Influence of Temperature on Evolution of Coaxial ZnO/Al₂O₃ One-Dimensional Heterostructures: From Core–Shell Nanowires to Spinel Nanotubes and Porous Nanowires

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In this paper, we present the influence of temperature on the Kirkendall effect-related evolution of coaxial ZnO/Al₂O₃ one-dimensional heterostructures based on a solid-state reaction. Controllable fabrication of spinel ZnAl₂O₄-based nanotubes and porous nanowires can step-by-step be achieved from ZnO/Al₂O₃ core–shell nanowires with a change in the reaction temperature. In particular, we demonstrate that the formation of completely hollow nanotubes in this system is not strictly limited to a fixed stoichiometry of ZnO/Al₂O₃ required for the spinel-forming reaction when an annealing temperature of 800 °C is employed. Combined with atomic layer deposition, the wall thickness of the formed nanotubes can be further precisely tailored and defined. Our finding provides an effective route to fabricate spinel nanotubes as well as nanotube arrays on a large scale.

1. Introduction

Tubular nanostructures have attracted considerable attention due to their potential application in electronics, optoelectronics, catalysis, and controlled release. To be able to meet such suitable applications, nanotubes of a wide range of solids including carbon, metals, semiconductors, and/or insulators have been fabricated.¹ Until now, a variety of routes has been developed for the fabrication of nanotubes, where the most widely applied are vapor-phase synthesis using a catalyst,²,³ template-based methods,⁴,⁵ and thin-film rolling.⁶ Recently, our group reported a new approach to produce tubular nanostructures such as spinel ZnAl₂O₄ nanotubes, where a thermally induced interfacial solid–solid reaction of ZnO/Al₂O₃ core–shell nanowires can directly be used to fabricate single-crystalline ZnAl₂O₄ nanotubes based on the Kirkendall effect.⁷ Similar phenomena toward hollow nanospheres have been demonstrated by other groups. Alivisatos et al. first reported the preparation of hollow CoS nanoparticles by the sulfidation of Co nanoparticles in solution based on the Kirkendall effect.⁸ The Kirkendall effect is a classical phenomenon in metallurgy. Initially, it describes a nonequilibrium mutual diffusion process through an interface of two bulk materials accompanied by the simultaneous occurrence of a vacancy diffusion to compensate for the unequal material flow. Voids can be formed at the interface as a result of condensation of excess vacancies. Since nanoscale systems involve a spatial confinement, high surface-to-volume ratios, and greater crystalline perfection relative to the bulk counterparts, void formation can be enhanced due to a more localized vacancy supersaturation. After a net material flux across the interface by a preferred outward diffusion, a single void is possible that can be supported at the center of the nanoscale materials. Such a concept of the nanoscale Kirkendall effect provides the methodology for producing hollow nanostructures composed of different compounds,¹⁰–¹⁵ as also was outlined in a recent review article.¹⁶

Moreover, continuous interest in the nanoscale Kirkendall effect has initiated new experimental findings of the influence of the surface diffusion on the formation of hollow ZnAl₂O₄ nanostructures.¹⁷ Derived from the available experimental results, an ideal size parameter was also proposed for the formation of completely hollow nanotubes. For instance, if a 10 nm-thick alumina shell is grown by atomic layer deposition (ALD), a critically narrow thickness range of 10–15 nm for the ZnO nanowire core is indispensable for achieving the complete transformation from core–shell structures to nanotubes at an annealing temperature of 700 °C.¹⁷ However, first of all, preparing ZnO nanowires with a uniform diameter is still a challenge, and second, the reliability of the whole process on temperature is still unknown. Therefore, if one desires the fabrication of spinel nanotubes on a large scale, the careful examination of this process and its dependence on core–shell ratios as well as reaction (diffusion) temperatures is necessary.

In this study, we investigated the dynamic morphology evolution of ZnO/Al₂O₃ core–shell nanowires by controlling the synthesis temperature. On the basis of the previous findings of the Kirkendall effect and the surface diffusion effect on the production of ZnAl₂O₄ spinel nanotubes from a ZnO/Al₂O₃ core–shell structure, we attempted to present a clear portrait of the diffusion processes that accompanies the chemical transformations under different temperatures. In contrast to the results our group described before, it was found for the first time that the formation of a completely hollow spinel nanotube is not strictly limited to a constant stoichiometry of ZnO/Al₂O₃ core–shell structures at a higher reaction temperature of 800 °C. A further increase of the temperature to 900 °C led to the formation of porous nanowires. Besides the clarification of the related mechanism, we extend this synthetic method to epitaxially grown ZnO nanowires to produce arrays of spinel nanotubes under optimal conditions.

