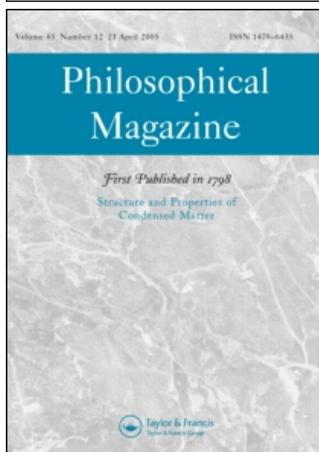


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## Growth of self-assembled ZnO nanowire arrays

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This paper reports on ZnO nanowires arrays synthesized using Sn as a catalyst. The Sn particles were produced from the reduction of SnO<sub>2</sub> powders via a vapour-solid growth process. Control of growth conditions led to the formation of ZnO nanowire arrays, radial nanowire ‘flowers’ and uniaxial fuzzy nanowires. ZnO nanowire–nanobelt junctions were also grown by changing the growth direction. As-grown nanowire arrays could be fundamental materials for investigating physical and chemical properties at nano-scale dimensions.

### 1. Introduction

ZnO, a piezoelectric material and wide bandgap semiconductor (3.37 eV) with a large exciton energy (60 meV) at room temperature, is an important and versatile functional semiconductor material. New phenomena and novel properties are expected at the nanoscale due to the size-confinement effect. As a result, since the first discovery of ZnO nanobelts [1], considerable effort has been devoted to the synthesis and characterization of ZnO nanostructures. ZnO nanospring [2, 3], nanoring [4], nano-propeller [5], nano-sisal [6], nanocomb [7, 8] and aligned nanowire arrays [9], among others, have been found for single-crystal structured ZnO. Devices, such as field emission transistors (FET) [10, 11], nanolasers [12] and cantilevers [13] have also been demonstrated. In addition, the coupling between semiconduction and piezoelectricity enable ZnO nanowires to work as nanogenerator for converting mechanical energy into electric energy [14], which has great potential for harvesting energy from the environment and self-powering nanodevices. Due to the semiconducting and piezoelectric properties combined with the excellent thermal and chemical stability of this functional material, various nanostructures and novel applications are expected to be demonstrated in the near future.

Growth of ZnO nanostructures can be achieved through various techniques, such as chemical vapour deposition (CVD) [15], metal-organic chemical vapour deposition (MOCVD) [16], physical vapour deposition (PVD) [1, 17], hydrothermal process [18], thermal decomposition [19], etc. Among them, PVD can produce various nanostructures with excellent crystallinity and has been adopted widely. Two basic growth modes have been proposed for ZnO nanostructures grown via the PVD process, including vapour–solid (VS) and vapour–liquid–solid (VLS) growth.

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VS can result in the most versatile morphologies; however, it has limited control on the location, growth direction or even size of the nanostructures. In comparison, facilitated with metal catalysts, VLS can provide better control, which benefits many applications with well-defined nanowire size and growth pattern.

This paper demonstrates some novel ZnO nanostructures grown using Sn as catalyst. The morphology, structure and possible growth processes of the self-assembled nanowires are illustrated.

## 2. Experimental method

The ZnO nanostructures were synthesized through a simple vapour-transport deposition process in a single-zone horizontal tube furnace equipped with an alumina tube, water-cooled end caps, rotary pump system, a UV laser system as an assistant heating source and a gas-controlling system. During the synthesis the temperature, pressure, atmosphere and evaporation time were controlled. Serving as source materials, commercial ZnO, SnO<sub>2</sub> and graphite powders (1.62, 1.51 and 0.12 g, respectively) were mixed, ground and then loaded into an alumina crucible, which was placed in the middle of the alumina tube. Placed 'downstream' at a lower temperature region in the tube, a single crystalline (111)-plane silicon wafer served as a substrate for the growth and collection of ZnO nanostructures. The alumina tube was sealed with two water-cooled end caps, which maintained a desirable temperature gradient across the tube, from the middle to the end, during the synthesis. The alumina tube was placed under vacuum (~1 Pa) for several hours before introducing Ar gas. The pressure was allowed to increase to and maintained at 150 Torr (~20 kPa) throughout the synthesis process. The temperature in the middle of the tube was gradually elevated to 1100 or 1150°C and maintained at the peak temperature for 20–30 min. The sublimated vapour from the source was transported by flowing Ar towards the Si substrate. Moreover, an additional target source can be placed near the substrate and be ablated by pulse laser to provide extra vapour. Local growth conditions near the substrate led to the formation of various nanostructures. The resultant ZnO nanostructures were characterized by a LEO1530 field emission scanning electron microscopy (SEM), a LEO 1550 SEM attached to an Oxford Inca Drycool EDS detector and Hitachi HF2000 transmission electron microscopy (TEM).

