Atomic layer deposition of ZnS nanotubes

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Abstract

We report on the growth of high-aspect-ratio ($\geq$300) zinc sulfide nanotubes with variable, precisely tunable, wall thicknesses and tube diameters into highly ordered pores of anodic alumina templates by atomic layer deposition (ALD) at temperatures as low as 75 °C. Various characterization techniques are employed to gain information on the composition, morphology and crystal structure of the synthesized samples. Besides practical applications, the ALD-grown tubes could be envisaged as model systems for the study of a certain class of size-dependent quantum and classical phenomena.

(Some figures in this article are in colour only in the electronic version)

Functional nanostructures are currently subjects of increasing interest. This is mainly due to the recent advances in nanofabrication techniques and a better control on the confinement geometry and growth conditions of the low-dimensional systems. In this respect, semiconducting nanowires are of particular importance. On the one hand, they can be utilized in highly efficient optical, electronic, biological and sensing devices and, on the other hand, they can equally be exploited as model systems for the study of generic solid-state phenomena [1, 2].

Here, we report on the highly size-controlled synthesis of zinc sulfide (ZnS) nanotubes (NTs) by atomic layer deposition (ALD) and characterization of the tubes thus obtained. By selection of suitable precursors and through utilization of surface chemistry reactions, ZnS nanotubes are grown onto the pore walls of perfectly ordered porous anodic alumina templates. The diameter and length of the hollow pores in the anodic alumina membrane which serves as a template for the tubes can be adjusted by optimization of the anodization conditions in the process of template fabrication. The wall thickness of the tubes, subsequently, is defined through the chemical deposition parameters such as the type of the precursors used, the growth temperature and the deposition time.

Bulk zinc sulfide is a group II–VI direct wide-bandgap semiconductor. At room temperature, it has a fundamental energy gap of about 3.7 eV between $\Gamma_{15}$ and $\Gamma_1$ symmetry points in its cubic crystal (zinc blende) phase. The corresponding value for the less frequently appearing hexagonal form (wurtzite) is 3.9 eV [3]. In contrast to most other binary semiconductors, ZnS can be doped both by donors and by acceptors to lead to either n- or p-type electrical conduction. Due to its optical properties, it is also a material of choice in certain optoelectronic applications. These include, among others, exploitation of ZnS as a phosphor or scintillation material, or its use in the fabrication of infrared filters. Still, contrary to its closest counterpart, ZnO, which has been studied extensively in the nanoscale [4], investigations on zero- and one-dimensional ZnS nanostructures have been relatively scarce to date. Recent progress in this direction involves fabrication of ZnS nanowires by an intermittent laser ablation–catalytic technique [5], exploitation of single-source molecular precursors [6], pulsed laser vaporization [7] and vertical catalytic growth on alumina templates [8], as well as chemical vapor deposition [9]. Correspondingly, ZnS tubular structures have been synthesized by utilization of ZnO nanowires and their chemical manipulation [10], thermo-chemical process [11], chemical growth of ZnS films onto carbon nanotube templates [12], surfactant micelle-template-induced reactions [13], solid-state chemical reactions [14], high-temperature chemical vapor deposition (CVD) [15], metal–organic chemical vapor deposition [16] and hydrothermal methods [17]. Furthermore, alternative avenues, such as rolling of certain layered materials into the tubular forms, have
been explored recently [18] and can possibly be examined for the fabrication of ZnS nanotubes as well. Yet, most of the above-mentioned approaches result in growth of bundles, may involve high-temperature reactions or have their strong limitations with respect to the accurate size and distribution control of the synthesized structures. Also, the majority of these techniques can only be utilized to synthesize either wire or tube geometries, but not both. Here, we report for the first time on fabrication of ZnS nanotubes by ALD. This approach can be equally used to obtain nanowires. In what follows, we will first explain the ZnS nanotube fabrication process and will then introduce the results of the experimental characterizations performed on the obtained structures.

First, to optimize deposition conditions in the ALD process, we examined SiO$_2$/Si wafers and commercially available anodic aluminum oxide (AAO) membranes. The latter had a distribution of pore diameters in the range 30–300 nm. The experiments were further carried out by use of home-made highly ordered alumina matrices, as is discussed below.

AAO templates were electrochemically fabricated by anodizing pure Al in acidic electrolytes. Highly ordered pores with average diameters of about 30, 45 and 200 nm were obtained by use of sulfuric, oxalic and phosphoric acid solutions, respectively. Precise control on the pore size and the interpore distances can be achieved by variation of electrolyte concentration, temperature and current density through anodized aluminum. The length of pore channels, up to 100 μm, was tailored by anodization time. More details on AAO template fabrication are given elsewhere [19, 20].

ALD is a bottom-up fabrication technique suitable for deposition of highly conformal thin films [21, 22]. In each self-limiting cycle of an ALD process, reactants in vapor phases are guided alternately into a vacuum chamber and are let to react on the exposed surface. Since, ideally, within each deposition cycle, only one monolayer is formed, the deposition will be highly conformal and its thickness can be accurately tailored by defining the number of cycles. In the case of a nanotube geometry, this will lead to a homogeneous radial coating of the walls and will allow precise control over the formed NT wall thickness. As precursors, we used diethylzinc, Zn(C$_2$H$_5$)$_2$ (purchased from Strem), and hydrogen sulfide, H$_2$S (from Sigma Aldrich). Diethylzinc was chosen over the other widely used precursors, such as zinc chloride [ZnCl$_2$], zinc acetate [Zn(CH$_3$COO)$_2$] or zinc oxy-acetate [Zn$_2$O(CH$_3$COO)$_3$], for two reasons. On the one hand, its use is less prone to lead to the ageing phenomena encountered in some practical applications [23], while on the other hand it has smaller molecules than those of most other metal–organics. The latter implies a better diffusivity along the narrow pore channels in AAO membranes and facilitates fabrication of high-aspect-ratio structures. Diethylzinc was kept in a stainless steel bottle with an air-tight valve at room temperature. