Metal/Semiconductor Core/Shell Nanodisks and Nanotubes**

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The low melting point of Zn and the high melting point of ZnO, as well as their hexagonal crystal structures, present great advantages for designing and fabricating various metal/semiconductor core/shell nanostructures. By controlling the kinetics in the Zn and ZnO system, the lower-energy facets, and the oxidation rates of different surfaces, we can control the fabrication of Zn/ZnO core/shell single-crystal, polycrystalline, and mesoporous nanodisks, as well as a variety of ZnO nanotubes. The oxidation of a Zn nano-object leads to the formation of Zn/ZnO core/shell nanodisks. A lower oxidation temperature results in the formation of a single-crystal-like Zn/ZnO core/shell structure, while a higher oxidation temperature leads to the formation of textured and even polycrystalline nanostructures. A re-sublimation process of Zn in the core leaves a ZnO shell structure. This is an approach for synthesizing metal/semiconductor core/shell or composite nanostructures. This article offers a detailed description of the kinetics controlling the procedures, the nanostructures obtained, their morphological and crystal structures, and their formation mechanisms.

1. Introduction

Zinc oxide is an important functional material possessing semiconductivity and piezoelectric and pyroelectric properties.[1-4] As a semiconductor, its direct bandgap is as wide as 3.37 eV, equivalent to that of GaN. Together with a large excitation binding energy (60 meV), it exhibits near-UV emission and transparent conductivity at room temperature and above. Its non-central symmetrical crystallographic structure leads to piezoelectricity as well as pyroelectricity, which make it a promising candidate for building electromechanically coupled sensors and transducers. The design and rational control of the synthesis of functional nanostructures with different morphological configurations is the cornerstone for further utilizing nanoscale building blocks for multifunctional nanodevice systems.

ZnO has a wurtzite structure with a hexagonal unit cell. Owning to the three fastest growth directions, <0001>, <0110>, and <2110>, as well as the ±(001) polar surfaces induced phenomenon, a diverse group of ZnO nanostructures has previously been grown for ZnO, including nanowires/nanorods,[6,8] nanotubes,[7,10] nanobelts,[11] nanosprings,[12] nanohelixes,[13] nanorings,[14] nanobowls,[15] nanopropellers,[16] nanodisks,[17,18] nanoplatelets and sheets,[19] etc. Wet chemistry and solid–vapor processes are the two main approaches for synthesizing ZnO nanostructures. ZnO probably has the richest family in the entire field of one-dimensional (1D) nanostructures, including carbon nanotubes. The synthesis and understanding of the growth of ZnO nanostructures and their applications are at the leading edge of today’s research in nanotechnology.

The partner of ZnO in this work, metallic Zn, also has a hexagonal structure. Also of importance is that ZnO tends to grow epitaxially on the surface of Zn via an oxidation process, forming Zn/ZnO metal/semiconductor core/shell structures.[20,21] In this work, by using a solid–vapor synthetic approach, and taking advantage of selective oxidation on the surfaces of the as-formed Zn nanostructures, we present the synthesis, structure, and growth process of various Zn/ZnO core/shell nanostructures, from single crystal nanodisks, polycrystalline nanodisks, and mesoporous nanodisks, to a variety of ZnO nanotubes. The results suggest that, by controlling the oxidation process, different morphological configurations of metal/semiconductor core/shell nanostructures can be produced. The newly synthesized nanostructures, composed of textured and aligned nanocrystallites of ZnO, could be fundamental building blocks for fabricating piezoelectric resonators and sensors.

2. The Structure of Zn and ZnO

Zinc is a metallic element with a low melting point of 419 °C, and a vaporization point of 907 °C in atmosphere.[22] It has a hexagonal crystal structure with lattice constants of $a = 0.2665$ and $c = 0.4947$ nm. It has the following low energy facets: {0110}, {2110}, and {0001}. Naturally, it can form faceted structures, such as hexagonal rods/wires, enclosed by the six crystallographic equivalent {0110}/{2110} side facets and with {0001} facets at the ends.[23]

Zinc oxide has a wurtzite structure with a hexagonal unit cell (space group P6₃mc) and lattice parameters $a = 0.3296$ and $c = 0.5206$ nm.[24] ZnO is dominated by ionic bonding and its structure can be simply described as a number of alternating

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[2] We thank the NSF (grant DMI 0403671), the NASA Vehicle Systems Program, the Department of Defense Research and Engineering (DDR&E), and the Defense Advanced Research Projects Agency (Award No. N66001-04-1-8903) for their support.
planes composed of tetrahedrally coordinated O$^{2-}$ and Zn$^{2+}$ ions, stacked alternately along the c axis. The tetrahedral coordination in ZnO results in a non-centrosymmetric structure that is responsible for piezoelectricity. Another important characteristic of ZnO are the polar surfaces that are produced by the net ionic charges of the Zn$^{2+}$-terminated facets and O$^{2-}$-terminated surfaces. The most common polar surfaces are the basal planes [0001],[25,26]

Owing to the similar hexagonal crystal structures of Zn and ZnO, ZnO tends to have an epitaxial orientation relationship with the Zn base crystal during oxidation, resulting in Zn/ZnO core/shell structures.[19,20] However the large lattice mismatch of 23.7% in the basal plane makes it impossible to form large ZnO crystals covering the Zn surface. Instead, ZnO nanocrystals are formed as islands, preserving the same orientation as the Zn crystal, and gaps/ pores are left between the nanocrystals owing to large local mismatch strain. Understanding of this process has led to the successful fabrication of the textured, self-assembled ZnO nanocages reported previously.[20] This process will be used herein to illustrate the formation of Zn/ZnO as well as ZnO nanostructures.

Our synthesis is based on a solid–vapor phase process. Different synthetic conditions were chosen to obtain different morphological structures. It is, however, striking to discover that, based on a similar physical deposition, controlling experimental conditions can produce a series of ZnO configurations, such as nanodisks and nanotubes. Detailed results and discussion follow.

3. ZnO Nanodisks

By tuning the synthetic parameters in this study, various configurations of disk-like ZnO nanostructures were achieved. The vapor-phase-transport synthetic parameters are: the source materials, ZnO powders + graphite; the evaporation temperature, 1100–1150 °C; the vaporization time at the peak temperature, 30–60 min; the time pause for 0–10 min at 1000 °C (this step was designed for a comparative study with tubular nanostructures, to be presented in Section 4) during the cooling process; and the pressure, 20–400 mbar (1 bar = 10$^5$ Pa). In the temperature zone we are interested in, disk-like nanostructures were observed to be aggregated into clusters. The observed ZnO nanodisks can be classified into four types of morphology, with slightly different composition: textured core/shell Zn/ZnO nanodisks, “single-crystal-like” textured ZnO nanodisks, nanostructured polycrystalline ZnO disks, and mesoporous ZnO disks. The as-deposited samples were collected at a temperature range of 400 to 600 °C.

3.1. Textured Zn/ZnO Core/Shell Nanodisks

In a typical synthesis, evaporating a mixture of ZnO and graphite at 1100°C for 30 min (pressure controlled around 20 mbar) resulted in textured disk-like ZnO and core/shell Zn/ZnO nanoparticles (Figs. 1–4). It is worth noting that this process had high reproducibility and high yield.

Figures 1a–d are a series of scanning electron microscopy (SEM) images displaying the disk-like ZnO nanostructure. A low-magnification SEM image of the densely grown disks with uniform size of 1–2 μm is illustrated in Figure 1a. These disks are always connected to zigzag-shaped nanowires. The side-view, magnified image of a ZnO nanodisk in Figure 1b clearly demonstrates that each disk has a regular hexagonal-faceted

![Figure 1](image-url)
Figure 2. a) TEM image of two overlapping hexagonal nanodisks and b) the corresponding single crystal [0001] diffraction pattern from a disk. c,d) TEM images of nanowires growing out of the top and side surfaces of a ZnO disk.

Figure 3. a,b) Bright-field and corresponding dark-field TEM images, respectively, of a Zn/ZnO core/shell nanodisk composed of ZnO nanocrystals.  c) The corresponding diffraction pattern of the nanodisk, which is composed of two sets of [0001] diffraction spots from Zn and ZnO, respectively, showing their epitaxial orientation relationship. d) HRTEM image from the disk showing 2D Moiré fringes.  e) HRTEM lattice image displaying the side wall of the ZnO and the middle Zn core, where the two arrowheads point out the interface between the Zn core and ZnO shell.

