



## Facilitating ZnO nanostructure growths by making seeds for self-catalytic reactions

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### ARTICLE INFO

#### Article history:

Received 26 September 2011

Received in revised form

14 December 2011

Accepted 26 December 2011

Available online 4 January 2012

#### Keywords:

Zinc oxide

Nanowire

Thermal annealing

Tetrapod

### ABSTRACT

Long and straight single-crystalline ZnO nanowires were successfully synthesized on ZnCl<sub>2</sub>-coated Zn foils in oxygen environment by using simple thermal annealing processes. With relatively low reaction temperatures (410 and 700 °C), nanowires whose lengths and diameters are up to ~50 μm and 10–100 nm were obtained. We found that ZnO seeds created from ZnCl<sub>2</sub> played an important role in facilitating the ZnO nanowire growth via self-catalytic reactions. Systematic studies by altering critical synthesis factors that determine shape, length, diameter, and density of the nanowires were performed in order to unveil the growth mechanisms. We also compared the nanowires synthesized from Zn foils with tetrapod ZnO nanostructures synthesized from Zn powders at various temperatures.

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### 1. Introduction

ZnO is an important semiconducting and piezoelectric material that has great potentials in the field of molecular electronics, optoelectronics, piezoelectric sensors, transducers, and resonators [1–9]. For example, its piezoelectric properties are suitable for sensor and actuator applications due to a large electromechanical coupling and the lack of the central symmetry in the wurtzite structure. It is a semiconductor that is transparent to visible light but can be made electrically conductive by doping Mn, Al, Ti, Cd, Se, Ga, and N [8,10,11]. One-dimensional (1D) ZnO nanostructures such as nanotubes and nanowires have been synthesized by using several different methods [10]. For example, Zn or ZnO powders could be evaporated to obtain ZnO nanostructures at relatively high temperature (over ~900 °C) by using thermal annealing [12,13]. Aligned ZnO nanowires were grown on sapphire substrate with Au/Sn as a catalyst via a vapor–liquid–solid (VLS) method [9,10,14]. A low-temperature hydrothermal method was also used to grow short (2–8 μm) ZnO nanowires [15]. With relatively low synthesis temperatures below ~500 °C, wire-like structures are typically shorter than several microns or/and require a long reaction time (more than several hours) with a relatively low number density [16]. It is necessary to use high temperatures up to ~1400 °C [12] to grow long wire-like

structures. In addition, tetrapod structures instead of wire shapes were often obtained at temperatures below 1000 °C. There have been several papers regarding the growth mechanisms of these nanostructures but they do not clearly provide the mechanisms with experimental results [17–21].

In this study, we present a simple method that facilitates ZnO wire growths from Zn foils. This method employs a thermal annealing process in oxygen at relatively low temperatures such as 410, 700, and 850 °C. With the 700 °C growth temperature, relatively long nanowires whose lengths and diameters are ~50 μm and ~100 nm were obtained in 60 min. The growth rate is high, which is estimated to be ~800 nm/min. At the higher temperature, 850 °C, long (~100 μm) microwires (diameter ~1 μm) with rough surfaces were synthesized. We found that nanowire synthesis was significantly improved by using ZnCl<sub>2</sub>, which played an important role in creating nucleation sites for growing long straight nanowires. The length, diameter, and density of ZnO nanowires were controlled by varying annealing temperature and time. Furthermore, we obtained tetrapod structures by using the same annealing conditions from only Zn powders (without ZnCl<sub>2</sub> or other chemicals other than oxygen gas). These nanostructures were compared to identify the growth mechanisms that initiated such dramatic morphology differences.

### 2. Sample preparation and experimental procedures

Zinc foils (Sigma-Aldrich, purity 99.9%) were diced into pieces (~1.5 cm × 1.5 cm × 0.2 mm), and then ultrasonically cleaned in

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**Table 1**

Twelve different synthesis conditions to obtain ZnO nanostructures with Zn foils or Zn powders. ZnCl<sub>2</sub> was dissolved in water and spin-coated on the selected foils.

