- 13. J. Q. Hu, Y. S. Bando, J. H. Zhan, X. L. Yuan, T. Sekiguchi, and D. Golberg, Adv. Mater. 17, 971 (2005).
- 14. Y. Wu, J. Xiang, C. Yang, W. Lu, and C. M. Lieber, Nature 430, 61 (2004).
- 15. S. Minko, A. Kiriy, G. Gorodyska, and M. Stanmm, J. Am. Chem. Soc. 124, 10192 (2002).
- 16. K. Keren, M. Krueger, R. Gilad, G. B. Yoseph, U. Sivan, and E. Braun, Science 297, 72 (2002).
- 17. M. G. Warner and J. E. Hutchison, Nat. Mater. 2, 272 (2003).
- H. A. Becerril, R. M. Stoltenberg, D. R. Wheeler, R. C. Davis, J. N. Harb, and A. T. Woolley, J. Am. Chem. Soc. 127, 2828 (2005).
- 19. M. H. Kim, S. K. Im, and O. O. Park, Adv. Funct. Mater. 15, 1329 (2005).
- 20. D. Wang and H. Möhwald, Adv. Mater. 16, 244 (2004).
- 21. P. D. Yang, Nature 425, 243 (2003).
- 22. S. Myung, M. Lee, G. T. Kim, J. S. Ha, and S. H. Hong, Adv. Mater. 17, 2361 (2005).
- 23. J. Y. Lao, J. Y. Huang, D. Z. Wang, and Z. F. Ren, Nano Lett. 3, 235 (2003).
- 24. P. X. Guo and Z. L. Wang, Appl. Phys. Lett. 84, 2883 (2003).
- 25. X. P. Gao, Z. F. Zheng, H. Y. Zhu, G. L. Pan, J. L. Bao, F. Wu, and D. Y. Song, Chem. Commun. 1428 (2004).
- 26. A. Umar, S. Lee, Y. H. Im, and Y. B. Hahn, Nanotechnology 16, 2462 (2005).
- 27. J. Y. Lao, J. G. Wen, and Z. F. Ren, Nano Lett. 2, 1287 (2002).
- 28. P. X. Gao and Z. L. Wang, J. Phys. Chem. B 106, 12653 (2002).
- 29. F. Xu, K. Yu, M. R. Shi, Q. Y. Wang, Z. Q. Zhu, and S. H. Huang, J. Nanosci. Nanotechnol. 6, 3794 (2006).
- 30. F. Caruso, Adv. Mater. 13, 11 (2001).
- 31. J. Wang, K. P. Loh, Y. L. Zhong, M. Lin, J. Ding, and Y. L. Foo, Chem. Mater. 19, 2566 (2007).
- 32. L. J. Fu, H. Liu, H. P. Zhang, C. Li, T. Zhang, Y. P. Wu, R. Holze, and H. Q. Wu, *Electrochem. Commun.* 8, 1 (2006).
- 33. V. Salgueirino-Maceira, M. A. Correa-Duarte, M. Spasova, L. M. Liz-Marzan, and M. Farle, Adv. Funct. Mater. 16, 509 (2006).
- 34. Z. Liang, A. Susha, and F. Caruso, Chem. Mater. 15, 3176 (2003).
- X. Cheng, S. Liu, L. Lu, X. Sui, V. Meynen, P. Cool, E. F. Vansant, and J. Jiang, *Micro. Meso. Mater.* 98, 41 (2007).
- 36. H. Zhou, T. Fan, and D. Zhang, Micro. Meso. Mater. 100, 322 (2007).
- 37. S. Y. Gao, H. J. Zhang, X. M. Wang, R. P. Deng, D. H. Sun, and G. L. Zheng, J. Phys. Chem. B 110, 15847 (2006).

- 38. Y. Yang, Y. Chu, Y. P. Zhang, F. Y. Yang, and J. L. Liu, J. Solid State Chem. 179, 470 (2006).
- 39. P. X. Gao and Z. L. Wang, J. Am. Chem. Soc. 125, 11299 (2003).
- 40. G. Z. Shen, Y. Bando, and C. J. Lee, J. Phys. Chem. B 109, 10578 (2005).
- 41. H. B. Lu, L. Liao, J. C. Li, D. F. Wang, H. He, Q. Fu, L. Xu, and Y. Tian, J. Phys. Chem. B 110, 23211 (2006).
- 42. K. M. Sulieman, X. T. Huang, J. P. Liu, and M. Tang, Nanotechnology 17, 4950 (2006).
- 43. X. Wang, P. Gao, J. Li, C. J. Summers, and Z. L. Wang, Adv. Mater. 14, 1732 (2002).
- 44. T. Gao, Q. Li, and T. Wang, Chem. Mater. 17, 887 (2005).
- 45. W. W. Wang, Y. J. Zhu, and L. X. Yang, Adv. Funct. Mater. 17, 59 (2007).
- 46. S. K. Panda, A. Dev, and S. Chaudhuri, J. Phys. Chem. C 111, 5039 (2007).
- 47. J. Geng, B. Liu, L. Xu, F. N. Hu, and J. J. Zhu, Langmuir 23, 10286 (2007).
- 48. H. San, B. Jang, T. Kim, S. M. Oh, and T. Hyeon, Adv. Funct. Mater. 15, 1845 (2005).
- 49. X. W. Lou, Y. Wang, C. Yuan, J. Y. Lee, and L. A. Archer, Adv. Mater. 18, 2325 (2006).
- 50. H. Masuda, K. Yasui, and K. Nishio, Adv. Mater. 14, 1031 (2000).
- 51. J. Liang, H. Chik, A. Yin, and J. M. Xu, J. Appl. Phys. 91, 2544 (2002).
- 52. R. Zhu, Y. T. Pang, Y. S. Feng, G. H. Fu, Y. Li, and L. D. Zhang, Chem. Phys. Lett. 368, 696 (2003).
- 53. X. Y. Mei, M. Blumin, D. Kim, Z. H. Wu, and H. E. Ruda, J. Cryst. Growth 251, 253 (2003).
- 54. G. Q. Ding, W. Z. Shen, M. J. Zheng, W. L. Xu, Y. L. He, and Q. X. Guo, J. Cryst. Growth 283, 339 (2005).
- 55. H. Chik and J. M. Xu, Mater. Sci. Eng. R 43, 103 (2004).
- 56. K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspon, and U. Gösele, Nano Lett. 2, 677 (2002).
- 57. X. Mei, D. Kim, H. E. Ruda, and Q. X. Guo, Appl. Phys. Lett. 81, 361 (2002).
- 58. H. Masuda and K. Fukuda, Science 268, 1466 (1995).
- 59. G. Q. Ding, M. J. Zheng, W. L. Xu, and W. Z. Shen, Nanotechnology 16, 1285 (2005).
- 60. G. Patermarakis and K. Moussoutzanis, Electrochim. Acta 40, 699 (1995).
- 61. W. L. Xu, M. J. Zheng, G. Q. Ding, and W. Z. Shen, Chem. Phys. Lett. 411, 37 (2005).
- 62. W. Lee, M.-C. Jeong, and J.-M. Myoung, Appl. Phys. Lett. 85, 6167 (2004).
- C. Geng, Y. Jiang, Y. Yao, X. Meng, J. A. Zapien, C. S. Lee, Y. Lifshitz, and S. T. Lee, *Adv. Funct. Mater.* 14, 589 (2004).
- 64. K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, and B. E. Gnade, J. Appl. Phys. 79, 7983 (1996).
- 65. Y. X. Liu, Y. C. Liu, C. L. Shao, and R. Mu, J. Phys. D: Appl. Phys. 37, 3025 (2004).
- 66. D. W. Hamby, D. A. Lucca, M. J. Klopfstein, and G. Cantwell, J. Appl. Phys. 93, 3214 (2003).
- 67. G. Q. Ding, W. Z. Shen, M. J. Zheng, and Z. B. Zhou, Appl. Phys. Lett. 89, 063113 (2006).
- 68. W. S. Seo, H. H. Jo, K. Lee, and J. T. Park, Adv. Mater. 15, 795 (2003).
- 69. A. Murali, A. Barve, V. J. Leppert, S. H. Risbud, I. M. Kennedy, and H. W. H. Lee, Nano Lett. 1, 287 (2002).
- P. Nguyen, H. T. Ng, J. Kong, A. M. Cassell, R. Quinn, J. Li, J. Han, M. McNeil, and M. Meyyappan, Nano Lett. 3, 925 (2003).
- 71. J. Y. Lao, J. Y. Huang, D. Z. Wang, and Z. F. Ren, Adv. Mater. 16, 65 (2004).