Figure 4. a) HRTEM image recorded from a Zn/ZnO disk.  b,c) Fourier-filtered images of (a) showing the lattices from the Zn core and ZnO shell, respectively.

Normally emerging nanowire could also extend from the side edge of the hexagonal nanodisk (as displayed in Fig. 1c). In general, one surface of the nanodisk is rather smooth, while the other side is rough. The diameter of the nanodisk could be as small as 300 nm, and its thickness could be as little as 50 nm. The cross-section of the extended nanowire could also be irregular. Figure 1d shows a nanowire grown directly from the edge in the plane of the hexagonal disk (as pointed out by the arrowhead). The X-ray diffraction (XRD) spectrum of the as-prepared sample is shown in Figure 1e, which shows that the majority of the peaks come from ZnO and Zn, whose diffraction peaks are marked by “▲” and “◇”, respectively. The extra peaks were contributed by the alumina substrate used to collect the sample.

To determine the crystal structure of an individual nanodisk, systematic transmission electron microscopy (TEM) imaging and diffraction analysis was conducted. Figure 2a is a TEM image of two hexagonal nanodisks of ~3 μm in width. The corresponding electron diffraction pattern in Figure 2b is a single-crystal [0001] pattern of ZnO, which reveals that the top and bottom surfaces of the nanodisk are a pair of (0001) and (0001) c planes, while the six side facets are [0110]. Figure 2c is a TEM image showing a ZnO nanodisk with three normally extended nanowires from the edge of the side surface (A), the center of the bottom rough surface (B), and the edge of the opposite side surface (C). The size of the nanodisk is about 600 nm. The top view of a 2 μm nanodisk in Figure 2d displays two nanowires extending from the edge of the nanodisk.

Further TEM analysis was conducted to investigate the fine structure in the nanodisk. Figure 3a is a bright-field TEM image of a nanodisk, which shows that the dominant surface of the disk is rough. The corresponding dark-field TEM image in Figure 3b clearly demonstrates the surface roughness, where the thickness of the disk is 100–200 nm. It is indicated by a white arrowhead in Figure 1b that an extended nanowire with a similar hexagonal cross-section grew normal to the hexagonal nanodisk in the center area. It was also found that the
nanocrystals were exposed. The diffraction pattern is composed of two sets of [0001] diffraction patterns corresponding to elemental Zn and ZnO, between which an epitaxial orientation relationship is preserved. Figure 3d is a high-resolution (HR)TEM image recorded from the middle part of the nanodisk in Figure 3a. The image depicts a two-dimensional (2D) Moiré pattern with the electron beam parallel to the c axis of the two overlapping Zn and ZnO lattices. Considering that a Moiré fringe pattern is produced by two sets of parallel overlapped lattice planes of Zn and ZnO, respectively, there are three sets of intersecting Moiré fringes; every individual pattern is rotated with respect to the other by 60°, forming the Moiré pattern shown in Figure 3d. This is due to the epitaxial orientation relationship between Zn and ZnO, as well as the perfect alignment of the c axes. Considering the lattice mismatch between Zn and ZnO, the interfringe spacing of the Moiré pattern is about 1.30 nm, which corresponds to one Moiré fringe every 4.6 atomic planes of ZnO or 5.6 atomic planes of Zn. An HRTEM image from the edge of the hexagonal nanodisk is shown in Figure 3e. The lattice image displays the interface between the Zn core and ZnO shell, as indicated by two arrowheads. The upper part of the image reveals the lattice image of the ZnO shell, while the bottom part corresponds to the elemental Zn core. The ZnO shell is 1.5–2 nm thick.

To investigate the lattice structure at the Zn/ZnO interface further, the HRTEM image was digitally processed. By taking a Fourier transform of the raw image displayed in Figure 4a, selecting only the reflections from Zn and ZnO, two sets of images, corresponding to Zn and ZnO, respectively, are presented in Figures 4b,c. The Zn lattice is almost perfect, without much distortion, owing to the fact that Zn was the “mother” crystal formed first at the core. The ZnO was formed via oxidation, so the lattice exhibits imperfection due to the multiple nuclei of the oxide grains on the surface. Mismatch dislocations and strains are apparent in the lattice image of the thin ZnO shell (see Fig. 4c).