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2. Experimental Procedures

2.1. Methods. ZnO nanowires with various diameters were grown by a vapor transport method using Au nanoparticles as the catalyst. Detailed experimental conditions have been described previously.18 For the epitaxial growth of ZnO nanowires, GaN/Si was used as a substrate, on which a thin Au film was deposited as the catalyst. Subsequently, the ZnO/Al2O3 core–shell nanowires were fabricated by depositing thin Al2O3 films on the as-prepared ZnO nanowires by ALD (Savannah 100, Cambridge Nanotechnology Inc.). Trimethylaluminum [Al(CH3)3, TMA] and water were selected as the aluminum precursor and oxygen reactant sources, respectively. The deposition was begun with a substrate temperature of 150 °C and a background pressure of 0.15 Torr. During each deposition cycle, TMA and water were alternately introduced into the ALD chamber in pulses of 0.3 and 1.3 s, respectively. An exposition time of 20 s and a successive purge time of 20 s under an Ar stream (10 sccm) were employed for both precursors. The time of 20 s and a successive purge time of 20 s under an Ar chamber in pulses of 0.3 and 1.3 s, respectively. An exposition time of 20 s and a successive purge time of 20 s under an Ar stream (10 sccm) were employed for both precursors.

2.2. Instruments. The obtained nanostructures were characterized and analyzed using SEM (JEOL, JSM-6300F), TEM (JEOL, JEM-1010; Philips, CM20T), and high-resolution TEM (JEOL, JEM-4010). Scanning energy-dispersive X-ray spectra were obtained using a Philips CM20FEG scanning TEM instrument.

3. Results and Discussion

3.1. Formation of ZnO/Al2O3 Core–Shell Nanowires. First, we investigated the deposition of Al2O3 layers on ZnO nanowires. Figure 1a is a SEM image of the ZnO nanowires coated with a thin layer of Al2O3 by using 66 ALD cycles. The core–shell nanowires have a broad size distribution, with diameters ranging from 40 to 200 nm. TEM investigation (Figure 1b) shows an individual ZnO nanowire (dark contrast) covered by a layer of amorphous Al2O3 (light contrast). The Al2O3 layer has a very uniform thickness of 10.3 nm along the ZnO nanowire. The precise control of the shell thickness is attributed to the sequential and self-limiting ALD process, which avoids any gas-phase reaction in the system and allows the target Al2O3 film to grow layer-by-layer around the ZnO nanowire. Therefore, the thickness of the Al2O3 shell can be accurately adjusted by the number of repeated ALD cycles. When we use a total number of 33, 66, 99, and 132 cycles, the Al2O3 layer deposited on the ZnO nanowire presents a conformal thickness of 5.1, 10.3, 15.5, and 20.5 nm, respectively, within the accuracy of few angstroms (see Supporting Information Figure S1). The dependence of the layer thickness on the ALD cycle number is illustrated in Figure 2c. From the linear relationship shown in the plot, the average growth rate of the Al2O3 layer is calculated to be 1.5 Å/cycle.

3.2. Annealing at Different Temperatures. To see how the synthesis temperature influences the nanotube formation, we used a series of ZnO nanowires coated by a 10.3 nm Al2O3 layer and annealed them at different temperatures but maintained the same period of 5 h. We denote the samples as samples A–E, which correspond to ZnO/Al2O3 core–shell nanowires annealed at 500, 600, 700, 800, and 900 °C, respectively.