## 3. Results and discussion

### 3.1. ZnO nanorod clusters

At a peak temperature of 1100°C, highly hierarchical ZnO nanowire arrays and uniaxial fuzzy nanowires were found on the Si substrate, which is in the temperature region 400–500°C. At the relatively lower temperature region of the Si substrate, numerous ZnO nanowire arrays grew from the surface, as shown in figure 1. Many ZnO nanowires were roughly perpendicular to the underneath of the Si substrate. At the same time, numerous nanowires grew radially from one spot. The inset in figure 1

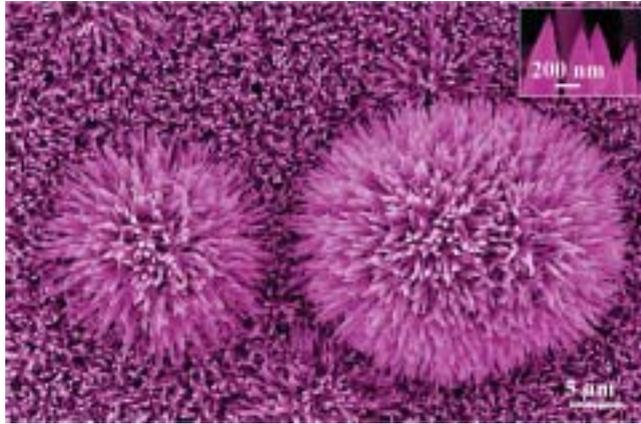


Figure 1. ZnO nanowire arrays and radial nanowire clusters, showing enlarged nanowire tips in the insets.

shows that the ZnO nanowires have a tapered front tip. Although, SnO<sub>2</sub> was introduced in the source materials and Sn is believed to serve as a catalyst in similar experiments [20], no Sn catalyst was found on top of the ZnO nanostructures. To further investigate the crystallographic structure of ZnO nanowires, TEM images of the nanowires are given in figure 2. Figure 2a shows a typical ZnO nanowire at this temperature region, which gradually increases towards the growth front and shrinks rapidly to form a sharp tip. The high resolution TEM image in figure 2b and the electron diffraction pattern in figure 2c confirm that the ZnO nanowire has a wurtzite structure and the growth direction is along [0001].

Surprisingly, a more complex ZnO nanowire assembly was found in a higher temperature region on the same Si substrate. Figure 3a shows numerous ZnO nanowires growing radially from a common axis. Due to this 3-dimensional structure and ultra-dense growth, high yields of ZnO nanowires can be achieved. In addition, a close examination reveals that the ZnO nanowires at the root of this cluster are slightly longer than those at the top. Moreover, the morphology of the tip of the nanowires also varies from the bottom to the top of the cluster. From the squared areas in figure 3a, figures 3b and c represent ZnO nanowires from the top and bottom part, respectively. The ZnO nanowires in figure 3b have diameters of 300–400 nm, a relatively rough surface and truncated hemispherical tips. In comparison, the ZnO nanowire in figure 3c have diameter of 300 nm or less, a smoother surface and flat tips composed of multiple small ‘fingers’. This difference is also observed in TEM characterization. Figures 4a and b show two types of ZnO nanowires, dissociated from the bottom and top of the cluster, respectively. The insets of figures 4a and b show electron diffraction patterns from the corresponding nanowires, indicating that all ZnO nanowires grow along the [0001]-direction. The HRTEM in figure 4c from a ‘finger’ in figure 4b suggests the single-crystallinity of wurtzite-structured ZnO nanowires and verifies the growth direction along [0001]. Although the ZnO nanowires have a blunt end, the component fingers have a very sharp, tapered tip, which could be useful as a field emitter [21].

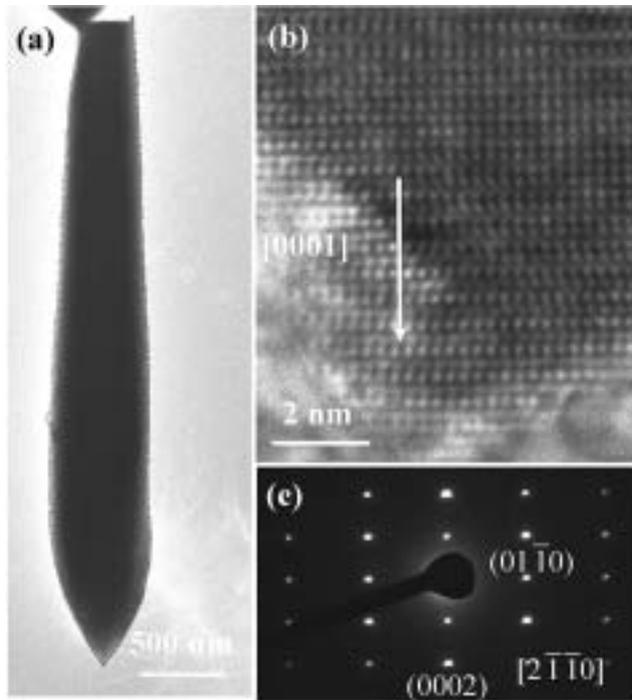


Figure 2. (a) TEM image of a nanowire taken from the ZnO nanowire array. (b) HRTEM image taken from the tip of the nanowire in (a). (c) Electron diffraction pattern of the nanowire showing a [0001] growth direction.

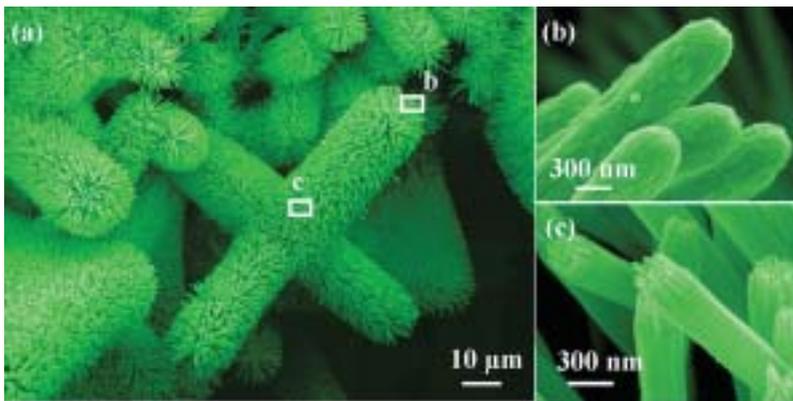


Figure 3. (a) Uniaxial fuzzy nanowire clusters from a higher temperature region. (b, c) Enlarged images of nanowires from white squared area in (a).

### 3.2. Assembly of ZnO nanorods clusters

To further study the effect of temperature on ZnO nanostructures, other experiments were performed with peak temperature of 1150°C at the centre and 550–650°C at the Si substrate. Self-assembled ZnO nanowire–nanobelt arrays were found on

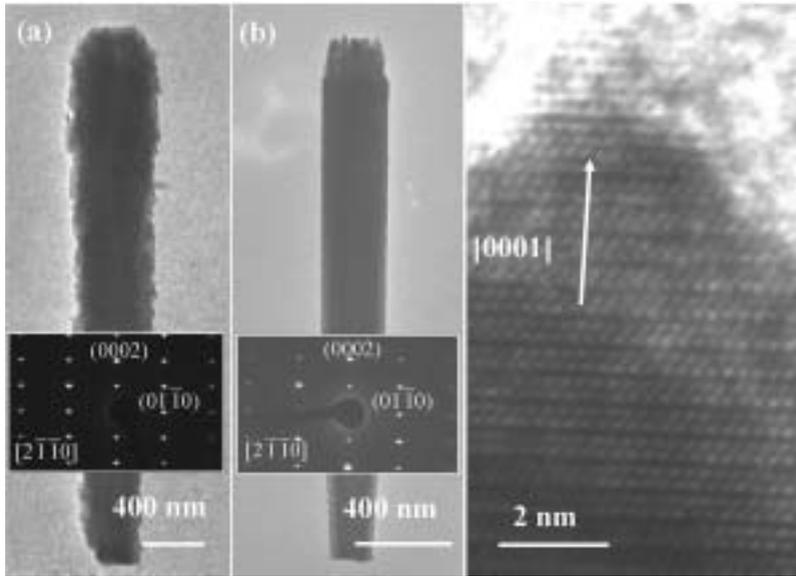


Figure 4. (a, b) TEM images and corresponding electron diffraction patterns of nanowires from uniaxial fuzzy nanowire cluster. (c) HRTEM image taken from the tip of the nanowire in (b).

the substrates. In addition, a new ZnO nanostructure assembly, shown in figure 5, was discovered on the same substrate in a higher temperature region (600–650°C). The backbone of this nanostructure assembly remained the nanowire–nanobelt junction. More importantly, numerous ZnO radial nanowire clusters grew on the main trunk, resembling a bloom of flowers on branches. An enlarged image of one cluster in the inset of figure 5 clearly shows that all nanowires have a very uniform body and tapered tip. In addition, some ZnO nanowires have a small Sn ball at the end of the tip, while others have none. These ZnO nanowire clusters were mainly found on the nanowire–nanobelt junction backbones. Further studies of nanowire–nanobelt junctions are necessary to understand these nanowire clusters.

Figure 6 shows TEM characterization of a typical nanowire–nanobelt junction structure. More interestingly, numerous smaller secondary ZnO nanowires grew from the nanobelts, as indicated by the white arrowheads in figures 6b and c. The TEM image and electron diffraction pattern confirms that nanowires and nanobelts are of the same crystal unit and have a wurtzite structure. Sharing the common  $\pm(2\bar{1}\bar{1}0)$  plane, ZnO nanowires and ZnO nanobelts grew along the  $[0001]$ -direction and  $[01\bar{1}0]$  (and equivalent) direction, respectively. ZnO nanobelts have  $\pm(0001)$  planes as side surfaces. In addition, the ZnO nanobelt in figure 6b clearly indicates that secondary ZnO nanowires grew from one side only and rarely from the opposite surface. A high-resolution TEM image of the ZnO nanobelt and secondary nanowires, from the white squared area in figure 6a, is shown in figure 6c, indicating that the ZnO nanowires grew epitaxially from the nanobelt in the  $[0001]$ -direction. All secondary ZnO nanowires display a single-crystalline structure with a diameter of about 6 nm.

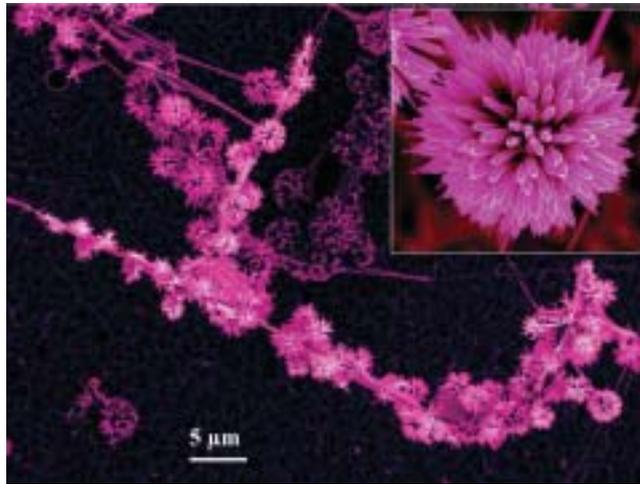


Figure 5. Flower-like nanowire clusters on the nanowire–nanobelt junction with inset showing an enlarged image of a flower-like nanowire cluster.

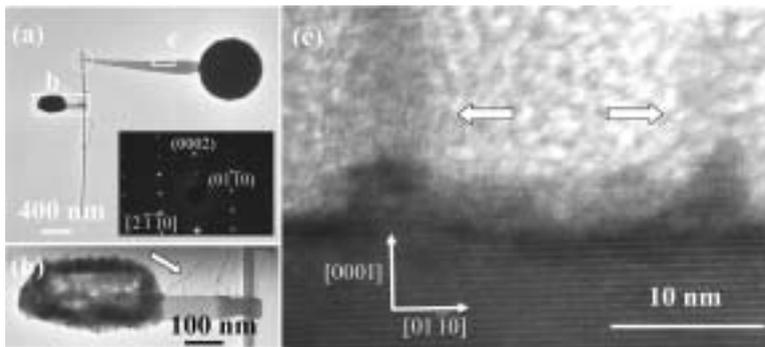


Figure 6. (a) TEM image of a nanowire–nanobelt junction structure. Inset: electron diffraction pattern taken from the white circled area. (b) A nanobelt branch clearly showing asymmetrical, secondary ZnO nanowire growth from the upper surface, as indicated by white arrowhead. (c) HRTEM image taken from the white squared area in (a), showing the single-crystal structure and growth directions of  $[01\bar{1}0]$  and  $[0001]$  for the nanobelt and nanowire, respectively. White arrowheads indicate the secondary nanowires.

#### 4. Discussion

ZnO nanowires can be easily grown via a the vapour–liquid–solid (VLS) process with Sn catalyst on the tip [5, 22] or occasionally at the root [23]. In the absence of other metal catalysts, ZnO nanowires can be grown via a vapour–solid (VS) process and a self-catalytic effect may play a role in nanostructure formation [24]. The morphology and growth direction of nanostructures are determined by growth kinetics, which can be controlled though pressure, growth temperature, etc. In this experimental setup, ZnO and SnO<sub>2</sub> powders give off Zn, ZnO, Sn and O vapours under the reduction of

graphite [5] and these vapours are transported to the substrate via the flow of carrier gas. Due to differences in chemical activity between Sn and Zn, SnO<sub>2</sub> is dissociated into Sn and O vapour before ZnO. Accordingly, at an early stage of synthesis, Sn and O vapour is the dominant source with small amounts of Zn and ZnO vapour. Sn vapour condenses on the surfaces of the Si substrate to form various liquid Sn balls. At higher temperatures, a few ZnO wires are also formed in the early stages but are quickly surrounded by a liquid Sn layer or balls as a result of the inflow of Sn-rich vapour. At lower temperatures, less ZnO wires are formed due to the low Zn and ZnO vapour concentrations. Sn vapour decreased quickly as a result of consumption of the SnO<sub>2</sub> source powder. As the Zn and ZnO vapour concentrations increase in the synthesis region, ZnO nanowires start growing from the Sn balls on the Si substrate and from Sn layer or balls on the few early grown ZnO nanowires. Under current growth conditions, ZnO growth along [0001] is greatly enhanced and growth along other directions is mainly suppressed, which explains why only ZnO nanowires are observed along [0001] in TEM characterization. ZnO nanowires grown from tiny Sn balls on the Si substrates at the lower temperature range form nanowire arrays, as shown in figure 1. Due to agglomeration, the larger Sn balls can simultaneously catalyze numerous ZnO nanowires and result in radial ZnO nanowire clusters, as shown in figure 1, which is similar to the growth of highly aligned silica nanowires from molten gallium balls [25]. In comparison, Sn balls or liquid Sn layers on the ZnO wires in the higher temperature range also absorb the inflowing Zn vapours and initiate fuzzy growth of ZnO nanowires around the common axis, resulting in the highly hierarchical ZnO nanostructure assemblies, shown in figure 3. A slightly better vapour source at the top of the assembly might result in a rougher surface, larger diameter and different tip morphology compared with ZnO nanowires at the lower part of this assembly.

In comparison, the nanostructures in figures 5 and 6 follow a slightly different process. In this experimental setup, the Si substrate is closer to the centre and the peak temperature is also higher. As discussed earlier, ZnO nanowires are formed before the furnace reaches a peak temperature of 1150°C. Under these growth conditions, other growth directions are also possible, resulting in the ZnO nanobelt branches along [01 $\bar{1}$ 0], shown in figure 6, with  $\pm(0001)$  as side surfaces. It is well-known that Zn-terminal polar surfaces are chemically active, while the opposite O-terminal polar surface is inert during growth [24]. The self-catalyzed growth from (0001) surfaces only results in the asymmetrical growth of secondary ZnO nanowires from one side of the ZnO nanobelt. In addition, the Sn balls at the tip of the ZnO nanobelts and other places can also initiate considerable growth of the most favourable ZnO nanowires along [0001], leading to the flower-like nanowire clusters.

## 5. Conclusion

By evaporating a mix of ZnO, SnO<sub>2</sub> and graphite, highly hierarchical 3-D nanostructures were synthesized. Sn particles from the reduction of SnO<sub>2</sub> serve as catalysts and initiate the growth of ZnO nanowires. Under these growth conditions, growth along [0001] is dominant and other directions are suppressed.

ZnO nanowire arrays and radial nanowire cluster were initiated from a large Sn particle and fuzzy ZnO nanowire with a common axis grown. Moreover, manipulating the synthesis kinetics can result in the formation of nanowire–nanobelt junctions at an early stage. The consequent fast growth of ZnO nanowires around Sn particles result in the flower-like nanowire clusters. A study of the nanostructures revealed the underlying growth mechanism, which is important for engineering nanoscale assemblies.

### Acknowledgements

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