3.2. Nanostructured Polycrystalline ZnO Disks and Mesoporous ZnO Disks

To investigate the effect of pressure variation on the formation of ZnO nanodisks, we increased the pressure from the original 20 mbar to 200 mbar, and kept the other parameters as described in Section 3.1. It was interesting to discover that similar hexagonal disk-like nanostructures of ZnO were grown in clusters in the temperature range 400–600 °C. Typically, three types of nanodisk were observed under SEM as the substrate temperature increased from 400 to 600 °C: single crystal ZnO nanodisks, polycrystalline nanodisks, and mesoporous nanodisks.

Figure 5a shows a cluster of densely packed ZnO nanodisks, found in the 400 °C area, which have a uniform size of around 5 μm. Between the nanodisks are many tiny nanowires. The magnified SEM image in Figure 5b clearly shows that the thickness of each nanodisk is about 10 nm. Figure 5c shows that on one large surface of a nanodisk, secondary growth of nanowires is clearly visible (as indicated by the arrowhead). The typical low-magnification TEM image in Figure 5d is a front projection view of a ~5 μm wide nanodisk. The corresponding enlarged image of the left corner of the nanodisk in Figure 5e reveals its grainy and patch-dominated surface, an indication of a possible polycrystalline structure. In Figure 5f, the corresponding electron diffraction pattern shows the surface to be textured by self-assembled ZnO nanocrystals that are approximately oriented in the same direction.

As the local growth temperature increased to ~500 °C, the morphology and structure of the disks changed. In Figure 6a, it is shown that more densely packed ZnO nanodisks/nanowires form a large cluster with a flower-like morphology. The nanodisks tend to be wavy (Figs. 6b,c) instead of the flat nanodisks collected in the low 400 °C temperature region (Figs. 5b,c). To determine if the nanodisks still kept the single-crystal-like textured structure, TEM results are displayed in Figures 6d,e. Figure 6d is a TEM image showing two curved nanodisks with a diameter around 10 μm; between
them there are quite a few Zn nanowires. The difference between Zn and ZnO nanowires is that the former are curly and the latter are straight. The selected-area electron diffraction pattern shown in Figure 6e is from a local, small part of a curly nanodisk. The ring pattern clearly shows that the nanodisk is made of nanocrystallites that are randomly oriented. This is very different from the single-crystal-like textured structure of the nanodisks collected in the lower-temperature zone.

As the local temperature increased to ~600 °C, it was found that mesoporous nanodisks were the dominant morphological configuration. Figures 7a,b show two low-magnification SEM images of the mesoporous nanodisks, which retained a uniform hexagonal shape. The disks were as thin as tens of nanometers, and the pores were ~50 nm in diameter. Figures 7c,d are respectively the TEM image and the corresponding electron diffraction pattern of a mesoporous nanodisk. The mesoporous feature is apparent, where the nanometer-sized grains are uniformly distributed and interconnected to form a “net-like” structure. The electron diffraction pattern proves the random orientation of the nanocrystallites that compose the mesoporous disk.

**Figure 6.** a) A flower-like cluster of packed ZnO nanodisks interconnected by nanowires. b) A magnified SEM image showing flower-like nanodisks with curved, large surfaces. c) Curved flakes of nanodisks with a uniform thickness as thin as ~30 nm. d) A typical TEM image of two curved nanodisks with nanowires surrounding them. e) The corresponding electron diffraction pattern revealing the polycrystalline structure of the curved nanodisk.

**Figure 7.** a,b) Mesoporous nanodisks with a uniform hexagonal shape, small thickness (tens of nanometers), and porous structure. c,d) TEM image of a mesoporous nanodisk and its corresponding electron diffraction pattern, respectively. The inset in (c) is a magnified TEM image showing the pores with a size about 50 nm.