- 72. C. H. Liang, G. W. Meng, Y. Lei, F. Phillipp, and L. D. Zhang, Adv. Mater. 13, 1330 (2001).
- 73. Z. W. Pan, Z. R. Dai, and Z. L. Wang, Science 291, 1947 (2001).
- 74. Y. B. Li, Y. Bando, and D. Golberg, Adv. Mater. 15, 581 (2003).
- 75. P. Guha, S. Kar, and S. Chaudhuri, Appl. Phys. Lett. 85, 3851 (2004).
- 76. Y. Ohhata, F. Shinoki, and S. Yoshida, Thin Solid Films 59, 255 (1979).
- 77. F. Y. Li, L. Zhang, and R. M. Metzger, Chem. Mater. 10, 2470 (1998).
- 78. Y. Xu, G. E. Thompson, G. C. Wood, and B. Bethune, Corrosion Sci. 27, 83 (1987).
- 79. P. P. Mardilovich, A. N. Govyadinov, and N. I. Mukhurov, J. Membrane Sci. 98, 131 (1995).
- 80. Y. Yamamoto, N. Baba, and S. Tajima, Nature 289, 572 (1981).
- 81. W. L. Xu, M. J. Zheng, S. Wu, and W. Z. Shen, Appl. Phys. Lett. 85, 4364 (2004).
- 82. J. Choi, Y. Luo, R. B. Wehrspohn, R. Hillebrand, J. Schilling, and U. Gösele, J. Appl. Phys. 97, 4757 (2003).
- 83. G. Q. Ding, W. Z. Shen, M. J. Zheng, and D. H. Fan, Appl. Phys. Lett. 88, 103106 (2006).
- 84. D. H. Fan, G. Q. Ding, W. Z. Shen, and M. J. Zheng, Micro. & Meso. Mater. 100, 154 (2007).
- 85. Y. Omura, Spectroc. Acta Pt. A 54, 507 (1998).
- 86. M. Mizuguchi, M. Nara, K. Kawano, and K. Nitta, FEBS Lett. 417, 153 (1997).
- 87. T. Gao, G. W. Meng, and L. Zhang, J. Phys.: Condens. Matter 15, 2071 (2003).
- 88. H. Chen, M. H. Gullanar, and W. Z. Shen, J. Cryst. Growth 260, 91 (2004).
- 89. S. Nakamura, M. Saito, L. F. Huang, M. Miyagi, and K. Wada, Jpn. J. Appl. Phys. 31, 3589 (1992).
- 90. X. Y. Kong, Y. Ding, R. S. Yang, and Z. L. Wang, Science 303, 1348 (2004).
- 91. E. Mirica, G. Kowach, P. Evans, and H. Du, Cryst. Growth Des. 4, 147 (2004).
- 92. Y. Zhang, H. B. Jia, R. M. Wang, C. P. Chen, X. H. Luo, D. P. Yu, and C. L. Lee, *Appl. Phys. Lett.* 83, 4631 (2003).
- 93. G. J. Exarhos and S. K. Sharma, *Thin Solid Films* 270, 27 (1995); X. L. Xu, S. P. Lau, J. S. Chen, G. Y. Chen, and B. K. Tay, *J. Cryst. Growth* 223, 201 (2001).
- 94. M. Saito, M. Shibasaki, S. Nakamura, and M. Miyagi, Opt. Lett. 19, 710 (1994).
- 95. D. H. Fan, Z. Y. Ning, and M. F. Jiang, Appl. Surf. Sci. 245, 414 (2005).
- 96. G. Q. Ding, W. Z. Shen, M. J. Zheng, and Z. B. Zhou, Nanotechnology 17, 2590 (2006).
- H. B. Jia, Y. Zhang, X. H. Chen, J. Shu, X. H. Luo, Z. S. Zhang, and D. P. Yu, *Appl. Phys. Lett.* 82, 4146 (2003).
- 98. A. K. Kulkarni, K. H. Schulz, T. S. Lim, and M. Khan, Thin Solid Films 308-309, 1 (1997).

- 99. D. H. Fan, W. Z. Shen, M. J. Zheng, and Y. F. Zhu, J. Phys. Chem. C 111, 9116 (2007).
- 100. W. I. Park, D. H. Kim, S. W. Jung, and G. C. Yi, Appl. Phys. Lett. 80, 4232 (2002).
- 101. J. J. Wu and S. C. Liu, J. Phys. Chem. B 106, 9546 (2002).
- 102. D. F. Liu, Y. J. Xiang, Z. X. Zhang, J. X. Wang, Y. Gao, L. Song, L. F. Liu, X. Y. Dou, X. W. Zhao, S. D. Luo, C. Y. Wang, W. Y. Zhou, G. Wang, and S. S. Xie, *Nanotechnology* 16, 2665 (2005).
- 103. W. C. Elliott, P. F. Miceli, T. Tse, and P. W. Stephens, Phys. Rev. B 54, 17938 (1996).
- 104. J. B. Baxter, F. Wu, and E. S. Aydil, Appl. Phys. Lett. 83, 3797 (2003).
- 105. J. Q. Hu and Y. Bando, Appl. Phys. Lett. 82, 1401 (2003).
- 106. H. J. Fan, R. Scholz, F. M. Kolb, and M. Zacharias, Appl. Phys. Lett. 85, 4142 (2004).
- 107. P. X. Gao, C. S. Lao, Y. Ding, and Z. L. Wang, Adv. Funct. Mater. 16, 53 (2006).
- 108. Z. L. Wang, X. Y. Kong, and J. M. Zuo, Phys. Rev. Lett. 91, 185502 (2003).
- 109. X. L. Zhang and Y. S. Kang, Inorg. Chem. 45, 4186 (2006).
- 110. D. H. Fan, Y. F. Zhu, and W. Z. Shen, J. Nanosci. Nanotechnol. 8, 6325 (2008).
- 111. H. Q. Yan, R. He, J. Pham, and P. D. Yang, Adv. Mater. 15, 402 (2003).
- 112. Y. H. Tong, Y. C. Liu, C. L. Shao, and R. X. Mu, Appl. Phys. Lett. 88, 123111 (2006).
- 113. R. P. Wang, G. Xu, and P. Jin, Phys. Rev. B 69, 113303 (2004).
- 114. G. W. Cong, H. Y. Wei, P. F. Zhang, J. J. Peng, X. L. Liu, C. M. Jiao, W. G. Hu, Q. S. Zhu, and Z. G. Wang, *Appl. Phys. Lett.* 87, 231903 (2005).
- 115. H. Pan, J. Z. Luo, H. Sun, Y. P. Feng, C. Poh, and J. Y. Jing, Nanotechnology 17, 2963 (2006).
- 116. W. S. Wang, L. Zhen, C. Y. Xu, B. Y. Zhang, and W. Z. Shao, Chem. Mater. 18, 3557 (2006).
- 117. Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, M. J. Mcdermott, R. T. Cygan, and L. J. Criscenti, *Nat. Mater.* 2, 821 (2003).
- 118. Y. F. Zhu, D. H. Fan, and W. Z. Shen, J. Phys. Chem. C 111, 18629 (2007).
- 119. R. A. McBride, J. M. Kelly, and D. E. McCormack, J. Mater. Chem. 13, 1196 (2003).
- R. C. Weast, (Ed.), "CRC Handbook of Chemistry and Physics," 69th edn. CRC Press, Boca Raton, Florida, 1988–1989.
- 121. Y. F. Zhu, D. H. Fan, and W. Z. Shen, J. Phys. Chem. C 112, 10402 (2008).
- 122. B. H. Stuart, "Infrared Spectroscopy: Fundamentals and Applications," Chap. 4. John Wiley and Sons, Ltd., 2004.
- 123. X. Y. Chen, W. Z. Shen, H. Chen, R. Zhang, and Y. L. He, Nanotechnology 17, 595 (2006).
- 124. B. Q. Cao, W. P. Cai, H. B. Zeng, and G. T. Duan, J. Appl. Phys. 99, 073516 (2006).
- 125. N. Ashkenov, B. N. Mbenkum, C. Bundesmann, V. Riede, M. Lorenz, D. Spemann, E. M. Kaidashev, A. Kasic, M. Schubert, M. Grundmann, G. Wagner, H. Neumann, V. Darakchieva, H. Arwin, and B. Monemar, J. Appl. Phys. 93, 126 (2003).
- 126. J. Schrier, D. O. Demchenko, and L. W. Wang, Nano Lett. 7, 2377 (2007).
- 127. A. Datta, S. K. Panda, and S. Chaudhuri, J. Phys. Chem. C 111, 17260 (2007).