

Diffusion-Induced Void Evolution in Core–Shell Nanowires: Elaborated View on the Nanoscale Kirkendall Effect

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Abstract: In 2006, our group reported the fabrication of ultra-long single-crystal ZnAl_2O_4 spinel nanotubes, starting from $\text{ZnO}/\text{Al}_2\text{O}_3$ core–shell nanowires, involving the nanoscale Kirkendall effect. In this feature paper, we introduce our up-to-date results on the design of porous and hollow 1D nanostructures following this solid-state interfacial reaction route. In particular, we present our recent understandings on void evolution induced by the unbalanced diffusion. We first give a short introduction on the distinctions of

core–shell nanowires in interfacial nanoreactions, in contrast to other systems. Then we discuss the roles of desorption, stress, and/or defects on void evolution and nanotube formation. Our results demonstrate that the stress- and defects-engineered diffusion mechanism can be used to specifically design hollow nanostructures, which will open up a new window in exploitation of the Kirkendall effect at the nanoscale.

Keywords: diffusion · oxides · reaction mechanisms · solid-state structures · zinc oxide

1. Introduction

The Kirkendall effect is a classical phenomenon in general metallurgy.^[1,2] Conceptually, this effect refers to a non-equilibrium mutual diffusion process through the interface of a couple of materials. It was assumed for a long time that, in metallic crystals, atomic diffusion occurs by a direct exchange mechanism or a ring mechanism. Both the mechanisms assume an interchange of A and B atoms with equal diffusion coefficients ($D_A = D_B$). In 1947, Kirkendall et al. for the first time suggested a difference in diffusion rates of two components, based on interdiffusion experiments by contacting Cu with α -brass plates.^[1] They demonstrated that atoms of different types naturally diffuse with unequal partial diffusion coefficients ($D_A \neq D_B$). Moreover, it was revealed that the unequal material flow was simultaneously accompanied by vacancy diffusion. Accordingly, interfacial voids are inclined to appear in the zone of the faster diffusing component of the solid diffusion couple.

At the macroscopic scale, the interfacial pores induced by the Kirkendall effect can only form a very heterogeneous ensemble. Since partial vacancies are consumed by numerous defects existent in macroscopic systems, the volume fraction of pores after interdiffusion is commonly much smaller than what is expected for the known material flows. From a traditional viewpoint, the formation of “Kirkendall voids” in alloys and solders is not a desirable process for metallurgical manufacturing because the porosity deteriorates the mechanical properties of the inter-

face. The main technological motivation for studying the Kirkendall effect in the past was to reduce its negative effect on adhesion or mechanical reliability at the respective interfaces.^[2]

However, the Kirkendall effect has presented its “constructive” applications for the generation and design of hollow structures in the nanoworld in recent years.^[3–5] Nanocrystals usually have a high surface-to-volume ratio and few defects, in contrast to their macroscopic counterparts. Once unequal interdiffusion occurs at the nanoscale, the net rate of vacancy injection will increase significantly. These vacancies are very likely to get supersaturated and coalesce into a single void. A classic example was shown by the Alivisatos group in 2004.^[3] It was reported that cobalt nanocrystals were transformed into hollow oxide or chalcogenide nanospheres after the reaction with oxygen, sulfur, or selenium in solution. The mechanism for the hollow structure formation was attributed to the dominant outward flow of cobalt through the

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oxide/sulfide shell induced by the so-called nanoscale Kirkendall effect.

The exploitation of the nanoscale Kirkendall effect has currently been regarded as a general route for the fabrication of hollow nanostructures from a large number of compounds.^[5] The beauty of this approach is that all the available data on diffusion rates in thin film diffusion

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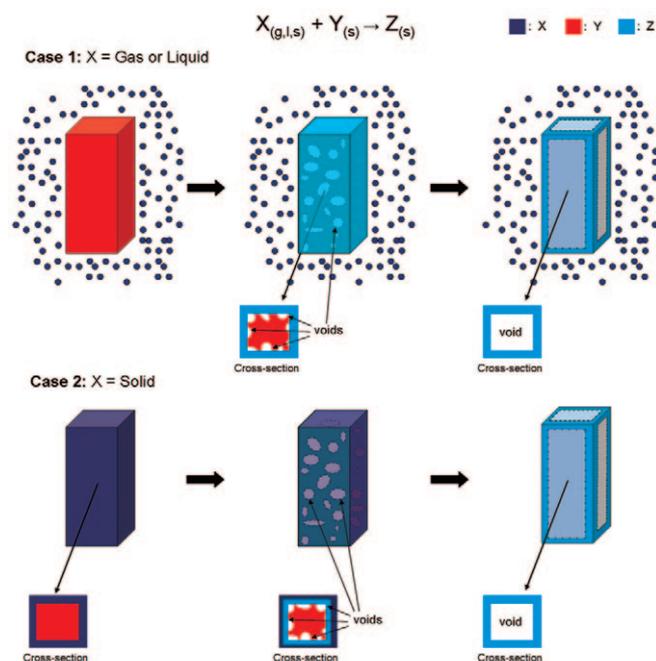
couples can readily be used to design starting structures, which can then be transformed into hollow nanostructures. For example, a self-diffusion process based on the Kirkendall effect can even happen in single-component couples, if the contacting couple layers are composed of different structures or have different electro- and thermomigration properties. When this self-diffusion mechanism was utilized at the nanoscale, hollow nanostructures like nanotubes were successfully converted from nanowires only through phase transformation.^[6] From a theoretical point of view, most extended concepts such as subsurface and grain boundary interdiffusion established for the “macroscopic” Kirkendall effect can readily be applied to elucidate vacancy fluxes and void evolution at the nanoscale as well.^[2]

In 2006 our group reported the fabrication of ultra-long single-crystal ZnAl₂O₄ spinel nanotubes, starting from ZnO/Al₂O₃ core–shell nanowires, involving the nanoscale Kirkendall effect.^[4] This nanotube formation process is based on an interfacial solid–solid reaction accompanying the formation of ternary oxide ZnAl₂O₄. In this article, we outline the recent progress in our laboratory in the design of porous and hollow 1D nanostructures following this solid-state interfacial reaction route. We first give a short introduction on the distinctions of core–shell nanowires in interfacial reactions induced by the nanoscale Kirkendall effect. Afterward, we discuss the roles of desorption, stress, and/or defects on void evolution and nanotube formation using our up-to-date results for illustration.

2. Core–Shell Nanowires in Interfacial Reactions

Interfacial reactions induced by the nanoscale Kirkendall effect generally include three types: solid–gas, solid–liquid, and solid–solid processes (Scheme 1). Solid–gas and solid–liquid reaction processes are very similar because both cases start with only one solid component in a diffusive couple. The second component is dispersed in a liquid phase or just a flowing gas.^[7–10] Therefore, they can be understood collectively as solid–fluid processes. The solid partner serves as both the precursor and the dimensionally controlling template for the transformation. When the reactants from the gas or liquid phase react with atoms/ions on the precursor surface, a new interfacial layer composed of the reaction product is formed. The “acquired” solid layer then works as a barrier to control the interdiffusion of the diffusive couple. If the outward diffusion of the solid component is favored due to the presence of this barrier layer, hollow nanostructures will finally form with the solid core gradually consumed.

For nanostructures like core–shell nanowires, the interfacial reactions follow the solid–solid process.^[4] This process is a little bit different from the above cases, because the interface between the two contacting phases has al-



Scheme 1. Schematic diagram of the transformation of nanowires to nanotubes via solid–gas, solid–liquid, and solid–solid processes by the nanoscale Kirkendall effect.

ready been established prior to the reaction.^[4,11] In view of this point, when core–shell nanostructures are used to investigate interfacial diffusion, it is easier to learn from the accumulated knowledge based on the traditional mechanisms involving the Kirkendall effect.

The core–shell nanowires used in our experiments are ZnO nanowires coated with a thin film of Al₂O₃, TiO₂, or SiO₂ by atomic layer deposition (ALD).^[12] The ZnO nanowires are single-crystalline, and are grown via vapor transport method using Au as a catalyst. Their diameter usually ranges from 10 to 200 nm. It is known that ALD is a sequential and self-limiting process, which avoids any gas-phase reaction in the system and allows a target film to grow conformal layer-by-layer even on 3D substrates.^[12] Therefore, the ALD coated oxide shells in our experiments are uniform and conformal in each case. Their thickness can be accurately adjusted by the number of ALD cycles.

Figure 1a schematically illustrates the fabrication process of ZnO/Al₂O₃ core–shell nanowires and their interfacial solid–solid reaction.^[4] Because the reaction is effectively a one-way transfer of ZnO into the Al₂O₃, it represents an extreme Kirkendall effect. Upon a suitable matching of the thickness of the core and the shell, highly crystalline single-phase spinel nanotubes can be formed via the stoichiometric reaction of ZnO/Al₂O₃. The TEM images in Figure 1b show single-crystalline ZnAl₂O₄ nanotubes obtained from ~15 nm ZnO nanowires coated with a 10 nm Al₂O₃ layer after annealing in air at 700 °C

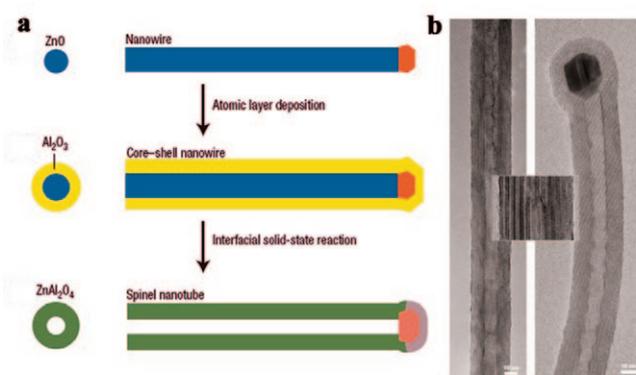


Figure 1. (a) Schematic diagram of the transformation of ZnO/Al₂O₃ core–shell nanowires to nanotubes by means of the Kirkendall effect. (b) TEM images of single-crystal ZnAl₂O₄ spinel nanotubes. Both are reproduced with permission from ref. [4].

for 3 h. Because of the conformal nature of the ALD Al₂O₃ layer, the same effect should occur in any other type of complex ZnO architectures, provided that the thickness of the Al₂O₃ layer is adjusted approximately to the diameters of the underlying ZnO. Figure 2a and b represents a branched tubular spinel nanostructure and a single-crystalline rippled spinel nanotube, respectively. These hollow structures were achieved from diverse ZnO nanostructures using the same ALD and annealing process, while the thickness of the coated Al₂O₃ layers was adjusted case by case. This strategy provides an opportunity to fabricate hierarchical hollow spinel nanostructures irrespective of their aspect ratios, which might enable applications beyond the reach of straight ones.^[13]

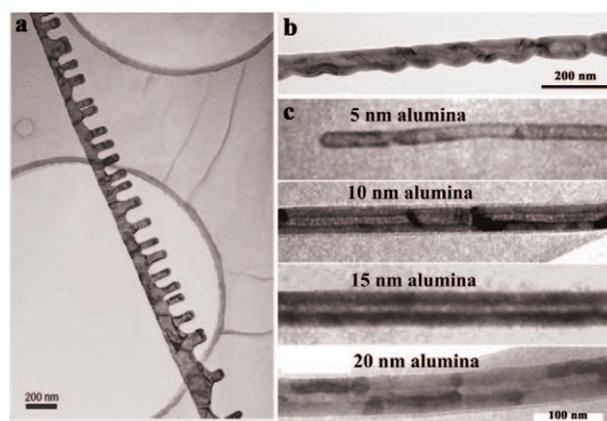


Figure 2. TEM images of (a) a branched tubular spinel nanostructure converted from a saw-like ZnO nanocrystal coated with a 10 nm Al₂O₃ layer (reproduced with permission from ref. [4]), (b) a rippled spinel nanotube converted from a rippled ZnO nanowires coated with a 20 nm Al₂O₃ layer, and (c) spinel nanotubes converted from ZnO nanowires coated with an Al₂O₃ layer of different thicknesses.

If the starting ZnO nanowires have a broad size distribution while the thickness of the Al₂O₃ layer is fixed, it can be expected that only partial ZnO nanowires can be transformed to phase-pure spinel nanotubes under the above reaction conditions.^[14,15] ZnO nanowires thicker than the fitting size will lead to the formation of unconsumed porous ZnO nanowires encapsulated by a spinel shell, which will be discussed in the next section. In contrast, nanotubes are formed for all the thinner ones. However, some nanotubes should be composed of ZnAl₂O₄ and remaining Al₂O₃ excess for this reaction. As seen in Figure 2c, when we increased the thickness of an ALD coated Al₂O₃ layer from 5, to 10, 15, and 20 nm for ZnO nanowires with a diameter of ~10 nm, completely hollow tubular structures were formed in each case after annealing in air at 700 °C. Considering the various thickness ratios of these ZnO/Al₂O₃ couples, the component of partial nanotubes presented here must be a mixture.

In the solid–gas or solid–liquid process, the supply of a “shell” material is sufficient and regulates the transformation reactions by the nanoscale Kirkendall effect. From an experimental point of view, it seems that the ALD-based solid–solid process is not so favorable for achieving completely hollow nanostructures with a pure phase if one starts from a core precursor with inhomogeneous sizes. In the case of ZnO/Al₂O₃ core–shell nanowires, such a core–shell interfacial reaction becomes suitable for large-scale synthesis of spinel nanotubes at 700 °C only for samples having a narrow diameter distribution. Nevertheless, this core–shell system is advantageous in the production of core–void–shell nanostructures by partly consuming the ZnO core. Given the fact that the thickness of the Al₂O₃ shell can be well tuned by ALD, the extent of reaction can be planned, which provides an important alternative compared to the only possible control being reaction time in the solid–fluid processes.

3. Void Evolution: Diffusion or Desorption?

Previous discussions on Kirkendall-type diffusions consider a continuous bulk diffusion of the growth species and vacancies governed by the Fick's first law:^[16]

$$J = -D\nabla c \quad (1)$$

where J is the flux of atoms, D the diffusion coefficient, and ∇c is the potential gradient of the atom concentrations. This indicates that the diffusion at the interface is driven by the concentration gradient. The pore enlarges only by aggregation of inward-flux excess vacancies at the center of the core. However, in most real experiments, voids are generated near the interface and separate the core from the inner surface of the product layer. In this case, bulk-like diffusion is limited, and the above formu-

lated diffusion mode become invalid. At the macroscopic scale it has already been found that interdiffusion occurred mainly along free surfaces and grain boundaries in Kirkendall-type thermal couples, which could serve as the fast diffusion paths and the sinks/sources of vacancies and dislocations.

As we discussed above, the solid–solid ZnAl₂O₄-forming reaction between ZnO and Al₂O₃ involves an extreme one-way diffusion of ZnO into Al₂O₃. Thus, the influence of interdiffusion can be ignored. This feature makes this system an ideal sample for investigating the void evolution induced by the nanoscale Kirkendall effect. The TEM image shown in Figure 3a outlines the morphologies

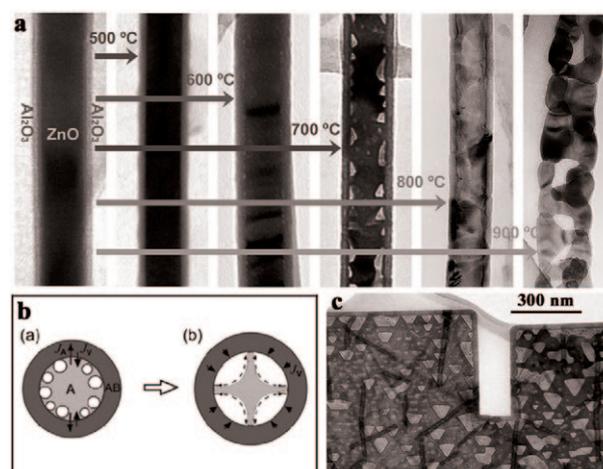


Figure 3. (a) Outline of ZnO/Al₂O₃ core–shell nanowires with an excess core for the solid-state reaction annealed at different temperatures (reproduced with permission from ref. [15]). (b) Generalized model for hollow structure formation based on the Kirkendall effect and subsequent surface diffusion (reproduced with permission from ref. [14]). (c) TEM image of a ZnO nanobelt coated with a 10 nm Al₂O₃ layer after annealing in air at 700 °C for 5 h.