### 3.3. Growth Mechanism of ZnO Nanodisks

In previous work on the textured polyhedral ZnO shell and cage structures,[29] the formation mechanism has been proposed to be a process composed of the solidification of liquid droplets, surface oxidation, and sublimation. In our current work, similarly, epitaxial oxidation on Zn surfaces is the fundamental process of forming the core/shell structure. Graphite was introduced into the raw materials to reduce the oxides into metals, as shown by Equation 1

\[ 2\text{ZnO(s)} + \text{C(s)} \rightarrow 2\text{Zn(g)} + \text{CO}_2(g) \]  

(1)

The sublimed Zn atoms are carried downstream by the Ar carrier gas. In the lower-temperature region, Zn atoms condense and form liquid clusters (as schematically shown in Fig. 8a), which tend to deposit fairly uniformly onto the alumina substrate. The liquid droplets quickly solidify on the substrate in the deposition temperature zone 400–600 °C. From a surface-energy point of view, the lowest energy facets for Zn are \( \{0001\} \), and then \( \{10\bar{1}0\} \) and \( \{2\bar{1}\bar{1}0\} \). Thus, faceted, single-crystalline Zn hexagonal disks tend to form, which are enclosed by \( \{0001\} \) top and bottom surfaces and \( \{10\bar{1}0\}/(2\bar{1}\bar{1}0) \) side surfaces, as shown in Figure 8b. Considering the lower local growth temperature, the residual oxygen in the growth cham-
Figure 8. Proposed growth model of the ZnO nanodisk (see text for details).

ZnO(s) → ZnO(g)  

Equation 2

At the lower-temperature region of ~400 °C, epitaxial surface oxidation is the major contributor to the growth of textured Zn/ZnO disks and ZnO disks. The difference between textured Zn/ZnO disks and ZnO disks is the degree of oxidation, whether incomplete or complete. Since the local temperature is low, a slow oxidation is likely, and a strong interaction with the Zn core is possible, resulting in a single-crystal-like structure (see Figs. 1–4).

On increasing the local growth temperature to ~500 °C, the oxidation rates are likely to be higher, resulting in a quick formation of larger ZnO nanocrystallites, and a non-uniform thickness of the ZnO nanodisks (Fig. 8c,II). In this case, the deposition of the ZnO vapor may become significant. It may directly deposit on the surfaces of the ZnO nanocrystals or form new nanocrystals on the nanodisks; thus, the epitaxial growth of ZnO nanocrystals is partially terminated because of the quick surface oxidation and the re-deposition of ZnO vapor at a faster rate, forming nanostructured polycrystalline objects (see Fig. 5).

When the local temperature is as high as ~600 °C, a resublimation of Zn is possible; the sublimation rate of Zn nanodisks may be so fast that the deposition of polycrystalline and nanostructured ZnO is not enough to cover the entire surface of the original Zn nanodisk. The areas covered or oxidized into ZnO are preserved, while the uncovered areas are resublimed, leaving behind a polycrystalline ZnO “skeleton” and the formation of holes or pores in the body of the nanodisks (Fig. 8c,III). In this case, mesoporous structured ZnO is formed (see Fig. 7).

The growth pressure could have a significant effect on the nanostructure morphology. Figures 1–4 and Figures 5–7 are the data acquired when the pressure in the growth chamber was set at 20 and 200 mbar, respectively. At 20 mbar, the limited amount of residual oxygen makes the temperature variation a dominating effect for the selective surface-oxidation process, leading to a morphological transition from Zn particles (non-oxidized), to Zn/ZnO core/shell textured nanodisks (incomplete selective oxidation), to textured (single-crystal-like) ZnO nanodisks (complete selective oxidation) in the temperature zone 400–600 °C. When the growth pressure was changed to 200 mbar, the amount of residual oxygen became significant, and the selective-oxidation process could be fully completed across the entire temperature range. However, the temperature variation became a dominant effect on the structural transition of the ZnO nanodisks, from textured, polycrystalline, to mesoporous and polycrystalline. In this transition process, excess oxygen led to the direct deposition of ZnO from the vapor phase. The epitaxial growth of ZnO shells on Zn nanodisks may be terminated, owing to the simultaneous deposition of randomly oriented ZnO nanocrystals on the selectively oxidized Zn base crystal. When the temperature reached 500 °C, the fast sublimation of Zn resulted in a mesoporous structure of polycrystalline ZnO nanodisks.

4. Microtubes, Nanotubes, and Nanotube Arrays of ZnO

4.1. ZnO Microtubes and Nanotubes

We now examine how the oxidation rate of Zn depends on the surface energy. To find out how the temperature influences the growth rate of different facets, the duration time at different temperatures was varied—the duration at 1150 °C was shortened to 5 min, and extended to 60 min at 1000 °C. The flow rate of Ar was 25 sccm, and the pressure was ~400 mbar. In this case, the growth at 1000 °C would be dominant. In a similar deposition area to where the nanodisks were collected, it was interesting to find that short microtubes were formed with clean, hexagonal-faceted surfaces. Figure 9a shows a top-side view of a typical hexagonal tube of ZnO approximately 3–5 µm in length, 2–3 µm in width, and with a wall thickness of ~200 nm. The enlarged open end of the tube is illustrated in
Figure 9. A series of SEM images displaying individual short microtubes with rough outer and inner surfaces. a,b) Low-magnification SEM images showing the outer hexagonal faceted surfaces and the inner rough and stepped surfaces of the ZnO tubes. c,d) Two short, micrometer-sized tubes with hexagonal facets.

Figure 9b, where the inner surface of the tube is stepped, rough, and without facets, revealing the possible sublimation process of the material from the center. Figure 9c displays the front view of a ZnO tube ~2 µm wide and ~4 µm long, with a rather sharply delineated inner surface, and the hexagonal facets are clean but not perfect. In Figure 9d, a tube ~4 µm high and ~4 µm in diameter is shown. The hollow core of the tube can be clearly seen, where the inner diameter at the entrance is larger than that in the middle of the tube, suggesting that the original material filling the core was not completely sublimed. It is evident from Figure 9 that the template for forming the tube was an hexagonal Zn rod; the oxidation of the surface formed the walls of the tube, and the re-sublimation of the Zn core created the hollow center.

At a higher deposition area, despite no visible trace of Zn core, sublimation was suggested—by the inset nanotube-tip in Figure 10a—and it is possible that lack of oxidation led to formation of only an incomplete shell. The sublimation of Zn was started, but not completed, leaving shallow microtube arrays with irregular shapes (Fig. 10a). The nanotubes were 50–100 nm long. Figure 10b gives a good illustration of randomly oriented, tubular-like structures of ZnO. Again, the enlarged nanotube in the inset has a clear trace sublimation in the inner surface, which is curved and stepped.

Similarly, upon adjusting the pressure to 300 mbar, more uniform nanotube arrays of ZnO were formed. As shown in Figures 11a,b, two rows of ZnO nanotube arrays with shallow entrance holes were grown. The “nanotubes” have a uniform diameter of 80–100 nm. A front view of a nanotube is shown in Figure 11c; the faceted outer surface and rougher inner surface are clearly observed.

Figure 10. a) An interconnected, irregular shaped nanotube array of ZnO. Inset shows the early stages of nanotube formation. b) Irregular shaped nanotubes in the form of clusters. The inset is a nanotube with hexagonal inner surface.

Figure 11. a) SEM image showing a uniform array of hexagonal ZnO nanotubes about 200 nm in diameter. b) Randomly distributed ZnO nanotubes around 100 nm in diameter grown on as-deposited micrometer-sized ZnO islands. c) A front-view SEM image showing the hexagonal cross-section and hollow inside of several nanotubes rooted on a ZnO island.
Further adjustment of the pressure to ~200 mbar in the synthesis led to the growth of high-quality tubular structures. As shown in Figure 12, four individual micrometer-sized tubes of ZnO are illustrated. Figures 12a,b show two microtubes with irregular shaped cross-sections. Figure 12a displays a microtube with a possible circular cross-section, and a rough side surface.

The stepped inner surface of the microtube in Figure 12b revealed that, despite a possible single-crystal structure, the formation of microtube still follows a possible sublimation process of core materials (see Section 4.3). Figures 12c,d give a more clear depiction of two intact, smooth, long freestanding microtubes of ZnO, which should be single crystals. Two typical TEM images showing a Zn/ZnO core/shell nanocable and a ZnO nanotube with residual Zn core inside are respectively displayed in Figures 12e,f. The diameters of both the nanocable and nanotube are 50–100 nm. The residual Zn inside the tube and inner wall is apparent in Figure 12e. The inset select-area nanodiffraction patterns indicate that they are single crystals with the same orientation, and that they grew along the c axis.

4.2. ZnO Nanotube Arrays on ZnO Cages

As illustrated above, the low melting point of Zn and the high melting point of ZnO have given us hints for the controllable design and fabrication of various functional, nanostructured ZnO nano-objects. Controlling the growth kinetics would allow us to control the formation process of the Zn/ZnO system. Lower-temperature synthesis of 1D ZnO nanostructures is very attractive, because it offers the hope of integrating the process with other synthetic and fabrication processes. Here, we demonstrate the case of the synthesis of nanotube arrays on large shells.

In the deposition region at a growth temperature of around 450 °C, ZnO nanotube arrays on ZnO cages were observed, as shown in Figure 13a. Microspheres of ZnO with sizes ranging between 10 and 50 µm grew freestanding on alumina substrates. Radical branched needles surround the central microsphere (Fig. 13b). A broken microsphere in Figure 13c reveals that the microsphere is a hollow, shell-like structure, inside which radially distributed nanotube arrays with a uniform diameter of ~1.5 µm grew directly out of the inner-cage surface. The outer surface of the ZnO cage is covered by radially extruding nanotube arrays of ZnO (Fig. 13d). Further close examination of the inner surface of ZnO cage found that, besides the hexagonal nanotubes, some wavy ZnO nanowalls are present. A typical TEM image of a broken nanotube from a hollow ZnO cage is shown in Figure 13f, where the hollow interior is...
in a visible bright contrast. Its corresponding electron diffraction pattern, shown in the inset (bottom), proves its single-crystal growth along the [0001] direction.

It is interesting to discover that the outer surfaces of some ZnO cages are enclosed by regularly arranged, hexagonal, pyramid-like domains; the six intersection lines of the pyramid are visible from the front (Fig. 14a). Each pyramid is about 2 μm wide and 1–1.5 μm high. On the tip of each ZnO pyramid, there is usually a single, outstanding nanorod ~300 nm wide and ~600 nm high (Figs. 14b,c). A single nanotube, with a diameter of ~200 nm was sometimes observed at the tip of the pyramid (Fig. 14d) in place of the nanorod.

![Figure 14. a–c) A series of SEM images displaying a collection of hexagonal-based pyramids of Zn/ZnO. On each island there is only one nanorod or nanotube grown on its top. d) A closer image of a nanotube at the tip.](image)

**4.3. Growth Mechanism of ZnO Microtubes and Nanotubes**

Three important factors are dealt with in this study: the kinetics in the Zn and ZnO system, the lower energy facets, and the oxidation rates of different surfaces. The oxidation rates on different crystal surfaces as well as in different temperature regions are distinct. The Zn surface with the lowest energy, such as the [0001] planes, tends to be the most stable, and may resist oxidation, while the higher-energy surfaces, such as [1010], are likely to have a higher oxidation rate. It is evident from the above experimental results that the selective and epitaxial oxidation growth of ZnO on a Zn rod is an effective way to design and synthesize tubular nanostructures of ZnO in dimensions ranging from nanometers to micrometers.

Similar to the growth mechanism proposed in Section 3.3 for ZnO nanodisks, a growth mechanism for ZnO nanotubes is illustrated in Figure 15. The first step (Fig. 15a) is still the necessary vapor-transfer of reduced Zn droplets by Ar gas to the deposition area where the temperature is ~400–500 °C. A faster growth along the c axis direction leads to the formation of hexagonal-based Zn rods (Fig. 15b). Since the Zn [0001] surfaces have lower energy than the [1010]/[2110] surfaces, they are more stable and resistive to oxidation. As a result, the side surfaces of the hexagonal nanorod are oxidized first, forming a ZnO shell. At the same time, since the low melting point Zn also has a lower vaporization temperature, the remaining Zn inside the rod can be re-sublimed through the open ends at the [0001] surfaces, leaving behind a ZnO tube that has relatively smooth facets, as defined by the Zn rod (Fig. 15c). The sublimation may not be complete, thus, the inner surface of the tube is rough, possibly with some residual Zn (see Figs. 9,12). If the sublimation is terminated at an early stage, the structures shown in Figure 11 would be formed.

The growth of the structures in Figures 13,14 are more complex, but they are still governed by the process illustrated in Figure 15. It is likely that a large Zn liquid droplet was deposited on the substrate, which was too large to be a single crystal, thus, a polycrystalline Zn ball was formed, but with many hexagonal pyramids forming on the surface, each of which was initiated from a Zn nuclei. Then, the small quantity of Zn vapor
could deposit on the surface at the tips of the pyramids to reduce the local surface energy, forming a hexagonal rod at the tip. Then, an oxidation and subsequent sublimation process, as illustrated in Figure 15, is possible, forming the tubular structure at the tip (see Fig. 14d).

There is no doubt that the temperature adjustment in Section 4.1 led to the growth of the tubular nanostructures of ZnO. Thus, the relative growth rates of different facets have been varied. The growth of nanostructures along the c axis rather than (1010)/(2110) was enhanced by extending the time at 1000 °C, while shortening the time spent at 1150 °C. A pressure adjustment from 400 mbar to 200 mbar is likely to promote the growth of tubular nanostructures.

5. Conclusions

The low melting point of Zn, and the high melting point of ZnO, along with their hexagonal crystal structures, give great advantages for designing and fabricating various metal/semiconductor core/shell nanowires. We dealt with three important factors in this study: the kinetics in the Zn and ZnO system, the lower-energy facets, and the oxidation rates of different surfaces. By using a solid–vapor synthetic approach, as well as by taking advantage of selective surface-oxidation on the as-formed Zn nano-object, textured ZnO nanostructures were synthesized. The growth and formation processes of single-crystal nanodisks, polycrystalline nanodisks, mesoporous nanodisks, and a variety of nanotubes of ZnO have been discussed. It is suggested that by controlling the oxidation process of different morphological configurations of Zn, different configurations of single crystalline to polycrystalline ZnO nano-/micrometer-scale objects could be achieved. The main conclusions can be summarized as follows:

i) Zinc and ZnO nano-objects can be simultaneously grown in a solid–vapor process. The Zn nanostructure is grown by a vapor–liquid–solid process, while ZnO is formed by a vapor–solid process. The nano-objects are mostly enclosed by the lower-energy facets: [0001], [1010], and [2110].

ii) The oxidation rate of the Zn surface is high for the [1010] and [2110] surfaces, but rather low for the [0001] surfaces.

iii) The oxidation of the Zn nano-object leads to the formation of Zn/ZnO core/shell nanodisks. A lower oxidation temperature results in the formation of a single-crystal-like Zn/ZnO core/shell structure, while a higher oxidation temperature leads to the formation of textured, and even polycrystalline, nanostructures. This is an approach for synthesizing metal/semiconductor core/shell or composite nanowires.

iv) Surface oxidation of the Zn nano-object and subsequent sublimation of the Zn core result in the growth of ZnO cage/shell/tube structures.

6. Experimental

The synthesis of ZnO nanodisks and nanotubes is based on a solid–vapor process by thermally vaporizing a source material, which is a mixture of ZnO powder and a reducing reagent, such as graphite powder. The source material was placed at the highest temperature zone of a horizontal tube furnace. Before heating to the desired temperature of 1100–1150 °C, the tube furnace was evacuated to ~10⁻¹ torr (1 torr = 133.322 Pa) to remove residual oxygen. During the synthesis, the Ar carrier gas was introduced at a flow of 25 scm. The products were deposited onto a polycrystalline alumina substrate placed in a lower-temperature zone under an Ar pressure of 10–300 torr. The duration time at 1100–1150 °C was 5–60 min. Upon cooling, a pause at 1000 °C for 0–60 min was conducted. Any variation in growth conditions is specified where different nanostructures are presented in the text.

For the synthesis of nanotube arrays on ZnO cates, a low-temperature synthetic method was used. Zn powder (~2 g) as the source material was placed at the peak-temperature region of a horizontal tube furnace. The temperature was controlled at 550–600 °C, pressure ~10 mbar, Ar flow rate: 10 scm, O₂ flow rate: 3 scm, and duration held at peak temperature ~2 h.

Field-emission (FE)SEM (field-emission TEM Hitachi HF-2000 at 200 kV and JEOL 4000EX high-resolution (HR)TEM at 400 kV), XRD (Philips PW 1800 with Cu Kα radiation), and energy-dispersive X-ray spectroscopy attached to the SEM and TEM, respectively, were used to investigate the morphology, crystal structure, and composition of as-grown nanostructures.

Received: May 16, 2005

By controlling the kinetics in the Zn/ZnO system, the lower energy facets, and the oxidation rates of different surfaces, Zn/ZnO core/shell single-crystal, polycrystalline, and mesoporous nanodisks, as well as a variety of nanotubes of ZnO can be fabricated (see Figure). The kinetics controlling the procedures and the formation mechanisms of the nanostructures are reported.