Growth of Hierarchical CdS Nanostructures on Fluorine-Doped Tin Oxide Glass Substrate

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ABSTRACT: Hierarchical CdS nanostructures were grown on fluorine-doped tin oxide glass via a physical vapor transport method. Tin from the substrate catalyzed the growth of a flower-like hierarchical structure that consisted of a stem and branches at a growth temperature of 280 °C. The stem nanowires grew along ⟨001⟩ with a rare zinc blende structure while branched nanowires grew along ⟨0001⟩ with a wurtzite structure. A modified vapor–solid–solid mechanism dominated by the diffusion of source species along the surface of the quasi-liquid shell of the catalyst while keeping its crystalline solid core was proposed based on the finding of a faceted core–shell Sn catalyst. The tetragonal β-phase Sn structure was observed and may induce the epitaxial growth of zinc blende CdS nanowires through a thin quasi-liquid interface owing to the close lattice match to zinc blende CdS. In contrast, branches were grown via a vapor–liquid–solid mechanism by Sn catalysts, which were vapor-transported from the higher temperature zone of the substrate, and condensed on the side wall of the stem nanowire.

1. INTRODUCTION

II–VI nanostructures, such as ZnO, ZnS, CdS, and ZnTe, possess unique characteristics highly desirable for novel optoelectronic devices.1 These material systems usually have wurtzite (WZ) crystal structures and show morphological variations including nanowires, nanobelts, nanosprings, nanosheets, and nanosaws due to the nature of polar surfaces.2,3 In particular, a hierarchical nanostructure with a stem and multigeneration branches has attracted much attention as a system with promising functionality specifically for solar cells, photocatalysts, sensors, and supercapacitors.4–6 The functionality mainly comes from the extremely large surface area of the nanostructure. There have been various attempts including sequential seeding, multistep solution growth, phase transition, self-catalyzed growth, and the use of a screw-dislocation-driven method via vapor–liquid–solid (VLS) (or vapor–solid–solid (VSS)) and solution–liquid–solid mechanisms to realize hierarchical nanostructures as classified by Cheng et al.4 Most of the methods relied on a multistep process for secondary/tertiary branch formation on preformed stem nanowires. However, the multistep process may have potential problems such as low yield and contamination. CdS nanostructures, one of the most notable and promising types of II–VI nanostructures, have been extensively investigated for the realization of nanowire lasers, photodetectors, and other optoelectronic devices.7–11 Previously, we reported a Sn-catalyzed synthesis of CdS nanowires without resorting to conventional Au catalysts that presumably degrade the optical properties owing to the formation of nonradiative recombination centers.12 Sn, as an alternative catalyst with a low melting temperature (232 °C), may facilitate low-temperature VLS growth. Unlike the published studies using catalysts from foreign sources in the forms of pure Sn or Sn alloys,13–15 here we achieved flower-like hierarchical CdS nanostructures on fluorine-doped tin oxide (FTO) glass substrates utilizing Sn catalysts from the substrates. The nanostructures on transparent conducting oxide glass substrates are extremely advantageous for novel optoelectronic devices16 but require lower growth temperatures for vapor-phase growth than the strain point temperatures (e.g., ∼500 °C for commercial glass and ∼666 °C for expensive display glass) to avoid glass substrate deformation. The energetic plasma species may provide a way to circumvent the requirement of high temperatures. Indeed, Si nanowires on conducting glass substrates have been achieved using nanoparticle Sn/In catalysts formed with hydrogen plasma assistance.16,19 However, here we grew hierarchical CdS nanostructures on FTO glass substrates at far lower temperatures (∼280 °C) than the glass strain point temperatures even without any foreign catalyst and plasma assistance.

2. EXPERIMENTAL METHODS

Hierarchical CdS nanostructures were grown via a physical vapor transport method employing a conventional single-zone...
furnace with a 1 in. diameter quartz tube (Lindberg Blue M Mini-Mite). A quartz boat containing CdS powder (100 mg, Alfa Aesar, 99.999%) was placed in the center zone where the CdS source temperature was set to 750 °C. Long FTO glass substrates (40 mm × 12 mm × 2.3 mm, Sigma-Aldrich) were cut and cleaned and then placed 14−18 cm downstream from the center. Figure S1 in the Supporting Information shows the schematic of the physical vapor transport system and its temperature profile, which was obtained by calibration with a thermocouple. According to the profile, the temperature range of the substrates was 280−630 °C. First, the system was evacuated by a mechanical pump for 0.5 h (base pressure ∼10−2 Torr), followed by the introduction of N2 carrier gas balanced with 10% H2 at a flow rate of 200 sccm. The ramp-up time to 750 °C was 15 min, and another 1 h was used as growth time while maintaining a pressure of 500 Torr. The sample was cooled to room temperature while maintaining the flow of carrier gas.

The morphologies of the as-grown hierarchical CdS nanostructures were observed by a field-emission scanning electron microscope (FESEM, JEOL JSM-6700F). X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (PANalytical, X'Pert Pro). Transmission electron microscope (TEM) specimens were prepared by immersing samples in an ethanol-filled vial, which was sonicated for 10 s to separate the hierarchical CdS nanostructures from their glass substrates; these nanostructures were then dispersed onto a carbon grid. Low- and high-resolution TEM images were obtained by a TEM (JEOL, JEM 2010). Energy-dispersive X-ray (EDX) spectra and mapping images were obtained by an EDX system (Oxford Instruments, INCA) attached to the FESEM and TEM.

Microphotoluminescence (µ-PL) measurements of individual hierarchical CdS nanostructures were taken using a home-built µ-PL system. An Ar+ laser (488 nm) was filtered and guided into a modified commercial microscope (Olympus BX60M) with a commercial Raman filter cube (Semrock). The filter cube consisted of an excitation filter (edge steepness: <1.0 nm), emitter filter (bandwidth: <1.9 nm), and dichroic beam splitter. The laser beam was focused to a spot (spot diameter: ∼3.2 μm) by an objective lens (Olympus ×50, N.A. = 0.75). Using a commercial dual-port attachment, images were taken by using a charge-coupled device (CCD, Imaging Source DBK41AF02) with simultaneous spectroscopic measurements. For spectroscopic measurements, the µ-PL signal was introduced into a multimode fiber using a fiber-launching module. Then, µ-PL was dispersed using a 0.5 m monochromator (Dongwoo Optron, MonoRa-500) and detected by a Peltier-cooled spectroscopic CCD camera (Andor, iDus DV401A). For single-nanostructure measurements, nanostructures were transferred to SiO2-coated Si substrates by casting and drying of a liquid drop containing them. All measurements were performed at room temperature.

Figure 1. (a, b, d) FESEM (45°-tilt) images of as-grown hierarchical CdS nanowires. (c) X-ray diffraction patterns of the hierarchical CdS nanostructures grown on FTO glass substrates.
3. RESULTS AND DISCUSSION

Figures 1a,b show images highlighting the nanowire’s hierarchical morphology. A flower-shaped CdS nanostructure intentionally colored in Figure 1a consists of two parts: a nanowire with a primary catalyst (upper) and numerous nanobelts (lower), which are similar to a pistil with stigma and a corolla with petals in a natural flower. All nanowires/nanobelts have catalysts on their tips indicating that the growth is preceded by a VLS (or VSS) mechanism. Hereafter, we denote the upper segment as segment-P (i.e., pistil-like segment) and the lower segment as segment-C (i.e., corolla-like segment). Figure 1b emphasizes another type of the nanostructure’s morphology in segment-C, which has several nanowire branches varying in diameter along a certain direction. Figure 1c shows an XRD pattern of the hierarchical CdS nanostructures. The majority of the diffraction peaks can be easily indexed to the WZ crystallographic structure of CdS (JCPDS 89-0440), most of them are superimposed upon the ZB peaks of CdS. Figure 1d shows a large-area 45°-tilt FESEM image of the as-grown hierarchical CdS nanostructures at the temperature region (280 °C, see the temperature profile in Figure S1) emphasizing morphological uniformity, whereas such hierarchical structures are not observed at higher temperature regions (310−490 °C) in the same substrate (Figure S2).