of a ZnO/Al₂O₃ core–shell nanowire with excess core for the solid-state reaction annealed at different temperatures. Upon annealing at 600 °C even for a very long time (12 h), only small voids with a fairly uniform size distribution intersecting the interface are observed, indicating the homogeneous nucleation and growth of Kirkendall voids in the initial stage via a bulk diffusion process.^[15] Due to kinetic reasons, it is very difficult to observe the growth of these voids into large ones at this temperature.

When the reaction is performed at 700 °C, multiple voids with large sizes appear at the interface as a result of the adequate outward diffusion of ZnO accompanying the complete transformation of the Al₂O₃ shell into ZnAl₂O₄. Since surface diffusion coefficients are normally several orders of magnitude larger than their bulk counterparts, a faster kinetics for the void growth is favored.^[14] Therefore, the enlargement of the initial Kirkendall voids at this stage is dominated by surface diffusion of the ZnO

core along the pore surface, which is shown schematically in Figure 3b. Because surface diffusion is strongly dependent on the diffusing energy of atoms on each facet, such an evolution manner usually makes the resultant voids irregular in shape and size. Figure 3c shows a TEM image of a 10 nm Al_2O_3 coated ZnO nanobelt after annealing in air at 700 °C for 5 h. In view of this 2D nanostructure, one can conclude that most interfacial voids evolving from the single-crystal ZnO substrate by surface diffusion are not only “faceted” but have homothetic shapes, too.

From the reaction point of view, it is clear that the residual ZnO cores cannot diffuse outwards any more because no chemical driving force exists after the complete consumption of the Al_2O_3 shell. However, when the annealing temperature is increased to 800 °C, hollow nanotubes are formed even if the initial ZnO nanowires are thicker than necessary for the stoichiometric reaction with the former shell (Figures 3a and 4). We suggest that this effect is caused by reactive desorption of ZnO at higher temperatures. When the reaction temperature is further increased, for instance, to 900 °C, the tube wall collapses due to thermodynamic instability,^[17] as seen in the right hand image of Figure 3a.

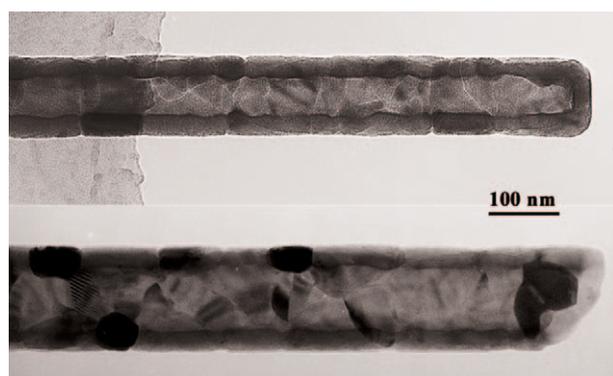


Figure 4. TEM images of spinel nanotubes converted from different sized ZnO nanowires coated with the same 10 nm Al_2O_3 layer. The solid-state reaction was performed at 800 °C in air for 5 h.

The images of the ZnAl_2O_4 nanotubes shown in Figure 4 confirm that the formation of nanotubes at 800 °C from ZnO nanowires with different ZnO excess amounts is conducted by the desorption process. In both cases demonstrated here, the entire tube wall is composed of multiple crystal domains. The present abundant grain boundaries facilitate the diffusion of the unconsumed ZnO to the spinel surface, which will be further desorbed. Allowing for these facts, the latter desorption process in the above case cannot be regarded as a Kirkendall-type diffusion, because the diffusion counterpart of the ZnO core (the Al_2O_3 shell) no longer exists. This process is somewhat similar to the calcinations of oxide-coated organic nanowires. However, the desorption of ZnO nano-

objects becomes much easier if an interfacial reaction is triggered or just in the presence of some functionalized coatings.^[18] We evidenced that slight ZnO desorption also happened at a reaction temperature of 700 °C. Thus, nanotube formation in the temperature window of 700–800 °C for this system is induced either by the nanoscale Kirkendall effect only, or by its synergistic role with desorption.

Therefore, it is important to distinguish the origin of voids observed after an interfacial reaction process,^[18,19] especially when the diffusion coefficients of a couple have not been identified. In our previous work, we reported that multitwinned Zn_2TiO_4 nanowires can be synthesized via the solid-state reaction of ZnO nanowires with a thin TiO_2 shell (5 nm in that case).^[20] The multitwinned nanostructures are proposed to develop via the oriented attachment of preformed spinel nanobricks, as shown schematically in Figure 5a. Zigzag features of the Zn_2TiO_4 nanowires with multiple microfaceted twin subunits are exhibited in Figures 5b–d. It was revealed that the TiO_2 is first incorporated into the ZnO lattice as segregation and then reacts into individual spinel crystallites

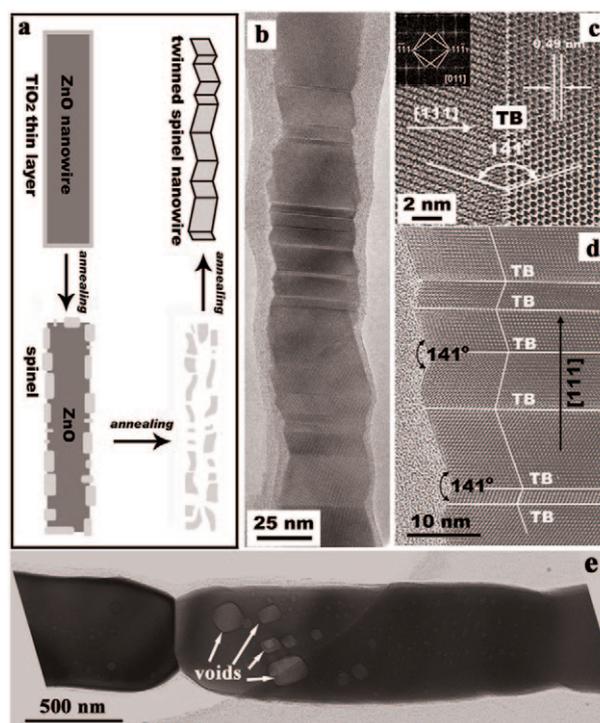


Figure 5. (a) Schematic diagram of the growth process for multitwinned Zn_2TiO_4 nanowires from ZnO/ TiO_2 core–shell nanowires by annealing at high temperatures. (b) TEM image showing the zigzag morphology of Zn_2TiO_4 multitwinned nanowires by solid-state reaction of ZnO/ TiO_2 core–shell nanowires at 900 °C for 8 h. Note that the twinning is non-periodic. (c) A closer view at one twin boundary and the corresponding FFT pattern. (d) Several twinning boundaries with a fixed zigzag angle of 141°. All are reproduced with permission from ref. [20]. (e) TEM image of a Zn_2TiO_4 nanowire with many voids in its interior.

through lattice rearrangement. Finally, these spinel bricks assemble into oriented solid multitwinned nanowires, with the unreacted ZnO decomposing and evaporating through the gaps in the bricks. Unlike the reaction of ZnO/Al₂O₃ nanowires, no voids or tubular structures appear at the ZnO/Zn₂TiO₄ interface at the initial reaction stage, indicating that the interdiffusion rates of ZnO and TiO₂ are comparable or the diffusion rate of the latter is bigger (not restricted to bulk diffusion). However, when ZnO nanowires coated with a 17 nm TiO₂ film were annealed at 800 °C, cavities were frequently found in the center of formed Zn₂TiO₄ nanowires. One typical image is shown in Figure 5e, in which a number of voids with different sizes can be clearly detected. We assume that the voids originate from the desorption of the unreacted ZnO during calcinations at high temperatures, where partial vacated interspaces are enveloped by the spinel bricks via oriented attachment and coalescence (Ostwald ripening). In other words, in principle the void formation in this system has no direct relation to the unbalanced interdiffusion based on the nanoscale Kirkendall effect.

4. Stress-Engineered Void Localization

For various Kirkendall effects, the elimination or building-up of atomic planes at the diffusion zone will lead to the generation of diffusion stresses, whose generation and relaxation can significantly affect the kinetics of interdiffusion, structural reconstructions, and interaction of defects at the interface. In this section we will discuss a flexible stress-mediated approach to design hollow nanostructures by intentionally positioning locally arranged nanovoids in core-shell nanowires.

The effects of stress on atomic diffusion and vacancy accumulation can be explained with a modified version of the Fick's first law adding a new stress related term to the initial concentration based term:^[21]

$$J = D \left[-\nabla c - \frac{c\nabla V}{kT} \right] \quad (2)$$

Here k represents the Boltzmann constant, T the temperature, c the concentration of the atoms, and ∇V the potential gradient of the force. This equation describes an atomic diffusion process with an additional stress gradient. Once a stress field created by an applied force is present, diffusion of atoms will occur along a negative stress gradient.

Generally, sharp corners greatly increase the stress concentration. The failure of many bi- and multi-material joints is known to initiate from one or more interface corners. For lattice-mismatched core-shell nanowires, it is revealed that the stress distribution in their interior is very

inhomogeneous. The stress maxima in the core usually occur in the corner region at the core-shell interface.^[22] Figures 6a and b show the geometry of the tip of a ZnO/Al₂O₃ core-shell nanowire and a 2D simulation of its

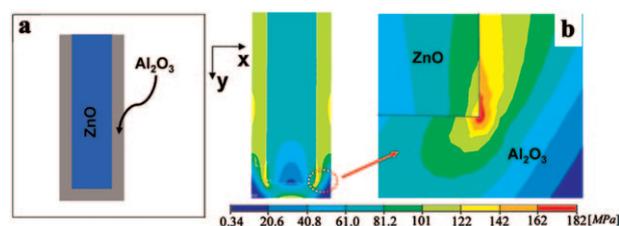


Figure 6. (a) Geometry of the tip of a ZnO/Al₂O₃ core-shell nanowire; (b) Simulated stress distribution at the tip of a ZnO/Al₂O₃ nanowire due to thermal expansion at 700 °C. The diameter of the core is 40 nm while the thickness of the shell is 12 nm. (Both are reproduced with permission from ref. [23]).

