

Shape-selective synthesis of II–VI semiconductor nanowires

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Polar II–VI semiconductors can nucleate in complex shapes ranging from nanowires to nanoribbons, nanosaws and multipods. Here we demonstrate the deterministic and fully reproducible shape-selective growth of several morphologies of CdSe and ZnTe nanocrystals by a steady-state vapour transport process. A simple pressure-based precursor-flow shutter excludes any effects of temperature ramping, ensuring reproducible shape selectivity for each set of deposition parameters. Once thermal gradients are eliminated, we show that the transition from one nanocrystal shape to another is controlled just by the interplay of precursor impinging on the substrate (ruled by the powder temperature T_p) and sample surface kinetics (ruled by the sample temperature T_s). Furthermore, a regime is found where seeded, epitaxial growth of CdSe nanorods becomes dominant over the conventional catalyst-assisted nucleation. This allows the fabrication of vertical nanorod arrays free of any metal contamination. Seeded growth of branched and tetrapod-like nanocrystals is also possible by further optimisation of the growth parameters.

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1 Introduction

High-aspect-ratio semiconductor nanostructures are of great interest due to their potential applications in electronics and photonics [1–3]. They can be grown in a variety of different shapes such as nanowires (NWs), nanoribbons (NRs), nanosaws (NSs) or multi-branched structures [3–6]. As post-growth manipulation of nanostructures is difficult and expensive, their full potential will only be realized when they can be directly grown into devices. Hence, there is the need for general approaches to achieve shape-selectivity and position-selectivity. Shape-selectivity is the deterministic control of the nano-structure morphology. Position-selectivity is the deterministic growth into specific device locations.

Vapour-transport in a single-zone quartz tube furnace is a widely employed approach to nanostructures synthesis [6–8]. In principle, it combines the advantages of both wet-chemistry and molecular beam techniques. However, this equipment does not normally provide flow shutters allowing for sharp growth interruptions (unlike, e.g., MBE). Thus, if care is not taken to overcome this issue, the nominal deposition parameters are not fully representative, since evaporation and deposition also occur during the temperature ramps and not just when the nominal steady state conditions are reached [8].

CdSe and ZnTe are direct bandgap II–VI semiconductors. When combined to form a heterostructure, they exhibit a type II band alignment [9], which makes them suitable candidates for photovoltaics applications [3, 9, 10]. In addition, their small lattice mismatch (0.4%, [9]) would allow the fabrication of dislocation-free nano-scale heterojunctions.

In this study, we vary the deposition conditions to synthesise CdSe and ZnTe nanostructures of different morphologies. A pressure-based precursor-flow shutter is used to ensure reproducible shape-

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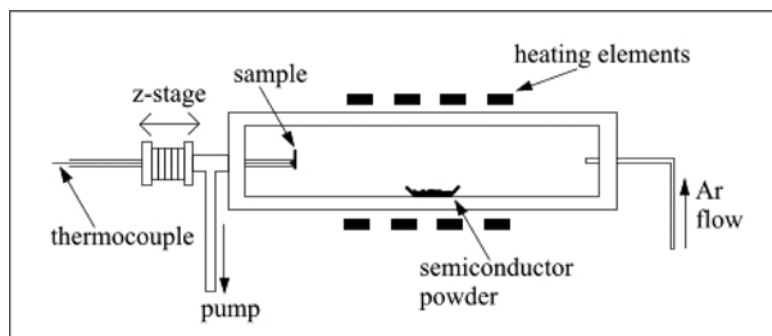


Fig. 1 Schematic diagram of the single-zone tube furnace used for the growth of CdSe and ZnTe nanostructures.

selectivity and fully representative synthesis parameters [8]. As previously demonstrated for CdSe [8], we show that the change in shape follows a general trend (as a function of powder and sample temperatures), which is applicable to other semiconductor compounds. Furthermore, by moving to a regime where seeded, epitaxial growth is dominant, we synthesise CdSe nanorods and branched-like structures, with a similar shape to those grown by wet-chemistry [11]. This process is completely catalyst free.

2 Experimental

CdSe and ZnTe nanostructures are synthesized by vapour transport in a horizontal tube, single-zone furnace reactor (Fig. 1). Commercial-grade semiconductor powder (Alpha Aesar, purity 99.99%) is loaded in a quartz boat and placed in the centre of the furnace. A thin Au layer (0.5 nm) is firstly patterned on a Si chip to act as catalyst for NW nucleation [12]. The substrate is positioned next to the downstream edge of the tube (where a steep temperature gradient is present during growth [8]) via a tubular quartz feed-through. The furnace is then pumped to a base pressure $<10^{-2}$ mbar. A 100 sccm Ar flow is admitted and the pressure is raised to 1 bar to suppress the diffusion of precursor vapor during the heating ramp [8]. This precursor-flow shutter allows to start (and stop) the synthesis only when steady state conditions are reached. When both powder and sample have thermalized to the target temperatures (T_p and T_s , respectively), the pressure is lowered to 100 mbar and the deposition started. The pressure is raised again to 1 bar during cooling, when the growth run is over and no further deposition is desired [8].

In addition to the pressure shutter, we want to underline some key features of our system (see Fig. 1) that ensure accurate control over the growth parameters. First, the hollow sample-holder feed-through allows *real-time* monitoring of the sample temperature. This is achieved with the insertion of a thermocouple in the tubular feed-through. Second, we use a drift-stage along the tube axis (z) in order to change on-the-fly the sample position without breaking the vacuum. This allows us to match exactly the substrate temperature required for any individual growth run with an accuracy of 1 °C.

Morphological and structural analysis on free-standing CdSe and ZnTe NWs and NSs is carried out by field-emission-gun scanning electron microscopy (FEGSEM), X-ray diffraction (XRD) and photoluminescence (PL). PL measurements were acquired by using an Ar-ion laser ($\lambda = 514.5$ nm) coupled to a micro-Raman RM1000 Renishaw system and using a 600 groves/mm grating.

However, the specific set of parameters varies depending on the material investigated (e.g. CdSe NWs grow around $T_p = 575$ °C, $T_s = 466$ °C, while $T_p = 625$ °C, $T_s = 533$ °C for ZnTe NWs).

3 Results and discussion

We investigate a wide range of powder and sample temperatures (520 °C $< T_p < 750$ °C and 400 °C $< T_s < 600$ °C, respectively) for the synthesis of CdSe and ZnTe nanostructures. In this range, no nucleation is observed on the bare Si substrate. As demonstrated elsewhere [8], by varying the growth conditions we

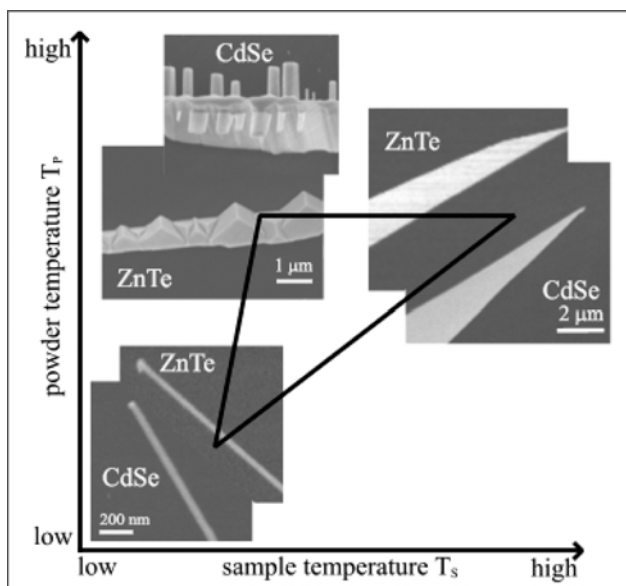


Fig. 2 Morphology of CdSe and ZnTe nanostructures as a function of T_p and T_s for catalyst-assisted growth. SEM images confirm that the occurrence of nanowires, nano-ribbons or nanosaws follows the same trend for both materials.

are able to synthesise CdSe nanostructures of several different morphologies. A combination of (T_p , T_s) can be found to grow thin and uniform CdSe NWs, ~50 nm in diameter, as shown in Fig. 2. Here, the wire diameter is determined by the catalyst particle. The same approach can be applied to synthesise ZnTe NWs, as shown in Fig. 2. Again, NWs grow catalytically from the Au pattern. By increasing both T_p and T_s , quasi one-dimensionality is lost and nanostructures morphology changes to NRs (see Fig. 2). On the other hand, by moving to a regime of high T_p and low T_s , anisotropic growth dominates. As shown in Fig. 2, CdSe nanostructures grown in these conditions present rectangular cantilever-like teeth, protruding from the backbone, all along their length. We see a similar behaviour for ZnTe, with the occurrence of NS morphology. However, a notable difference is the pyramidal shape of the ZnTe protrusions (see Fig. 2).

Further increasing T_p leads to a regime where nanorods and branched nanostructures are synthesised on the bare Si substrate. No metal catalyst is involved in such process but a self-formed seed of CdSe is found at the bottom of the structure. Figure 3 shows representative CdSe nanostructures grown in these conditions. Note that we can get branches lengths of the order of few microns for a given set of growth conditions ($T_p = 750$ °C, $T_s = 525$ °C). This length scale is much longer than that associated to nanostructures routinely synthesised by wet-chemistry [11] and may be of interest especially for photovoltaics applications [13].

The occurrence of one nanocrystal shape or another is determined by the interplay of precursor impinging on the substrate and thermal desorption at the sample surface [14]. NW morphology is the result of the dynamical equilibrium between these two competing processes, which allows the one dimensional growth catalysed by the metal seed to dominate. Moreover, as polar II–VI semiconductors are characterised by different adsorption coefficients (thus different growth rates) in different crystallographic directions [5, 6], one would expect this to be reflected in the nanostructure morphology within the epitaxial growth regime. For fixed substrate temperature, higher precursor flows enhance vapour adsorption, thus providing higher growth rates. Epitaxial growth is thus obtained by raising the powder temperature T_p . On the other hand, increasing T_s enhances the desorption and the surface mobility of the adsorbed atoms. Still, the increased desorption does not fully balance the increased adsorption. Epitaxial growth occurs in

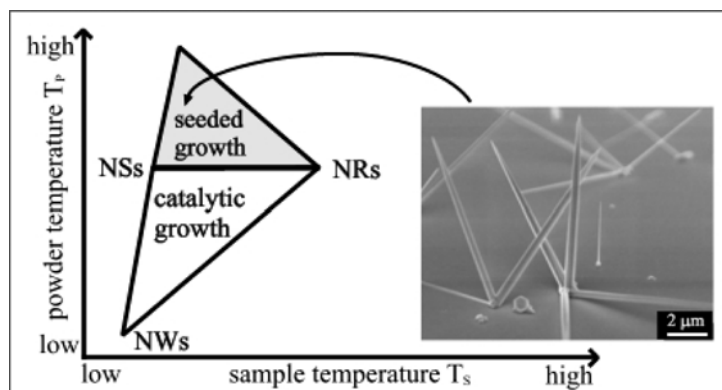


Fig. 3 SEM image of CdSe multi-branched nanostructures grown in epitaxial regime. Catalytic growth regime is also shown for comparison.

a layer-by-layer fashion when surface mobility is high enough to ensure proper migration and incorporation of adsorbed atoms. This is the “high T_p , high T_s regime” in Fig. 2, leading to a NR morphology. If T_s is lowered (for fixed T_p), surface mobility is decreased and epitaxial growth is no longer layer-by-layer. This leads eventually to three-dimensional (3D) nucleation and to a NS morphology (Fig. 2).

Non-catalytic growth of nanorods and other multi-branched nanostructures is possible only for very high semiconductor vapor density (high T_s), and relatively low T_p (Fig. 3). This is a case where 3D growth is pushed to the limit. At very high impinging flow rates, part of the vapor may initially condense on the Si substrate in spite of the low sticking coefficient, and then accumulate in nano- or micro-sized agglomerates. These agglomerates work as seeds for nanostructures formation, as further growth occurs along one or more favoured directions, likely to be defined by the crystallographic orientation of the seeds facets.

4 Conclusions

We synthesised different CdSe and ZnTe nanostructures by means of vapour-transport in a single-zone quartz tube furnace. A pressure-based shutter ensures reproducibility and full shape-selectivity. Once thermal gradients are eliminated, the transition from one nanocrystal shape to another is controlled just by varying two parameters: powder temperature (regulating the amount of precursor impinging on the sample) and substrate temperature (determining the sample surface kinetics). For a specific set of parameters, non-catalytical, seeded growth of nanorods and branched nanostructure is also achievable.

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