3.2.1. Annealing at 500 and 600 °C. Figure 2 demonstrates the evolution of the morphology at low temperatures (500 and 600 °C). Figure 2a shows the typical TEM image of sample A. At first glance, there is no significant change in the morphology of the core–shell nanostructure after reaction. Its corresponding electron diffraction (ED) pattern in Figure 2b shows the typical set of spots for single-crystal hexagonal ZnO with a growth direction of [0001]. The diffusive halo in the center of Figure 2b might originate from the amorphous alumina since it cannot be obviously crystallized at 500 °C. Nevertheless, from the magnified image of some core–shell nanowires, a number of small voids could be detected at the interface of ZnO/Al2O3 (Figure 2c). The nanowire interface became intersected in sample B (Figure 2d), where irregularly shaped voids are clearer as shown in Figure 2e,f. Nucleation of voids at the ZnO core is unlikely. Previously, Maezawa et al. reported the formation of an aluminate-type phase (i.e., surface spinel) even at a synthesis...
temperature of 400 °C. This interaction involves the diffusion of Zn ions into tetrahedral sites in a surface lattice of Al₂O₃ to form spinel-like structures. The scattered small voids along the interface of sample A can be understood as a consequence of the redistribution of zinc ions from the core into the alumina followed by coalescing vacancies to voids. This implies that the reaction begins at temperatures as low as 500 °C. The gradually developed voids at 600 °C in sample B indicate a greater diffusion of ZnO into the alumina subsurface. However, the diffusion is limited at this temperature. Indeed, no more change upon morphology took place even after the annealing of sample B for 20 h. Note that the tip of the core–shell nanowires is the preferential site for void evolution (Figure 2e), which may be related to a high interface energy near the boundary due to its highest curvature.

3.2.2. Annealing at 700 °C. Figure 3 presents the typical TEM images of sample C annealed at 700 °C. The main structural feature for the most part of the annealed nanowires was the encapsulation of the ZnO core in the spinel nanotubes (Figure 3a,b), which have been confirmed by structural analysis (data not shown). Large voids distributed along the interface clearly show the existence of bridge-like linkages between the residual ZnO core and the spinel shell. Completely hollow spinel nanotubes already could be found in this case, as shown in Figure 3c. As compared to the other 1-D structures (Figure 3a,b), these nanotubes have a very narrow outer diameter of 30–40 nm, consistent with the results reported before. Figure 3d sums up all the typical 1-D nanostructures of sample C, where the wall thickness of the differently sized nanostructures similarly falls into the range of 15–20 nm.

The Kirkendall effect-induced voids are initially formed from the bulk diffusion, which is driven by a 1-D steady-state bulk flux related to the concentration gradient. Since ZnO has been identified to be the dominant diffusing species in the ZnO/Al₂O₃ couple, the diffusion-controlled process will generate a series of voids at the interface with the spinel ZnAl₂O₄ formed.

Figure 2. (a and b) Low magnification TEM image and corresponding ED pattern of a typical sample A nanowire after annealing at 500 °C. (c) TEM image of end section of a sample A nanowire. (d) TEM overview of a typical sample B nanowire after annealing at 600 °C. (e and f) Magnified images from the end and middle sections of the nanowire shown in panel d.

Figure 3. (a–c) TEM images of typical 1-D nanostructures of sample C after annealing at 700 °C. (d) Outline of differently sized 1-D nanostructures of sample C.
Considering that the activation energy of the ZnO surface diffusion (158 kJ/mol)\textsuperscript{22} is much lower than that of bulk diffusion (347–405 kJ/mol),\textsuperscript{23} it is reasonable that the adatoms of the remaining ZnO will dominantly diffuse along the pore surface to the reaction front. With the gradual formation of ZnAl\textsubscript{2}O\textsubscript{4} through the one-way diffusion of ZnO, vacancies are continuously generated and flow inward. Once the ZnO core exceeds the amount required for a complete transformation of the Al\textsubscript{2}O\textsubscript{3} shell, unconsumed ZnO would still exist in the interior. As a result, interrupted tubes with segmented voids or mesoporous nanowires containing unequally sized voids would be formed. From an experimental point of view, reaction in a vapor or solution phase looks more favorable than a solid–solid reaction for achieving the complete transformation of the core since the supply of the shell material is sufficient under the former conditions. Thus, it seems that on this condition (700 °C), only for samples having a narrow diameter distribution, such a solid–solid reaction of core–shell nanowires will be suitable for a large-scale synthesis of nanotubes or for transferring a whole array of nanowires into spinel nanotubes.