stress distribution caused by thermal expansion at 700 °C. The stress calculations were performed using ANSYS finite elements analysis software. A very fine mesh (0.85 nm) was used to calculate the resulting thermally generated mechanical stress field with high resolution. The simulation result indicates that the highest thermal stress in the ZnO core appears at the interfacial corners.^[23]

When an excess ZnO core reacts with an Al₂O₃ shell at 700 °C through the nanoscale Kirkendall effect, the nearly identical concentration gradient of ZnO along the core-shell interface should induce a uniform void evolution at various sites. However, the large stress created on the corners can enhance the diffusion of ZnO away from these areas.^[23] This in turn enhances the vacancy flux towards this position. Also, the low radius of curvature favors outward diffusion of the core material. Therefore, vacancies more easily supersaturate and coalesce into voids at the corners. Since the surface diffusion of ZnO presents a faster kinetics for the void growth, a finally evolved void with a larger size is presumed to develop from an initial Kirkendall void whose nucleation is preferred. This conclusion is based on the precondition that the enlargement of the interfacial voids in the ZnO/Al₂O₃ core-shell nanowires cannot be achieved by void coalescence via a long-range migration due to the very low self-diffusivity of ZnO at 700 °C.

However, if the concentration gradient is very high, the influence of the stress might be hidden. For the ZnO nanowire and nanobelt coated by a 10 nm thin Al₂O₃ shell, shown in Figure 3, the stress effect on diffusion seems insufficient for the formation of large interfacial nanocavities localized at the high-stress positions. To magnify the role of stress, Equation 2 provides two possible alternatives:^[23] decreasing the concentration gradient

of the diffusing material or increasing the stress gradient at intended positions.

We first deposited a thinner, uniform 3 nm Al_2O_3 film on the ZnO nanowires by ALD. After annealing at 700 °C for 5 h, a very large interfacial nanocavity was exclusively formed at the tip of each core–shell nanowire, as shown in Figure 7a. Along the stem only very small voids

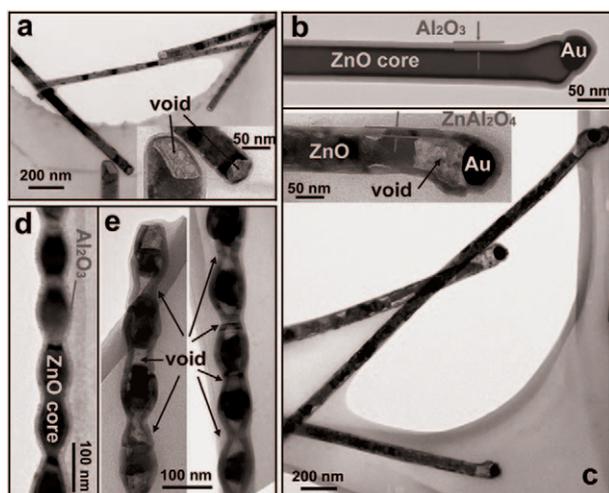


Figure 7. TEM images of (a) ZnO nanowires with a 3 nm thin Al_2O_3 shell after annealing at 700 °C for 5 h; gold-capped ZnO nanowires with a 12 nm thin Al_2O_3 shell before (b) and after (c) annealing at 700 °C for 5 h; rippled ZnO nanowires with a 12 nm thin Al_2O_3 shell before (d) and after (e) annealing at 700 °C for 5 h (Reproduced with permission from ref. [23]).

are observed in most cases. The reduction of thickness of the Al_2O_3 shell leads to a much more preferential void formation at the tips. It can be assumed that, once the reaction between the ZnO nanowire core and the 3 nm thin Al_2O_3 shell started, the concentration gradient of ZnO across the interface and the shell decreased more rapidly due to the reduced diffusion space for Zn^{2+} and O^{2-} . As a result, the geometry-induced stress influences the diffusion of ZnO and the nucleation of the Kirkendall voids to a greater degree. Finally, a large void is positioned at the region of the highest induced stress. During the void enlargement by surface diffusion, longitudinal diffusion of ZnO in the Al_2O_3 shell also occurred.

In the second experiment, 12 nm thin Al_2O_3 films were deposited on gold-capped ZnO nanowires (Figure 7b). After the reaction at 700 °C, a hollow section typically appeared at the gold/nanowire interface, as shown in Figure 7c. The introduction of gold obviously accelerates the diffusion of the adjacent ZnO nanowire core atoms. The gold/nanowire interface is a region of high stress due to large curvature and lattice mismatch. In this case, the contribution from the concentration gradient was “weakened” by the addition of a very large stress gradient, the

value of which is unattained only by the corner geometry of the ZnO/ Al_2O_3 core–shell nanowires.

When we started the process from rippled ZnO/ Al_2O_3 core–shell nanowires, ZnAl_2O_4 nanotubes with embedded ZnO nanocrystals were fabricated. Figures 7d and e show TEM images of 12 nm thin Al_2O_3 coated rippled ZnO nanowires before and after annealing, respectively. After annealing at 700 °C for 5 h, the core–shell nanowires were transformed into a pea-pod structure. Large nanocavities were only observed in areas where the nanowires are constricted to smaller diameters, which separate the remaining ZnO nanowire core into unconnected “nanopeas”. The rippled nanostructure indeed creates an oscillating stress field with a periodic fluctuation by thermal expansion. Its stress gradient is higher in the narrower sections of the nanowires compared to the wider sections. As a result, the void nucleation is more favorable at these positions and the pea-pod nanostructure is formed.

This Kirkendall effect-derived, stress-assisted diffusion process can be regarded as a general route to specifically design nanostructures with positioned large interfacial nanocavities. Greater regulation of a local chemical and physical environment is expected in nanostructures with controlled porosity, which is important for various applications.

5. Defect-Facilitated Nanotube Formation

It is known that defects such as grain boundaries and cracks formed during shell growth can also act as preferential nucleation sites for Kirkendall voids, which favor the outward diffusion of core materials. However, the defect profile of nanostructures is generally difficult to identify. This is the reason why we sometimes encounter very large voids in unpredicted positions in the diffusion-resultant ZnO/ ZnAl_2O_4 nanostructures. If we can purposely introduce defects into the core–shell interface of Kirkendall-type thermal couples, their void evolution should be facilitated, especially in cases where the void development requires a long nucleation period.

Similar to the formation of ZnAl_2O_4 nanotubes from ZnO/ Al_2O_3 core–shell nanowires, the reaction between the ZnO/ SiO_2 couple involves a one-way interfacial transfer of ZnO into the SiO_2 shell, which leads to the formation of a tubular Zn_2SiO_4 structure.^[24]

ZnO nanowires coated by ALD with a 15-nm SiO_2 layer were first annealed at 800 °C for 6 h in air. As shown in Figure 8a, the product presents few morphological evolutions, although a small quantity of superficial Zn_2SiO_4 has already been formed at this temperature. Only several tiny cavities appear in some ZnO/ SiO_2 core–shell nanowires due to the Zn_2SiO_4 -forming reaction. When the solid-state reaction was carried out in air at 900 °C for 6 h, partial core–shell nanowires were transformed into Zn_2SiO_4 nanotubes or discontinuous tubular

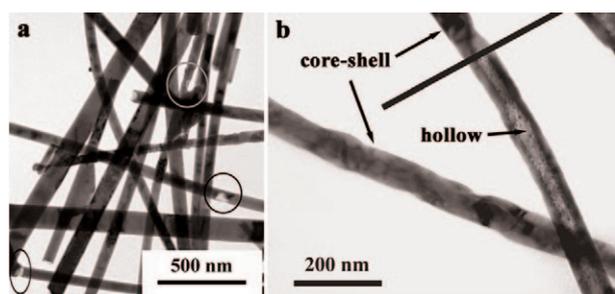


Figure 8. (a) TEM image of 1D nanostructures after annealing 15-nm SiO_2 layer coated ZnO nanowires ZnO/ SiO_2 core-shell nanowires at 800°C for 6 h in air. The circles highlight the positions of formed small cavities. (b) TEM image of 1-D nanostructures after annealing the same core-shell nanowires at 900°C for 6 h in air. Some nanostructures show a long tubular section connected to a core-shell section. The boundary is highlighted with the line.

nanostructures, indicating that the reaction at 900°C was still not complete. In Figure 8b, it is found that distinct dividing lines are observed in the intermediates along axial direction; that is, the 1D nanostructures formed are composed of evolved tubular sections and unchanged core-shell segments. In particular, no voids were detected at the interface of the core-shell remainders. Based on these observations, we assume that the ZnO/ SiO_2 solid-solid reaction induced by the bulk diffusion proceeds very slowly. This slow reaction rate is most probably attributed to the high bond energy of SiO_2 . Therefore, an extremely long time is required for the widespread nucleation of the initial Kirkendall voids. Once a large void preferentially formed at weak positions in the ZnO/ SiO_2 interface, for example at spots with high defects or high strains, a tubular section would rapidly develop from this gap by kinetically-favored surface diffusion. From this point, the formation of the Zn_2SiO_4 nanotubes presented here is actually triggered by a few preferentially generated interfacial voids rather than a randomly distributed void evolution at the ZnO/ SiO_2 interface, which is different from that in the ZnO/ Al_2O_3 system.

External forces, such as heat or an electron beam, can induce the transport of gold particles in a thin SiO_2 film.^[25] If a gold interlayer is present at the ZnO/ SiO_2 core-shell interface, the migration of gold in and through the SiO_2 shell should occur during an annealing process. The driving force for the motion should be the reduction in interface energy upon successive replacement of the interface ZnO-Au- SiO_2 by the Au- SiO_2 and the SiO_2 -Au-air interfaces. Based on this fact, we designed a ZnO-Au- SiO_2 sandwich nanowire structure and exploited the diffusion of the gold interlayer to influence the diffusion behavior of the thermal diffusion couple ZnO/ SiO_2 .

The ZnO-Au- SiO_2 nanowires were subsequently annealed at 900°C for 3 h in air. Most of the starting sandwich nanowires were transformed into Zn_2SiO_4 nanotubes decorated with gold nanocrystallites (right images in

Figure 9), although the reaction time was halved. A number of partly hollow structures even formed at 800°C . Obviously, the diffusion of ZnO into the SiO_2 shell and the resultant overall reaction rate can be accelerated by the presence of the gold interlayer and its temperature-dependent migration.