Figure 2a shows the side-view FESEM image of the cross section representing the distinctive regions composed of CdS nanostructures, CdS layer or columnar region, FTO, and glass substrate layers. The average height of the nanostructure is ~12 μm, and the thicknesses of the CdS and FTO layers are ~1 and ~0.5 μm, respectively. Figure 2b presents the magnified FESEM image of the cross section with an orange square for EDX mapping. The EDX maps in Figures 2f–j illustrate the elemental distributions of Cd, S, Sn, O, and Si in the orange region in Figure 2b. Figures 2c–e are the same images for easier comparison. As expected, Cd and S were distributed in the CdS layer and Si in the glass layers. In addition, O spread out in both the FTO and glass layers. Sn, a catalytic material, was interspersed in the center of the FTO layer.

Figure 3 shows the low-magnification TEM images near segment-P of a collection of as-grown hierarchical CdS nanostructures, most of which have a kinked region (blue arrow) and branch-petal regions (red arrow). Scale bars are 200 nm.

Figure 2. Side-view FESEM images of the as-grown hierarchical CdS nanostructures. (a) A cross-sectional image of the entire nanostructures, CdS layer or columnar structures, FTO, and glass substrate layers. (b) A magnified image near the orange square for EDX mapping. (c–e) Identical FESEM images of the orange square in (b) to assist in the direct comparison with EDX mappings. (f–j) EDX elemental mapping images of the orange square in (b).
observed in spectra of 3 (red), 4 (green), and 5 (magenta). Small Cd and S peaks in spot 2 were originated from the CdS region near the catalyst owing to the larger diameter of an electron-beam spot than that of a catalyst (∼15 nm).

Figure 5 shows the TEM images and fast Fourier transform (FFT) patterns of the hierarchical CdS nanostructures. The high-resolution TEM (HRTEM) image shown in Figure 5b corresponds to the interface region between the CdS kinked stem and Sn catalyst in Figure 5a. Figures 5c, 5d, and 5e show FFT patterns of areas 1 and 2 (yellow arrows in Figure 5a) and area 3 (yellow box in Figure 5b), respectively. Interestingly, the stem nanowire shows the structural transition at the kinking point. Figure 5c shows a ZB crystal structure (space group F43m) grown along the [001] direction as confirmed from 0.29 nm for the 002 spot (see Figure S3 for a detailed analysis), whereas Figure 5d shows a WZ structure grown along the [0001] direction in the kinked stem. The {111} surface of ZB and {0001} surface of WZ have atomically identical arrangements but exhibit different stacking sequences along the c-axis (i.e., ABCABC... sequence for ZB and ABABAB... sequence for WZ). Therefore, the {0001} surface for the kinked stem was grown out of {111} surfaces of ZB stems. The angles between cubic (001) and hexagonal (0001) would be 54.7° and 125°, which are consistent with the angles found in Figure 3. FFT analysis of branches showed the WZ structure grown along (001) as further confirmed from the angles between the stem and branches in Figure 3. The energy difference between WZ and ZB ($\Delta E_{W-ZB}$) was calculated to be around ~1.1 meV/atom, and WZ was slightly stable. WZ is highly preferred in CdS nanostructures as stated in previous reports. 

Considering its small energy difference, a number of reports describing the dependence of ZB, WZ, and their mixed phases on growth conditions should be found. However, the literature concerning free-standing ZB CdS is very rare. The ZB structure is occasionally observed in WZ nanowires owing to phase disorder. The core part in nano-tetrapods has a ZB structure while their arms have WZ structures. However, to this author’s best knowledge, there is only one report on a CdS nanowire with a ZB structure. In Au-catalyzed III–V nanowires, the most extensively studied system, a WZ phase is highly favored under the growth conditions of high supersaturation and small catalyst size (i.e., small diameter nanowire) even if ZB is usually stable in bulk. For a two-dimensional nucleus with monolayer height, nucleation events take place either at the center or the triple-phase boundary in a liquid-phase catalyst. When a nucleus forms at the triple-phase boundary, the part containing lateral facets replaces the pre-existing area of a liquid-phase catalyst having a higher surface energy. Thus, total energy lowering arises for this nucleation. Under conditions of high supersaturation and small catalyst size, the nucleation event at the triple-phase boundary is dominant, and WZ stacking is energetically favored as discussed by Glas et al. However, such an energy-saving mechanism may fail for low-surface-energy catalysts. Indeed, Cirlin et al. have reported the realization of pure ZB GaAs nanowires under moderate experimental conditions when self-catalyzed by Ga, one of the low-surface-energy metals (e.g., $\gamma_{LV}$ values for Sn, Ga, and Au are 0.575, 0.715, and 1.130 J/m², respectively, where $\gamma_{LV}$ is the surface energy of liquid metal). The nucleation event at the triple-phase boundary is effectively suppressed in the case of a Ga catalyst, and thereby the center nucleation is promoted. Considering that $\Delta E_{W-ZB}$ of GaAs is ~12.02 meV/atom and thus ZB is highly stable, ZB stacking is favored in the center nucleation. This model may be applied to explain the ZB phase of the CdS stem in this study considering the even lower $\Delta E_{W-ZB}$ value for Sn. However, even if the nucleation at the triple-phase boundary is effectively suppressed by using a Sn catalyst, WZ stacking would be still favored in CdS nanowires because of the energetic stability of WZ. Indeed, as stated in our previous report, all bimodal CdS nanowires with diameters in the wide range of 25–150 nm by using a SnS source grown under similar experimental conditions had a WZ phase with no exception. Thus, we consider the possibility of a VSS or modified VSS mechanism rather than a VLS mechanism to explain the ZB phase of the CdS stem.
In our previous study, the catalyst shapes were well fitted to truncated spheres, proving that a VLS mechanism was responsible for nanowire formation. However, we note the obvious faceting behavior of the Sn catalyst in Figure 5b, which has a very different shape from that of our previous report. The FFT pattern analyses in the central regions of the Sn catalyst in Figures 5e and 5f show that Sn catalysts have a tetragonal structure ($\beta$-phase Sn, space group $I\bar{4}$-amd) in spite of additional faint spots making a parallelogram inside the tetragonal spots in Figure 5f, probably due to locally precipitated orthorhombic SnO$_2$ (space group $Pbcn$, JCPDS 79-1063). It is noteworthy that the lattice mismatch between ZB CdS (lattice constant = 0.5832 nm) and $a$-axis Sn (lattice constant = 0.5831 nm, JCPDS 86-2264) is virtually absent. The catalyst diameters were investigated by examining low-magnification TEM images, and the histograms of the diameters for Sn catalysts from stems and branches are displayed in Figure 6. Stem catalysts have a broader diameter distribution (16.3% deviation) than do branch catalysts (6.8% deviation). This supports the idea that the origin of stems is different from that of branches. A model of tetragonal Sn nanocrystallites on FTO substrates may be proposed. The growth temperature of 280 °C reported here is rather nominal since the furnace has a steep temperature gradient in this region. The growth temperature could be lower. We speculate that ZB CdS nanowires grow by maintaining an epitaxial relationship with Sn nanocrystallites via a modified VSS mechanism. The major problem we encounter is the high growth rate of CdS nanowires. The growth rate via a VSS mechanism is 1 or 2 orders of magnitude lower than that via a VLS mechanism owing to the slow diffusion rate of source species through the solid-phase catalyst. If the surface and interface of the catalyst are in the quasi-liquid state while the core is still solid-phase, the source species that arrive on the surface may diffuse along the surface of the quasi-liquid shell and finally be incorporated into solid nanowires. The mass transport rate of surface diffusion can be comparable to that of bulk liquid diffusion as discussed by Wang et al. This is somewhat similar to a vapor–quasi-solid–solid model. In addition, we assume that the quasi-liquid shell is thin enough to maintain the epitaxial relationship with a solid CdS nanowire. The model presented here is in contrast with the model used to explain the epitaxial relationship between $\beta$-phase Sn and ZnO for Sn/ZnO nanowires by Ding et al. In their model, the growth of a nanowire/nanobelt proceeded via a VLS mechanism, but a Sn catalyst with a molten core and partially crystallized or atomically ordered shell guided nanowire growth. Then, the catalyst finally solidified to $\beta$-phase Sn by using an atomically ordered shell as a template. However, their model may not be applicable to our case because a strong driving mechanism for the growth of rare ZB nanowires is required while keeping a faceted catalyst. We observed a shell (thickness ~1.2 nm) structure in Figure 5b, and the volume fraction of this shell to the core (diameter ~28 nm) was ~0.26. If the shell contained Cd and S elements, such elements should have been detected by EDX measurements owing to the appreciable volume fraction (Figure 4b). Therefore, the shell consisted of Sn or SnO$_2$. The shell structure may be ascribed to postgrowth oxidation when exposed to ambient air. However, this possibility may be ruled out since such a prominent shell structure could not be observed in our previous study. We noted that the distance from the catalyst to the kink point is almost constant (~100 nm) after inspecting several nanostructures. Since a ZB phase is metastable, a growth disturbance may lead to a structural transition to a stable WZ phase. During the cooling process, the complete solidification of the shell occurs and may induce the structural transition. Assuming that all Cd species that grow into the kinked section (during cooling) were initially alloyed with the Sn nanoparticle under VLS mechanism, the initial atomic percent of Sn in the alloyed catalyst would be 28% considering ~100 nm long kinked section and the diameter of Sn catalyst. Noting that the Sn content traces the liquidus of Sn/Cd phase diagram, the estimated temperature (245 °C) is 35 °C lower than the growth temperature (280 °C). Considering the steep temperature profile in our system, the temperature is reasonable. The estimation probably supports the existence of quasi-liquid shell in the catalyst during growth.

On the other hand, Sn vapor from the high-temperature region of FTO layers (630 °C) is transported toward the cooler region and condenses on the side wall of the stem to form catalyst nanoparticles. Inspection of the branches revealed that they have a WZ phase, and catalysts are mostly polycrystalline. Their shapes are fitted to truncated spheres (Figure S4), and thus, branches seem to be formed via a conventional VLS mechanism. Figure 7 shows a $\mu$-PL spectrum from a single CdS nanostructure with the peak at 502 nm corresponding to...
The authors declare no competing financial interest.

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REFERENCES


ASSOCIATED CONTENT

Supporting Information
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Physical vapor transport system and temperature profile; FESEM images of CdS nanostructures at various substrate temperatures; a detailed FFT analysis of the ZB phase stem; high-resolution TEM image of a branch (PDF)

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Notes

4. CONCLUSIONS

We have investigated hierarchical CdS nanostructures grown on FTO glass substrates by physical vapor transport without any foreign catalysts. Flower-like structures with a stem and branches were grown by Sn catalysts supplied from FTO layers at a growth temperature of 280 °C. The stem nanowire grew along (001) with a ZB structure, which has rarely been reported, with a short kinked part (~100 nm) near the Sn catalyst, whereas branched nanowires grew along (001) with a WZ structure via a VLS mechanism. We infer that the ZB stem probably grew via a modified VSS mechanism, judging from the faceted core—shell Sn catalyst. The modified VSS mechanism was governed by the diffusion along the surface of the quasi-liquid shell. Epitaxial growth of ZB CdS proceeded through a thin quasi-liquid interface considering the close lattice match between ZB CdS and α-axis tetragonal β-phase Sn crystals. CdS nanostructures showed strong PL emission without impurity-related bands indicating high optical quality. The nanostructures reported here grown on conducting transparent glass without a foreign catalyst are highly useful for realizing novel optoelectronic devices.

Figure 7. Representative μ-PL spectrum of the CdS nanowire with the main peak at 502 nm and μ-PL image of a CdS nanowire with strong green-light emission (inset).

band edge emission. There is only strong band edge emission without impurity-related PL bands in the longer wavelength region, consistent with EDX observation. Furthermore, a μ-PL image in the inset of Figure 7 confirms the strong green-light emission from the CdS nanostructure.