3.2.3. Annealing at 800 °C. In the case of sample D involving 800 °C annealing, we find that all the core–shell nanowires were transformed into completely hollow nanotubes irrespective of their dimension ratio (Figure 4a). Hollow tubular structures were even formed for tapered nanowires (see Supporting Information Figure S2). Figure 4b shows the TEM image of two isolated nanotubes with a rather large diameter in the range of 100–110 nm. In both cases, the entire tube wall is composed of multiple crystal domains. However, the corresponding ED pattern clearly reveals that the tubular structure grows preferentially with the (111) planes of cubic ZnAl\textsubscript{2}O\textsubscript{4} perpendicular to the tube axis. The local composition of the nanotube was investigated with EDX spectra by line scanning across and along a nanotube axis (Figure 4c). The intensity profile of elements Al, Zn, and O across the nanotube presents a valley-like shape characteristic of completely hollow nanotubes. However, the nanotubes seem not to be composed of a pure spinel phase since we detected weak diffraction spots of hexagonal ZnO in the ED patterns (Figure 4b). This conclusion was further confirmed by EDX analysis. For a formed nanotube with a diameter of 70 nm (Figure S3a), the atomic ratio of elements Zn/Al is about 1.4:1, deviating from the theoretical value of 0.5:1 calculated from the chemical formula of ZnAl\textsubscript{2}O\textsubscript{4}. Thus, some Zn or ZnO is possibly mixed with the spinel.

![Image](image.png)

**Figure 4.** (a) Low magnification TEM image of spinel nanotubes with different diameters after annealing at 800 °C (sample D). (b) Two isolated spinel nanotubes and their corresponding ED pattern. (c) Intensity profile of Zn, Al, and O across and along one tube diameter. (d) Atomic-resolution TEM image of a spinel nanotube. (e and f) Images magnified from the selected area in panel d.
Nevertheless, the EDX line scanning parallel to the tube axis (Figure 4c) as well as the elemental mapping (Figure S3b) exhibits a quite uniform distribution of Zn, Al, and O in the whole region of the nanotube, and no enriched areas of Zn were found. Figure 4d illustrates an atomic resolution TEM image of a 110 nm-thick polycrystalline nanotube. From the magnified images near the tube-edge region (Figure 4e,f), the lattice image of a discrete crystalline wall with a thickness of around 15 nm can be observed. Although domains or grain boundaries with different crystal orientations exist, the (111) ZnAl<sub>2</sub>O<sub>4</sub> spinel plane with an interplanar spacing of 4.67 Å in the long single-crystalline sections is always vertical to the tube axis, consistent with the results of the ED pattern, pointing to a (111) texture. Note that we did not find any ZnO nanocrystals during our TEM investigations.

Evidently, a temperature of 700 °C assured a complete transformation of Al<sub>2</sub>O<sub>3</sub> and the corresponding ZnO involved in this solid–solid reaction. However, the excess ZnO core in the spinel nanotube was hardly affected at this temperature even after a longer annealing time. When the reaction temperature was increased to 800 °C, the diffusion of the remaining ZnO once frozen at 700 °C seems to be triggered. Krost et al. observed that epitaxial ZnO layers could be flattened at a high annealing temperature (900 °C).<sup>24</sup> Its mechanism was ascribed to a redistribution of ZnO clusters on the surface based on the Gibbs–Thomson effect. This means that the residual ZnO core with a very rough surface (see, i.e., Figure 3) might be unstable at a higher temperature such as 800 °C in our nanoscale system. The excess ZnO is likely to diffuse along the void surface toward the spinel wall and reach its outer surface, where most of it is desorbed or evaporated from the tube.<sup>25–27</sup> Some residual Zn and O ions are probably homogeneously dissolved in the spinel matrix similar to what is known for the MgAl<sub>2</sub>O<sub>4</sub> spinel system.<sup>28</sup> In this case, the formed tubular structures can be regarded as Zn-rich spinel nanotubes. Alternatively, ZnO might form a thin layer attached to the inner surface of the tube wall. Similar as to what was observed for the formation of nanospheres based on the Kirkendall effect, the spinel shell tends to crystallize in larger grains at a high reaction temperature of 800 °C.<sup>10,15</sup> The appearance of such a textured graining structure can be ascribed to the simultaneous nucleation of spinel at multiple contact points along the longitudinal axis of each nanowire induced by surface diffusion. Moreover, the lattice rearrangement from a wurtzite ZnO to a cubic ZnAl<sub>2</sub>O<sub>4</sub> during the migration of ZnO is another important reason. However, the formed ZnAl<sub>2</sub>O<sub>4</sub> nanotubes exhibit preferential ordering of the (111) planes perpendicular to the tube axis. For an fcc structure such as spinel ZnAl<sub>2</sub>O<sub>4</sub>, the surface energy of different facets follows {111} < {100} < {110}. Therefore, {111} is the dominant facet that encloses the crystal.<sup>29</sup> On the other hand, in addition to the textured graining structure, cation antiphase boundaries, a general phenomenon for a spinel system may be present.<sup>30</sup> The grain nucleated at different positions only generates cation stacking faults. The oxygen sublattice can remain identical on each side of the spinel grain, which also favors the orientation of the formed spinel nanotube.