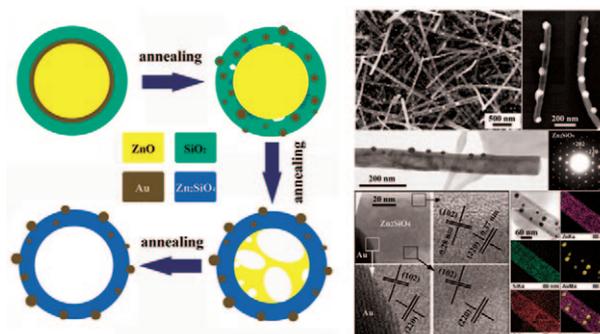


Figure 9. Left: The growth process for gold nanocrystallite-decorated Zn_2SiO_4 nanotubes formed from ZnO-Au- SiO_2 sandwich nanowires by annealing at high temperatures. Right: Images and ED/EDX characterizations of Au-decorated Zn_2SiO_4 nanotubes by annealing ZnO-Au- SiO_2 nanowires at 900°C for 3 h in air. (Both are reproduced with permission from ref. [24]).

In this process, heat first induced the disintegration of the gold interlayer into isolated nanocrystallites at the ZnO/ SiO_2 interface by dewetting. These nanocrystallites then gradually migrated from the interface to the outer surface of the SiO_2 shell. During the migration, surface diffusion of SiO_2 along the gold nanocrystallites took place, which filled the gold-vacated spaces in the shell. This mode is similar to the Stokes motion of a solid sphere in a viscous medium. Some small gold nanocrystallites might have grown larger owing to their collision and to Ostwald ripening.

As the fluidity of solid state SiO_2 is limited at temperatures far below its melting point, it is supposed that some vacancies induced by the motion of the gold nanocrystallites failed to be compensated in time. During annealing, these frozen vacancies would possibly fuse into large voids, some of which gather at the ZnO/ SiO_2 interface. Moreover, the surface diffusion of SiO_2 along different gold nanocrystallites resulted in an unequal thermal reconfiguration of the initial ALD-deposited SiO_2 shell. Abundant defects and weakened bonds would be produced in the interfacial SiO_2 , in contrast to the annealing process without the gold interlayer. Therefore, it can be inferred that the gold motion introduced additional voids, vacancies, and defects into the ZnO/ SiO_2 nanowire interface, which facilitated the nucleation of the Kirkendall voids at multiple positions by bulk diffusion. Once this initial void nucleation was adequately achieved, the ZnO nanowire core could rapidly diffuse into the SiO_2 shell along the interfacial void surfaces. Therefore, the forma-

tion of a Zn_2SiO_4 nanotube was accelerated. As for ZnO nanowires with large diameters, excess ZnO finally diffuses along the void surface toward the Zn_2SiO_4 wall and desorbs on its outer surface. The above proposed procedures are shown in the left image in Figure 9.

In this case, the interfacial defects are introduced by the heat-driven motion of the gold interlayer, which facilitates the initial nucleation of the Kirkendall voids and further accelerates the formation of the Zn_2SiO_4 nanotubes. This procedure simultaneously leads to the fabrication of a hybrid nanocomposite. If an organic interlayer is sandwiched at the interface, we expect that the same effect will take place during the combustion of the interlayer. Finally, phase-pure Zn_2SiO_4 nanotubes can be obtained under optimized conditions. Preparation of the organics-sandwiched conformal nanowires now becomes possible with recent developments on the ALD deposition of polymers.

6. Summary and Outlook

We briefly introduced the recent progress in our group on void evolution in core–shell nanowires by the nanoscale Kirkendall effect. In all the experiments, we used single-crystalline ZnO nanowires grown by vapor transport as core material.^[26] Different shells such as Al_2O_3 , TiO_2 , and SiO_2 were coated by ALD, which can achieve conformal deposition and precise thickness control. Using coaxial ZnO/ Al_2O_3 core–shell nanowires as an example, we revealed that the initial voids formed at the ZnO/ Al_2O_3 interface originate from the one-way migration of ZnO into the Al_2O_3 shell. The dynamics is accelerated at 700 °C, favored by the surface diffusion of ZnO along the present void surface. Completely hollow ZnAl_2O_4 nanotubes can be formed at this temperature, provided that the ZnO core is totally consumed by the solid–solid reaction. Recently, formation of coaxial ZnAl_2O_4 microtube nanolaminated assemblies was achieved by a so-named bi-directional Kirkendall effect based on the same ZnO/ Al_2O_3 system and a very similar ALD deposition and subsequent annealing procedure.^[27]

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 spinel nanotubes. We especially emphasized the difference between diffusion and desorption, both of which can contribute to formation of hollow structures. However, the latter has no direct relation to the Kirkendall effect.

Furthermore, we investigated the effect of stress and defects on void nucleation during solid–solid reactions through the nanoscale Kirkendall effect. Based on a stress-assisted diffusion process, new ZnO/ ZnAl_2O_4 nanostructures with positioned large interfacial nanocavities

were fabricated. In the last example demonstrated here, the presence of a thin gold layer sandwiched at the ZnO/ SiO_2 interface introduced many “artificial” interfacial defects during the solid–solid reaction, which facilitated the formation of Zn_2SiO_4 nanotubes.

Our results demonstrate that the stress- and defects-engineered diffusion mechanism, in combination with the Kirkendall effect, can be used to specifically design hollow nanostructures. This void engineering strategy can be further extended to other thermal diffusion couples. In our current work, all the produced ZnO-based ternary oxides are either wide bandgap semiconductors or typical phosphorous materials. Due to a large surface-to-volume ratio and symmetry breaking on the surface, the 1D nanoscale ternary oxides with novel properties different from their bulk counterparts are expected to find important applications in catalysis, sensing, and flexible electronic displays.^[26]

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