Synthesis condition	Annealing temperature (°C)	Annealing time (min)	Zn	ZnCl <sub>2</sub>
1	410	120	Foil	Spin coating
2	410	120	Foil	–
3	700	60	Foil	Spin coating
4	700	60	Foil	–
5	850	60	Foil	Spin coating
6	700	10	Foil	Spin coating
7	700	30	Foil	Spin coating
8	850	30	Powder	–
9	800	30	Powder	–
10	700	30	Powder	–
11	500	30	Powder	–
12	500	5	–	Spin coating

acetone, isopropanol, and deionized (DI) water, respectively. A catalyst solution was prepared by dissolving ZnCl<sub>2</sub> (Fisher Scientific, purity 97.8%) in DI water with a concentration of 5 mM. Then, the solution was spin coated several times at 1500 rpm for 20 s. The spin-coating process uniformly distributes tiny ZnCl<sub>2</sub> particles on the foil surface, serving seeds for growing nanowires. In addition, Zn powders (Fisher Scientific, purity 99.3%) were also used to grow ZnO nanostructures without further treatments.

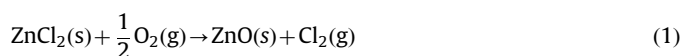
The samples were placed in a quartz or an alumina boat and inserted at the center of a 22-mm inner diameter quartz tube. Prior to heating a tube furnace (Lindberg/Blue M), ~50 sccm O<sub>2</sub> was flowed for 1 min in order to remove air or any residues that might be present in the tube. Subsequently, the furnace was heated up to the target annealing temperatures (see Table 1) at a rate of ~85 °C/min with a continuous ~5 sccm O<sub>2</sub> flow throughout the entire synthesis process. The samples grown by using the synthesis condition 8, 9, 10, and 11 were obtained at the same time while other conditions were experimented separately. The synthesis temperatures at different locations of the furnace tube were calibrated by using a K-type thermocouple. The temperature was 850 °C at the heating center (Condition 8) and ~800 °C in the area between 3 and 4 cm away from the center of the heating zone (Condition 9). The temperature dropped to ~700 and ~500 °C at the locations that are, respectively, 6 cm (Condition 10) and 10 cm (Condition 11) away from the center of the heating zone. At the end of the annealing, the furnace was naturally cooled at a rate of approximately 10 °C/min above ~200 °C and approximately 1 °C/min below ~200 °C [22,23].

Twelve different synthesis conditions were tested as listed in Table 1 for elucidating the influence of synthesis parameters on nanostructure growths and morphologies. The structure and composition of as-grown samples were analyzed by using an X-ray diffractometer (Bruker-AXS D8 VARIO) and a field-emission scanning electron microscope (SEM), FEI Quanta 600. For the X-ray diffraction (XRD) analysis of the samples grown from Zn foils, ZnO was ultrasonically detached from the foil in DI water. Then, the sample-containing solution was dispersed and dried on a quartz substrate several times. The sample was scanned from 2θ=20–80° with a step size and dwell time of 0.01° and 0.1 s, respectively. The nanostructures were detached by sonication in ethanol and then dispersed on grids for further structure analysis in a transmission electron microscope (TEM), JEOL 2010 with selective area electron diffraction.

### 3. Results and discussion

ZnO nanowires were successfully synthesized at 410, 700, and 850 °C (synthesis condition 1, 3, and 5 in Table 1) on the Zn foils

coated with ZnCl<sub>2</sub> as, respectively, shown in Fig. 1a–c. Prior to the annealing process, the Zn foils were smooth and flat. After the annealing process, the surface of the Zn foils became rough and white. It was observed that the length and diameter of the synthesized ZnO nanowires were increasing as the reaction temperature was raised. Nanowires synthesized at 410 °C are relatively short and small (~5 μm in length (*L*), ~50 nm in diameter (*D*)) compared to the nanowires synthesized at 700 °C (*L*~50 μm, *D*~100 nm) and 850 °C (*L*>100 μm, *D*~1 μm). The growth rates are high, which are estimated to be ~800 and ~1700 nm/min for 700 and 850 °C, respectively. The ZnO nanowires synthesized at 850 °C, which is close to the boiling point of Zinc 907 °C [24], have rough surfaces as shown in Fig. 1c. On the other hand, when Zn foils without the ZnCl<sub>2</sub> coating were annealed at 410 (Condition 2) or 700 °C (Condition 4), sparse and very short (~1 μm) nanowires (Fig. 1d, 410 °C) or thick and short nanorods (Fig. 1e, 700 °C) were observed. Without using ZnCl<sub>2</sub>, dense nanowires with long lengths and small diameters have not been obtained. This indicates that ZnCl<sub>2</sub> plays a crucial role in the ZnO nanowire growths. A suggested reaction is described as follows. The spin coating process distributes tiny ZnCl<sub>2</sub> particles on the foil surface. Upon heating, ZnCl<sub>2</sub> decomposes into ZnO and gas-phase Cl<sub>2</sub> above ~230 °C [25]:

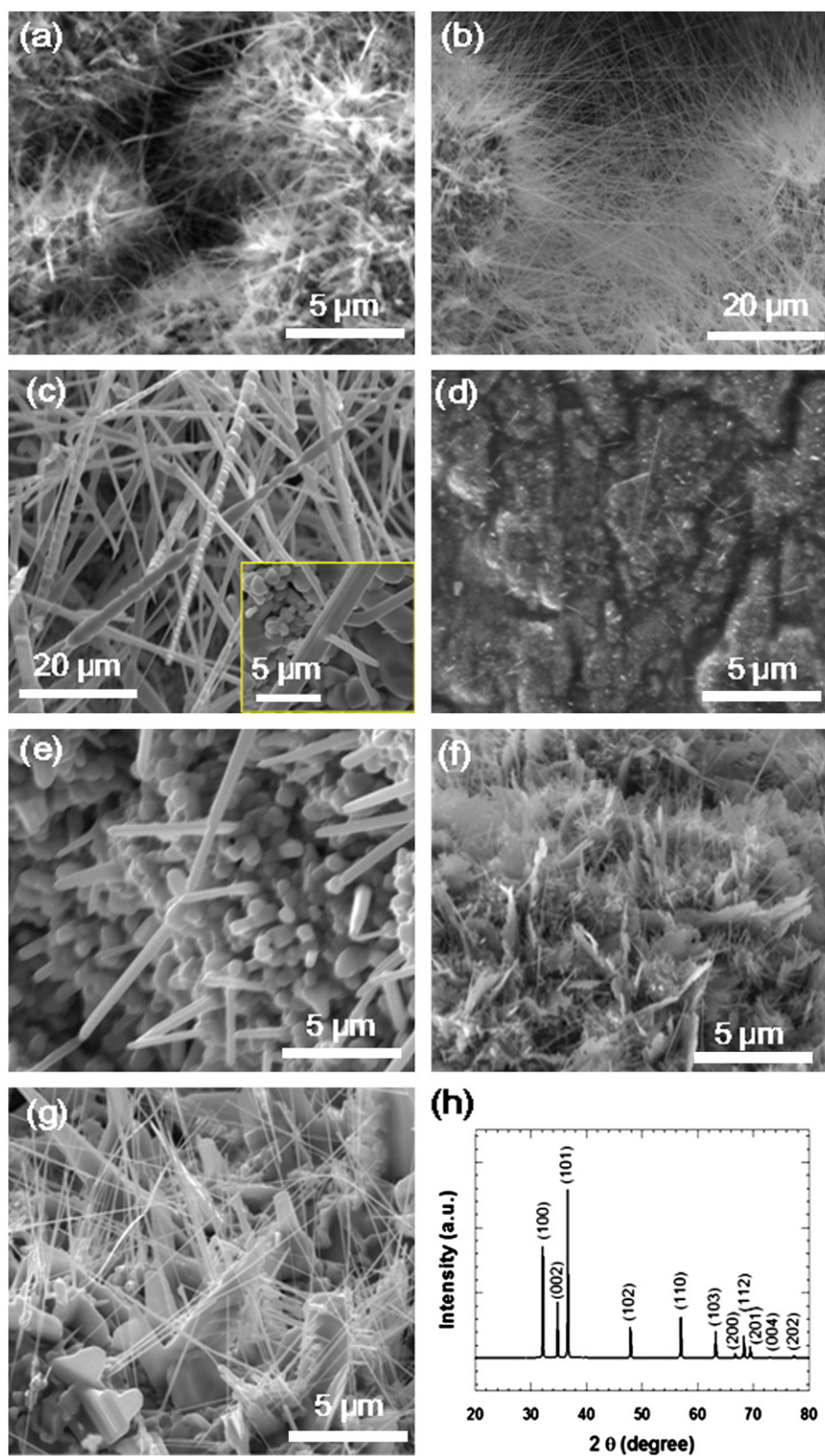


The gas-phase Cl<sub>2</sub> is removed by O<sub>2</sub> flow during the reaction process. Then, ZnO particles are deposited on the foil surface, serving seeds to facilitate nanowire growths. The density of the nanowires for ZnCl<sub>2</sub>-coated samples was high at the edge compared to the center of the foils. This also confirms the role of ZnCl<sub>2</sub> since ZnCl<sub>2</sub> concentration is relatively higher at the edge due to the centrifugal force and the surface tension of the aqueous ZnCl<sub>2</sub> solution.

The influence of the reaction time on the nanowire growth was also studied by varying the reaction time from 60 min (synthesis condition 3) to 10 and 30 min (synthesis condition 6 and 7) at the annealing temperature of 700 °C. After the 10-min annealing at 700 °C (Fig. 1f), a few micron long leaf-like nanostructures and nanowires were observed. With the longer reaction time, 30 min (Fig. 1g), longer nanowires and sheet structures were obtained.

XRD results of the nanostructures prepared by using the synthesis condition 1 in Table 1 are shown in Fig. 1h, which match the wurtzite structure of ZnO with lattice constants of *a*=0.324 and *c*=0.519 nm. Any chlorine-containing compounds including ZnCl<sub>2</sub>, Zn, or other impurities were not detected. Fig. 2 shows TEM images with a selected area electron diffraction (SAED) pattern of an individual ZnO nanowire synthesized by using condition 3 in Table 1. The growth direction of the particular nanowire is [1120], which is one of common growth directions for wire-shape ZnO nanostructures [16,26]. It is also possible that we have ZnO nanowires with other growth directions, [0001] and [0110], which are commonly observed from ZnO nanowires and nanobelts [10,27].

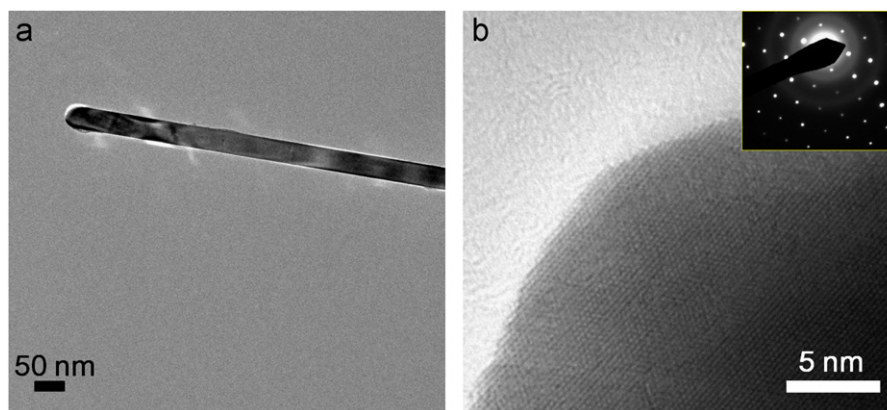
In order to study the nanowire growth mechanism with ZnCl<sub>2</sub>, SiO<sub>2</sub>-grown single-crystalline silicon and amorphous quartz wafer pieces coated with ZnCl<sub>2</sub> were annealed for 5 min at 500 °C. The short reaction is to identify if the ZnCl<sub>2</sub> becomes seeds to facilitate the nanowire growths. We used two different substrates, but the both reactions occurred on SiO<sub>2</sub>. This is because the quartz has a severe charging effect in a SEM, as opposed to less charging from the Si substrate. In addition, the atomically flat surface of the Si wafer is ideal for clearly observing the seeds. On the other hand, the quartz does not show XRD peaks whereas the crystalline Si wafer has a very large XRD intensity, which makes a XRD scan with a small amount of powder samples difficult. The concentration of



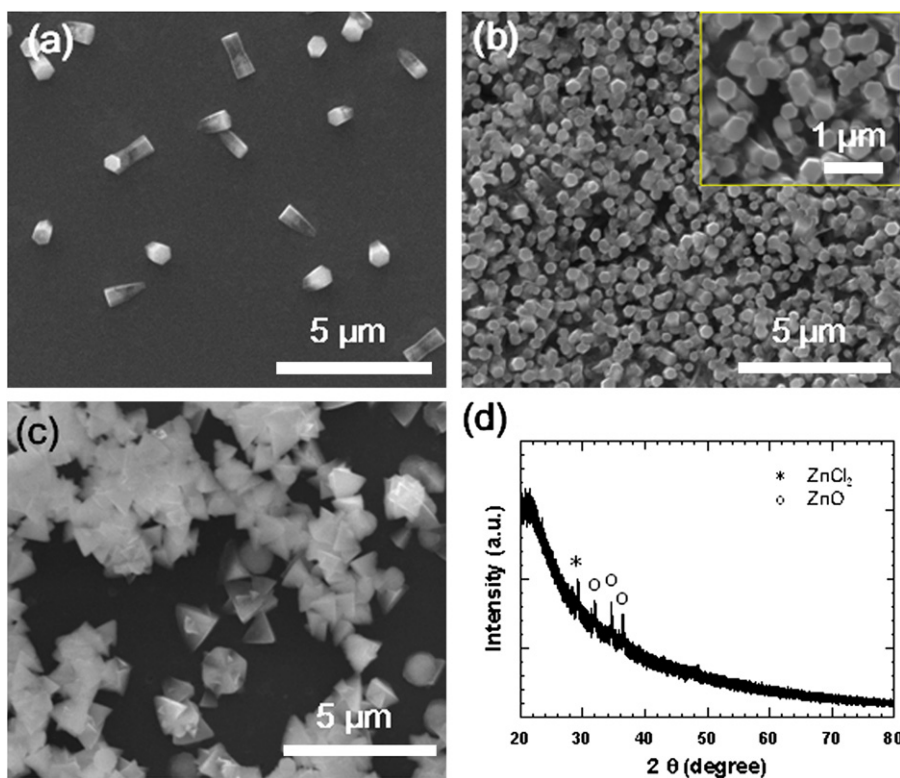
**Fig. 1.** Zn foils with  $\text{ZnCl}_2$  coating after thermal annealing at 410 °C for 120 min (a), 700 °C for 60 min (b), 850 °C for 30 min (c), 700 °C for 10 min (f), and 700 °C for 30 min (g). Zn foils without  $\text{ZnCl}_2$  after thermal annealing at 410 °C for 120 min (d) and 700 °C for 60 min (e). (h) A typical XRD pattern from the sample synthesized by thermal annealing at 700 °C for 60 min (synthesis condition 3 in Table 1).

the  $\text{ZnCl}_2$  solution and the coating method are the same as those used on the Zn foil. Figs. 3a–c show SEM images of different locations on the Si piece after the annealing. Near the center of the sample (Fig. 3a), low density nanorods with hexagonal cross-sections were observed, presumably due to the low density of

$\text{ZnCl}_2$  near the center after the spin coating process. Near the edge where the density is high, dense nanorods pushed each other, making them vertically erected (Fig. 3b). Additionally, residual tetragonal  $\text{ZnCl}_2$  particles were also found on the Si piece (Fig. 3c), indicating the wires were grown from the particles by reaction (1).



**Fig. 2.** (a) A ZnO nanowire synthesized by thermal annealing at 700 °C for 60 min (synthesis condition 3 in Table 1). (b) A high resolution TEM image that shows lattice patterns with a SAED in the inset.



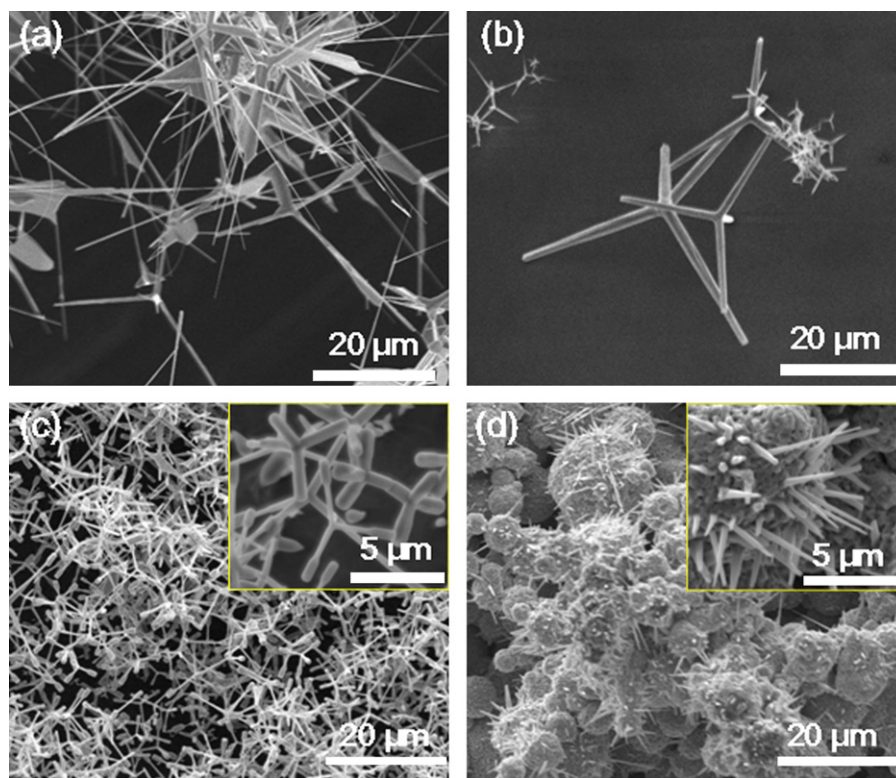
**Fig. 3.** ZnO nanostructures on a Si wafer coated with ZnCl<sub>2</sub> after thermal annealing at 500 °C for 5 min (a) near the center with low density ZnO, (b) near the edge with high density ZnO, (c) unreacted ZnCl<sub>2</sub> particles showing a tetragonal structure, (d) a typical XRD pattern of ZnCl<sub>2</sub> on a quartz wafer after thermal annealing at 500 °C for 5 min.

The XRD data of the sample on the quartz wafer (Fig. 3d) confirmed the presence of both tetragonal ZnCl<sub>2</sub> and hexagonal ZnO.

Zinc powders were also annealed in 5-sccm oxygen flow at four different temperatures with the synthesis conditions 8 (850 °C—Fig. 4a), 9 (800 °C—Fig. 4b), 10 (700 °C—Fig. 4c), and 11 (500 °C—Fig. 4d) in Table 1. With the synthesis temperature, 700 °C or higher, tetrapod nanostructures were obtained. At 850 °C growth temperature, a large amount of sheet structures were also observed (Fig. 4a). It was reported that the tetrapods have the zinc blend structure for the center and the hexagonal structure for the legs [28]. Nevertheless, the reaction mechanism for creating the morphology is still unclear. The sample annealed at ~800 °C (Fig. 4b) shows tetrapod nanostructures whose legs are tapered while the small tetrapods grown at ~700 °C (Fig. 4c) have legs with dumbbell-like shapes. On the other hand, Fig. 4d shows no tetrapod nanostructures but short nanorods grew out of

the surface of spherical Zn powders after the reaction at 500 °C. After this reaction, most of the powders remained dark rather than white, which indicates the reaction temperature is too low to have ZnO.

The experimental results show that the morphology of Zn even with the same thermal annealing method creates different ZnO morphologies—nanowires with foil substrates and tetrapods with powders. Here, we believe different growth mechanisms are responsible for the different morphologies. Our nanowires on the Zn foil with ZnCl<sub>2</sub> at 410 °C (Fig. 1a) were grown dominantly by a self-catalytic reaction [17,29]. Upon heating above the melting point of ZnCl<sub>2</sub> (292 °C [30]), ZnO seeds can be created as a result of reaction (1) (e.g., see Fig. 3a and b). Subsequently, when the temperature reaches the melting point of Zn (420 °C [24]), oxygen can be diffused into liquid-phase Zn, forming ZnO at the interface between the liquid Zn and ZnO seeds. Since ZnO



**Fig. 4.** ZnO nanostructures from Zn powders after thermal annealing at (a) 850 °C, (b) 800 °C, (c) 700 °C, and (d) 500 °C for 30 min.

grows along the preferentially favorable direction, ZnO becomes a wire shape. The ZnO seeds are self-catalysts to facilitate this reaction. When we used the same reaction temperature and time with only Zn foils (no ZnCl<sub>2</sub>), the growth rate was substantially suppressed as shown in Fig. 1d. We believe that this is due to the lack of the selective localized oxidation sites from which continuous Zn oxidation occurs to form wire shape structures. Without such selective sites, the whole Zn surface is likely to be evenly oxidized, resulting in continuous oxide films.

When the temperature was raised to 700 °C, long nanowires were synthesized on the ZnCl<sub>2</sub>-coated foil (Fig. 1b) as opposed to short nanorods with larger diameters from the sample without ZnCl<sub>2</sub> (Fig. 1e). With shorter reaction times (Fig. 1f and g), the length of the nanowires became shorter but the diameters were kept to be similar. This indicates the catalytic reaction is dominant since other growth reactions suggested in literatures are likely to make the diameter larger with longer reactions. For instance, a growth by Zn diffusion delivers Zn from the root to the tip of nanowires. Due to the slow diffusion coefficient of Zn in crystalline ZnO ( $10^{-16}$  cm<sup>2</sup>/s at 700 °C [31], which provides the diffusion length of 1–10 nm over the 30-min reaction time), it is necessary to have a faster (a few order of magnitude) diffusion through surfaces than that through crystalline ZnO [32,33]. Grain boundaries and defects could also be passages for a high rate diffusion. If this is the case in our experiment, it is likely that the diameter becomes noticeably larger since oxygen can be combined with Zn along the stem of the nanowires before diffused Zn reaches the tip.

With the higher temperature reaction at 850 °C (Fig. 1c), large diameters, ~1 μm were obtained. We also noticed irregular wire surfaces and branched wires, indicating Zn was also externally delivered to the reaction sites (called a vapor–solid reaction). Due to the high reaction temperature close to the boiling point of Zn (907 °C [24]), Zn is vaporized and converted into ZnO on the surface of the nanowires in the oxygen environment.

Simultaneous reactions (both self-catalytic and vapor–solid reactions) would have increased the reaction rate, resulting in long (~100 μm) wires.

On the other hand, the same reaction temperature (850 °C) with Zn powders instead of foils produced tetrapod and sheet structures. Since powders have larger surface area than foils, Zn powders can be easily vaporized at a temperature close to the boiling point. Then, the Zn vapor is likely to condense into ZnO in the oxygen flow (i.e., vapor–solid reaction). Here, the condensed ZnO has the zinc-blend structure from which thermodynamically preferred hexagonal wire-shape structure ZnO were grown, along the four different directions. The small and big tetrapods, shown in Fig. 4b, have very similar shapes, indicating that Zn was externally delivered to the reaction sites rather than supplied from the center. We believe that the tetrapods shown after 850 and 800 °C reactions (Fig. 4a and b) were not synthesized via liquid-phase Zn diffusion since could not find tetrapods whose centers are bigger than the diameter of the legs. When the reaction temperature was lowered to 700 °C, smaller tetrapods with only a few micron long legs were observed (Fig. 4c), presumably due to a reduced amount of vapor-phase Zn. Further decrease of the reaction temperature to 500 °C, which is too low to generate vapor-phase Zn, resulted in only rod-shape structures from the powders.

#### 4. Conclusion

Single-crystalline ZnO wire- and tetrapod-shape nanostructures were successfully synthesized from zinc foils or powders by using a simple thermal annealing method at atmospheric pressure. The influence of key synthesis parameters – reaction temperature, annealing time, and Zn source morphology (i.e., foil and powder) – on the nanostructure growth was systematically studied. Dense ZnO nanowires were easily obtained at a temperature as low as 410 °C

from ZnCl<sub>2</sub>-coated Zn foils. The length, diameter, and density of ZnO nanowires increased with a higher reaction temperature and a longer time. ZnCl<sub>2</sub> played a major role in facilitating the growth of the ZnO nanowires via self-catalytic reactions. It was observed that only short nanorods or no nanowires were obtained from Zn foils without ZnCl<sub>2</sub> coating. With the same annealing process, Zn powders were converted into ZnO tetrapod nanostructures via vapor–solid reactions and their size/morphology changes were highly temperature-dependent.

### Acknowledgments

The authors gratefully acknowledge financial supports from the US National Science Foundation (Award no. 0854467) and the National Research Foundation of Korea (the Pioneer Research Center Program) funded by the Ministry of Education, Science and Technology (MEST) (Grant no. 2010-0002231).

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