### 3.2.4. Annealing at 900 °C

When the reaction proceeded at 900 °C, dramatic changes upon the morphology were observed.
Figure 5a shows a typical SEM image, where porous nanowires with different diameters were observed. The TEM image in Figure 5b further demonstrates that the 1-D porous structure consists of crystalline domains with a string of voids included in the interior. In a theoretical study by Tu and Gösele, the thermal stability of the hollow nanostructures, especially those formed on the basis of the Kirkendall effect, was discussed. It was pointed out that a nanotube with thick walls should thermodynamically be rather unstable. To decrease the surface energy, atoms are inclined to diffuse from the nanotube outer surface to the inner region. Partial voids are finally eliminated, leading to the formation of a string of voids instead of a hollow cylinder for reducing its surface area. For the hollow spinel nanostructures generated at 900 °C, the high temperature would significantly increase the inner concentration of thermal vacancies under a negative pressure. These vacancies gradually went to the sink on the outer surface of the nanotube. Some parts of the wall, especially where the grain boundaries exist, will collapse. Eventually, discontinuous voids will be formed in the core.

3.2.5. Outline of 1-D Nanostructures Obtained at Different Annealing Temperatures. On the basis of the previous investigations, the influence of temperature on the conversion of single-crystalline ZnO nanowires covered by a 10.3 nm-thick Al2O3 layer is concluded in Figure 6. Importantly, it is revealed that a higher reaction temperature such as 800 °C can lead to the formation of completely hollow spinel nanotubes regardless of the initial core–shell diameter ratio. Besides, all the resulting nanotubes are characterized by an approximately identical wall thickness, which is determined by the deposited alumina layer.

3.3. Fabrication of Spinel Nanotubes with Thicker Tube Walls at 800 °C. Since the thickness of the alumina shell can be precisely tuned by ALD, a large-scale fabrication of ZnAl2O4-related nanotubes with an adjustable wall thickness is expected. To prove the concept further, ZnO nanowires were coated by a 20.5 nm Al2O3 layer. As shown in Figure 7a,b, all the core–shell nanowires could be transformed into completely hollow nanotubes after annealing at 800 °C for 5 h. From the inset of Figure 7b, the wall thickness was found to be 30 nm, as expected.

3.4. Large-Scale Fabrication of Vertically Arranged Spinel Nanotube Arrays at 800 °C. In a last experiment, we applied this method to vertically aligned ZnO nanowires for demonstrating vertically arranged spinel nanotube arrays. Figure 8a shows the SEM image of the as-prepared ZnO nanowire array grown on a GaN/Si substrate. After the ALD deposition of a 20.5 nm-
thick alumina layer and annealing at 800 °C for 5 h, the array structure is well-conserved (Figure 8b). TEM observations confirm that all the aligned 1-D nanostructures are textured grainy nanotubes independent of their diameter (Figure S4). Figure 8c shows an SEM image where open ends on the substrate are visible together with the corresponding nanotubes.

4. Conclusion

In summary, the evolution of coaxial ZnO/Al2O3 core–shell nanowires at different temperatures was studied in detail. The results reveal that the initial voids formed at the core–shell interface originate from the migration of ZnO based on the Kirkendall effect. The dynamics is accelerated at 700 °C, favored by the surface diffusion of ZnO along the present void surface. Completely hollow spinel nanotubes can be formed at this temperature provided that the ZnO core is totally consumed by the solid–solid reaction. At a higher temperature of 800 °C, the unconsumed ZnO core can be further removed via diffusion, desorption, and redistribution processes. Therefore, all the starting core–shell nanowires with various diameters are transformed into completely hollow nanotubes. The wall thickness is approximately determined by the initial thickness of the deposited alumina layer. Reactions at 900 °C lead to the formation of porous nanowires, which are derived from the collapsing of the spinel nanotubes due to their thermal instability. As the most important point, our results demonstrate that at a suitable reaction temperature, either freestanding or vertically aligned spinel nanotubes with a controllable wall thickness can be fabricated on a large scale via the Kirkendall effect-induced approach.

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Supporting Information Available: TEM images of ZnO/Al2O3 core–shell nanowires prepared by different ALD cycles, hollow tubular structures formed from tapered nanowires and spinel nanotubes formed on the GaN/Si substrate, and EDX spectrum and elemental mapping of spinel nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes