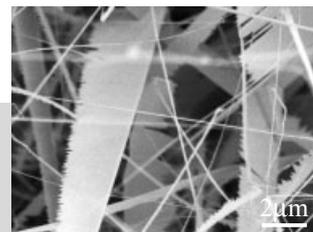


Road Map for the Controlled Synthesis of CdSe Nanowires, Nanobelts, and Nanosaws—A Step Towards Nanomanufacturing**

By *Christopher Ma* and *Zhong Lin Wang**



One-dimensional (1D) nanostructures of CdSe have been found to exhibit morphologies of nanowires, nanobelts, and nanosaws, but their synthesis is by trial and error. To meet the needs of large-scale, controlled, and designed synthesis of nanostructures, it is imperative to systematically find experimental conditions under which the desired nanostructures are synthesized reproducibly, in large quantity, and with controlled morphology. This article reports the first systematic study on the growth of 1D CdSe nanostructures by a vapor–liquid–solid (VLS) process by varying a wide range of experimental conditions. Over 150 experiments have been conducted to investigate the morphology dependence of three different types of nanostructures: nanowires, nanobelts, and nanosaws, over various substrate temperatures and pressures. The results of this work yield a road map for the controlled growth of 1D CdSe nanostructures. This research serves as a guidance and “menu” for scaling up of the synthesis of CdSe nanostructures. This is a key step towards the controlled synthesis of nanostructures to meet the needs of many industrial applications of nanomanufacturing.

Research in synthesizing semiconducting nanostructures is a forefront area in nanotechnology, because such materials can be applied in nanoelectronics, photonics, data storage, and sensing.^[1–3] To meet the needs of large-scale, controlled, and designed synthesis of nanostructures, it is vital to systematically find experimental conditions under which the desired nanostructures are synthesized reproducibly, in large quantity, and with controlled morphology. It is necessary to systematically investigate the underlying mechanisms that determine the morphology and dimensionality of one-dimensional (1D) nanostructures. This is an important step towards nanomanufacturing for future applications in industry. We have recently demonstrated the “phase diagram” for high-yield growth of aligned ZnO nanorods on nitride surfaces.^[4] In this paper, we use CdSe as an example to illustrate our recent progress towards nanomanufacturing.

CdSe has been investigated over the past decade for applications in optoelectronics,^[5] luminescent materials,^[6] lasing

materials,^[7] and biomedical imaging. CdSe is the most extensively studied quantum-dot material and is therefore regarded as the model system for investigating a wide range of nanoscale processes and phenomena in zero-dimensional nanostructures. Yet, despite numerous studies on CdSe quantum dots, there exist only a few papers reporting the synthesis and properties of 1D CdSe nanostructures.^[8–10] In particular, 1D nanostructures present the ability to experimentally address the fundamental issues of reduced dimensionality and quantum confinement in 1D systems.^[11,12] Control of the size and size distribution of CdSe nanocrystals is the most important parameter for CdSe quantum dots. In 1D nanostructures, CdSe has been found to exhibit morphologies of nanowires, nanobelts, and nanosaws.^[7] This article reports the systematic study on the growth of 1D CdSe nanostructures by a vapor–liquid–solid (VLS) process by varying the experimental conditions over a wide range. More than 150 experiments have been conducted in order to investigate the morphology dependence of three different types of nanostructures—nanowires, nanobelts, and nanosaws—on various substrate temperatures and pressures. The results of this work yield a road map for the controlled growth of 1D CdSe nanostructures. This research serves as a guidance and “menu” for scaling up the synthesis of CdSe nanostructures.

To investigate the relationships between morphology, temperature, and pressure of this material, the source temperature of the system has been held constant, while the pressure has been systematically varied to one of nine settings: 800, 700, 600, 500, 400, 300, 200, 100, and 4 mbar (1 mbar = 10² Pa).

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[**] Thanks are expressed for the support from SNSF grant DMR-9733160, the NASA Vehicle Systems Program and the Department of Defense Research and Engineering (DDR&E), and the Defense Advanced Research Projects Agency (Award No. N66001-04-1-8903).

This has been repeated for five different source temperatures: 850, 800, 750, 700, and 630 °C, yielding a total of forty five distinct experimental sets. To verify the reproducibility of our results, each of the experiments has been run a minimum of three times. The same size of gold particles has been used as the catalyst for growth. The temperature gradient for each of the source temperatures has been measured in order to correlate the morphology of the as-deposited materials with the local substrate temperature, as shown in Figure 1. By knowing the substrate position within the furnace, the local deposition temperature of each substrate could be determined using the calibrated temperature profile inside the furnace. A sampling

faces of the belt. The Cd-terminated (0001) polar surface is chemically active, but the Se-terminated (000 $\bar{1}$) surface is relatively inactive, thus, side teeth grow on Cd-terminated (0001) surfaces. This secondary growth mechanism has been extensively investigated in wurtzite-structured 1D ZnO and ZnS nanomaterials.^[14,15] Figure 2 gives examples of each type of CdSe morphology. X-ray diffraction clearly identifies the wurtzite structure of CdSe. Electron diffraction patterns reveal that all of the structures are single crystals and that the nanobelts and nanosaws grow along the [01 $\bar{1}$ 0] with top and bottom surfaces being $\pm(2\bar{1}\bar{1}0)$ (Figs. 2a,b). The nanowires, however, grow along the [0001] (Fig. 2c).

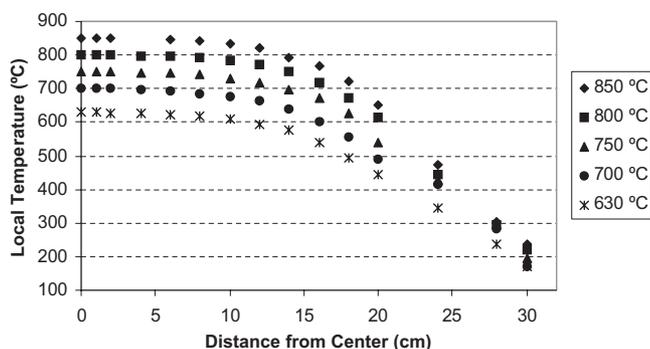


Figure 1. Calibrated temperature profiles inside the tube furnace for a heating temperature at the source site of 630, 700, 750, and 800 °C, as indicated.

of the morphology has been taken in a given temperature range to ascertain the population percentage of specific 1D CdSe nanostructures. The morphology and morphological distribution of the three types of nanostructures have been determined by using scanning electron microscopy (SEM). Each data point has been determined by counting 180 individual nanostructures.

To narrow the scope of this study, only 1D nanostructures grown via the VLS mechanism have been identified. This excludes all of the data from the experiments with a source temperature of 850 °C and most of the data from the 800 °C source-temperature experiments owing to growth of a CdSe polycrystalline film at high growth temperatures. The film acts as a buffer layer for the silicon substrates, whereby nucleation of 1D CdSe nanostructures is able to occur at the grain edges of the polycrystalline layer via a vapor–solid mechanism.

Three types of nanostructures have been observed throughout the study: nanosaws/nanocombs, nanobelts, and nanowires. The nanosaw and nanocomb structures have similar morphologies, in that their geometry is predicated upon a spontaneous polarization-induced asymmetric (SPA) growth mechanism.^[13] The nanosaws and nanocombs are belt-like and undergo a secondary growth process induced by the asymmetric growth behavior of the $\pm(0001)$ polar side sur-

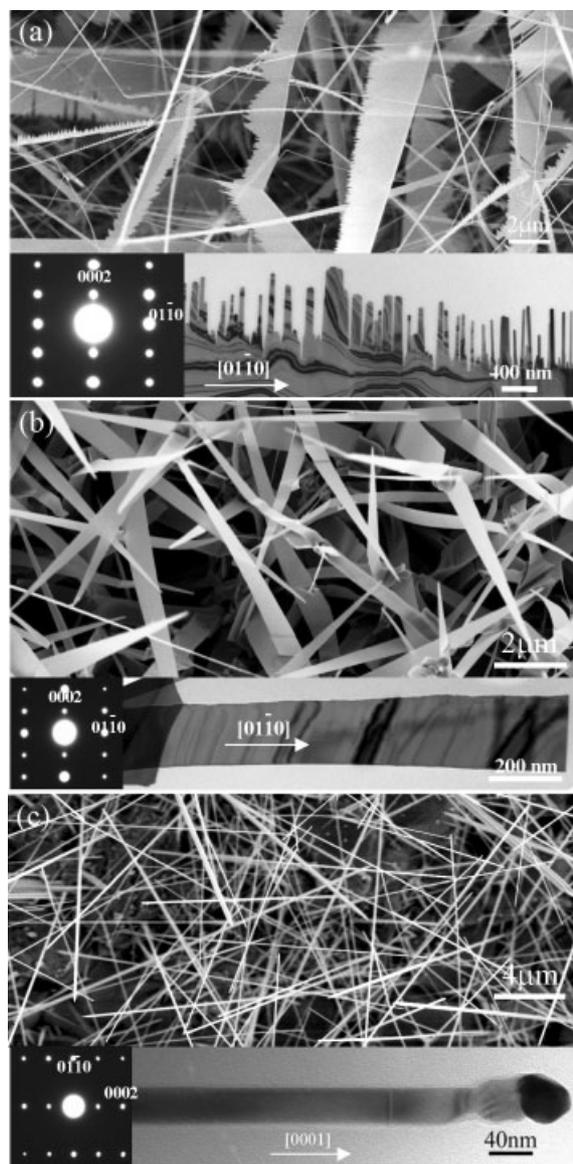


Figure 2. Typical SEM images of the morphologies of CdSe structures with their corresponding transmission electron microscopy (TEM) images (lower right) and electron diffraction patterns (lower left). a) Nanosaws/nanocombs, b) nanobelts, and c) nanowires.

To present the experimental data in an easy way, we have used different colors to represent the population percentages of the corresponding nanostructures received under the experimental conditions presented above. Figure 3 shows a plot of the population percentages of nanosaws/nanocombs at four different source temperatures. The horizontal axis is the pressure in the growth chamber, and the vertical axis is the temperature at the substrate. The graphs provide the local temperature ranges (vertical bars) at which nanosaw growth can be found and also give the popu-

lation percentages of that morphology at a given substrate temperature and pressure. The values for population percentages are an average of the three runs made at that particular pressure and source temperature; the bars on each graph represent multiple experimental runs that have been averaged to adequately clarify the large amount of information collected within this research and the experimental reproducibility. This same procedure has been used in plotting data for the nanobelt and nanowire structures in Figures 4,5, respectively.

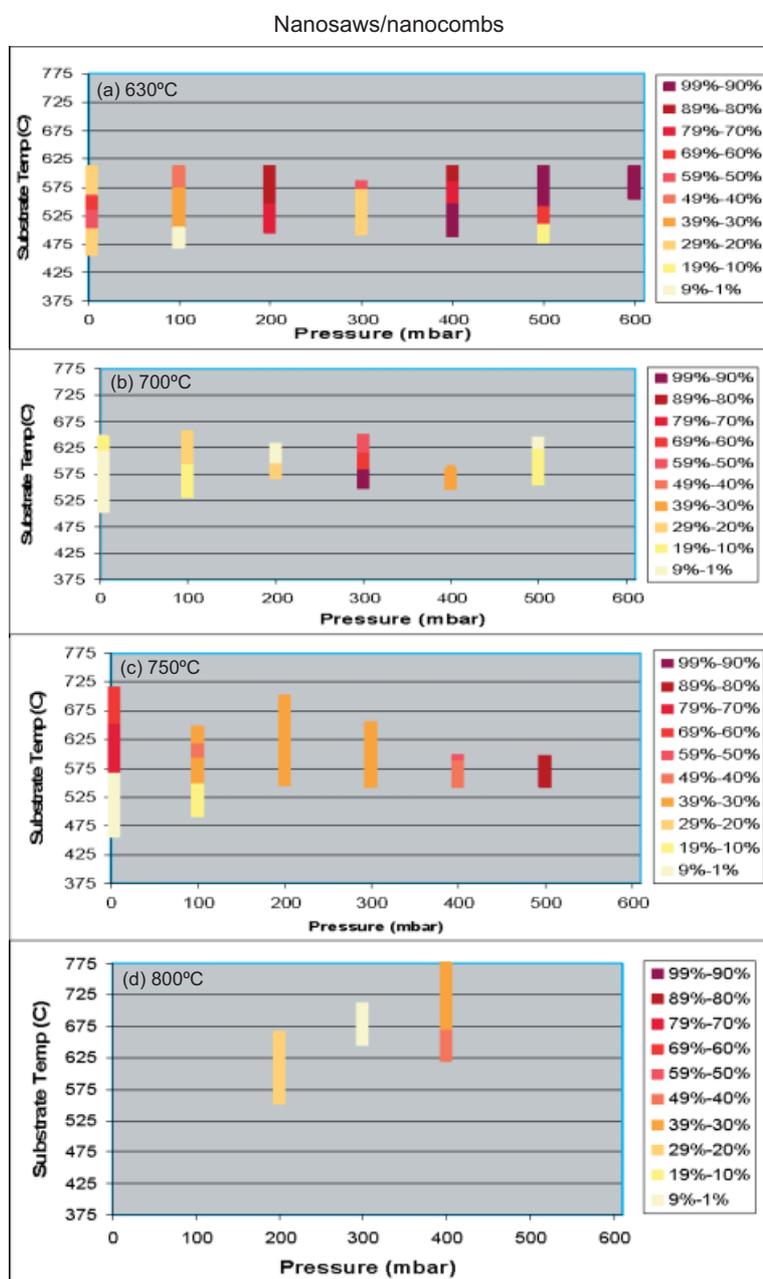


Figure 3. Population percentage of CdSe nanosaws/nanocombs as a function of substrate temperature and carrier gas partial pressure under a heating temperature at the source site of a) 630, b) 700, c) 750, and d) 800 °C.

Upon close examination of Figure 3, two trends relating to the population percentage become apparent. The first is pressure dependence. The highest population percentage of the nanosaw morphology can be consistently found at pressures of 300 mbar or higher. There appears to be a direct relationship between the observed population percentage of nanosaw structures and the overall system pressure; as the system pressure decreases, the population percentage of the nanosaw morphology also decreases, with the lowest population percentage of nanocombs and nanosaws being found when the system pressure is at its lowest, 4 mbar. This pressure–population–percentage relationship is independent of the source temperature.

Also independent of source temperature is the relationship between the population percentage and substrate temperature. At a constant pressure, the population percentage of the nanosaw growth decreases with decreasing local temperature. Typically, the highest population percentages of saw- and comb-like structures within any given run will be at the hottest zone of the deposition area.

In general, the population percentage of nanobelts increases as the local temperature decreases in the system (Fig. 4). The highest population percentage of nanobelts can be found at or near the coldest region in the deposition area. It may be that the lower synthesis temperature may not overcome the energy barrier required for stimulating the SPA growth on the Cd-terminated (0001) surface, leaving behind the nanobelt morphology. The population percentage of nanobelts decreases as the pressure increases. The population percentage of nanobelts is significantly larger at 4 mbar than at 500 mbar, regardless of the source temperature.

For nanowires, however, there is no distinct dependence on pressure (Fig. 5). The only discernable tendency is a consistently high population percentage of nanowire growth at higher temperatures and higher pressures. In the region of high temperature and high pressure, the morphology was almost completely dominated by nanowires.

The opposite trends in the population percentages of nanobelts and nanosaws versus pressure or temperature could be interpreted as follows: At

Nanobelts

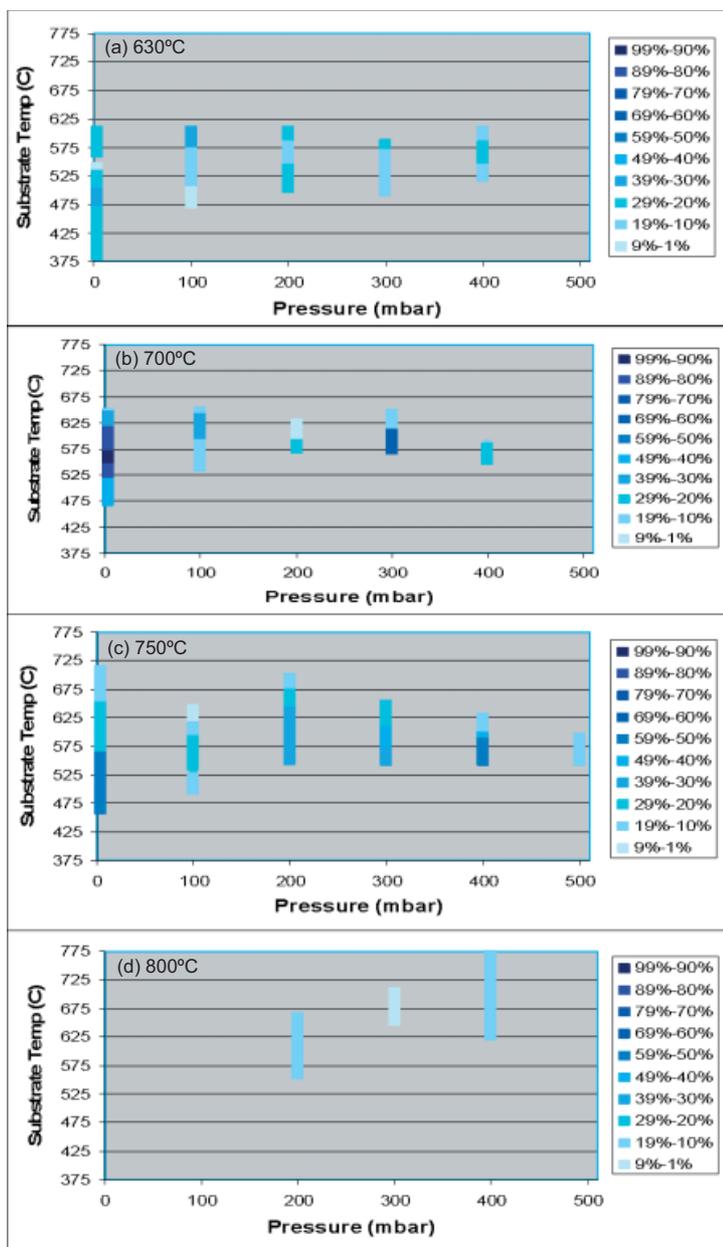


Figure 4. Population percentage of CdSe nanobelts as a function of substrate temperature and carrier-gas partial pressure under a heating temperature at the source site of a) 630, b) 700, c) 750, and d) 800 °C.

lower growth temperature, the nanobelts are formed. As the growth temperature increases, some of the nanobelts could be transformed into the saw shape due to the self-catalyzed SPA growth. As presented in Figure 2, the “teeth” of the nanocombs and the nanosaws are due to the secondary growth on the Cd-terminated (0001) surface. There may be an energy barrier associated with self catalysis of the Cd²⁺ ions that must be overcome in order to grow the teeth of the SPA structures. If there is insufficient thermal energy provided locally, the secondary growth process may be very slow. This could be the

basis for the decrease in population percentage of nanosaws at lower temperature.

There is one general trend throughout all experiments: the deposition occurs in approximately the same temperature range regardless of the temperature at the source materials. This means that the temperature at the source stimulates the vaporization of the source materials, and the subsequent growth is controlled by the local temperature and pressure at the substrate. There is an increase in the growth temperature range where deposition occurs with a decrease in the system pressure. In comparing the temperature ranges for deposition at 500 mbar to that at 4 mbar, the ranges for growth can increase by anywhere from a factor of two to a factor of 5.8. It should be noted that this trend does not apply to synthesis runs with a source temperature of 800 °C or higher because of the formation of thin films.

In summary, we have presented a systematic investigation on the synthesis parameters affecting the morphology of VLS-grown 1D CdSe nanostructures using gold as the catalyst. The relationship between morphology and pressure/temperature has been discussed, and a road map for guiding the synthesis has been defined. The main conclusions can be summarized as follows:

- The temperature at the source stimulates the vaporization of the source materials, and the subsequent growth is dominantly controlled by the local temperature and pressure at the substrate.
- There is an increase in the growth temperature range where deposition occurs with a decrease in the system pressure.
- Lower temperature at the source material (630 °C), higher chamber pressure (600 mbar), and 575 ± 5 °C substrate temperature produces the highest percentage of nanosaws/nanocombs.
- Lower temperature at the source material (700 °C), lower chamber pressure (4 mbar), and 575 ± 8 °C substrate temperature produces the highest percentage of nanobelts.
- Growth of nanowires is less restrictive and can be carried out at a wide range of temperatures and pressures.
- High source temperature favors the growth of nanowires rather than nanosaws and nanobelts.

In perspective, future nanomanufacturing requires controlled, designed, and large-scale synthesis of nanomaterials. To achieve this goal, the first step is to find out the “phase diagrams”^[4] and road maps for the synthesis of nanomaterials. The current research usually focuses on finding new growth phenomena and morphologies. The trend in the next five years will be controlled and large-scale synthesis at high yield and reproducibility. The research has to be systematic and complete. To meet this goal, a substantial amount of work is required to change our current approaches in nanomaterials synthesis. An alternative trend is

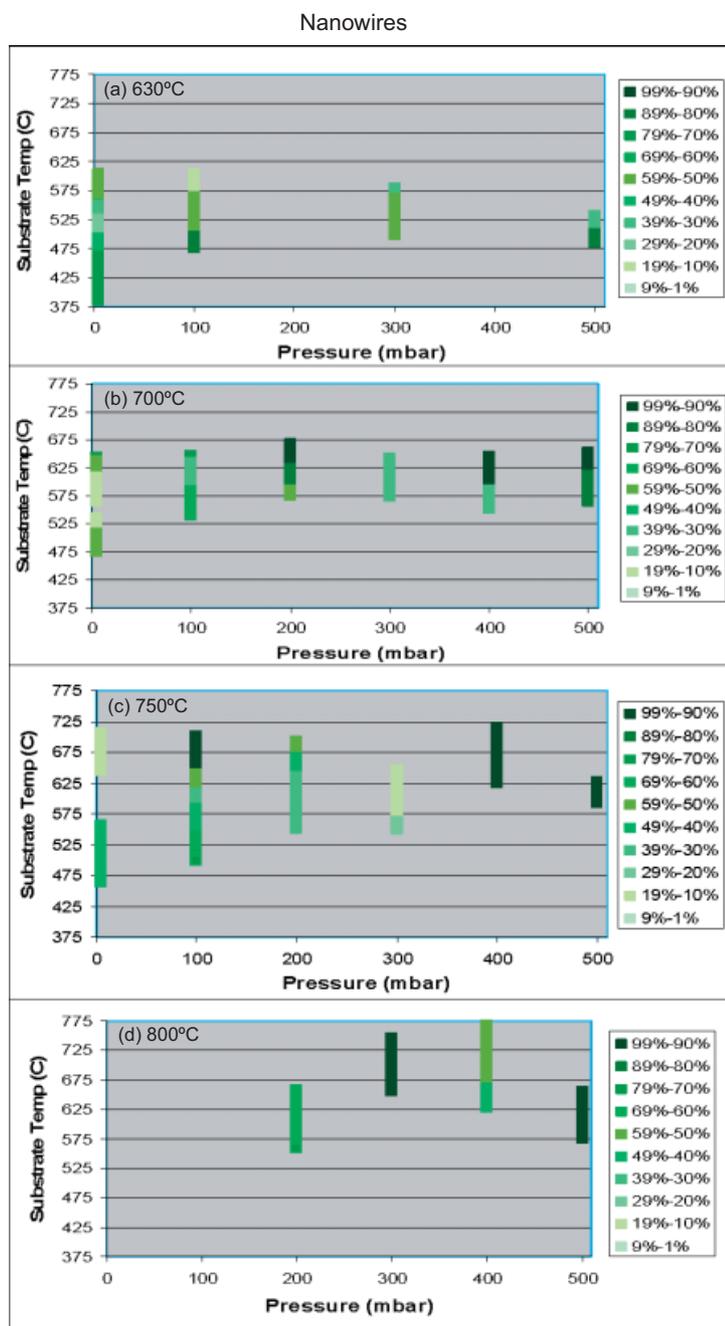


Figure 5. Population percentage of CdSe nanowires as a function of substrate temperature and carrier gas partial pressure under a heating temperature at the source site of a) 630, b) 700, c) 750, and d) 800 °C.

to use modeling in guiding materials synthesis. Statistical analysis techniques have been applied for the first time for modeling and optimizing the experimental parameters required for synthesizing desired nanostructures.^[16] This pioneering work has been done based on the experimental data presented in this paper, and will be published elsewhere. The future applications of nanomaterials in industry rely on nanomanufacturing.

Experimental

The CdSe nanostructures were synthesized through a thermal-evaporation process in a single-zone, horizontal tube furnace (Thermolyne 79300). A 30 in. (1 in. = 2.54 cm) polycrystalline Al₂O₃ tube (99.9% purity) with an inner diameter of 1.5 in. was placed inside the furnace. Commercial grade CdSe (Alfa Aesar, 99.995% purity, metal basis) was placed in the center of the tube and used as a source material. Single-crystalline silicon substrates with a 2 nm thermally evaporated non-continuous layer of gold were placed downstream of the source in order to collect the deposited CdSe nanostructures. Water-cooled aluminum endcaps were used to seal the system as a mechanical roughing pump purged the system of oxygen. After the chamber maintained a pressure of 2×10^{-2} torr (1 torr \approx 133 Pa) for an hour, the system temperature was raised to a designated set point at a rate of 20 °C min⁻¹. A nitrogen carrier gas was sent through the system at a rate of 50 sccm. Although the primary function of the carrier gas was to transport the sublimated vapor to cooler regions of the furnace, the secondary function of the gas was to build up the initial pressure of the system as well as to control the partial pressure of the vaporized source material. This ensured that the pressure of the system was constant throughout the entire synthesis process. The system was held at the set temperature and pressure for a period of 60 min and cooled to room temperature afterwards.

The as-deposited products were characterized and analyzed by SEM (LEO 1530 FEG) and TEM (Hitachi HF-2000 FEG at 200 kV).

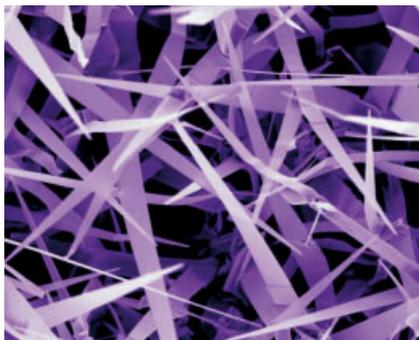
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RESEARCH NEWS

Nanostructures

C. Ma, Z. L. Wang* ■ – ■

Road Map for the Controlled Synthesis of CdSe Nanowires, Nanobelts, and Nanosaws—A Step Towards Nanomanufacturing



The first systematic study on the growth of one-dimensional CdSe nanostructures (see Figure) using a vapor–liquid–solid process by varying a wide range of experimental conditions is reported. The results yield a road map for the controlled growth of CdSe nanowires, nanobelts, and nanosaws, and it gives the guidance and “menu” for scaling up the synthesis of CdSe nanostructures.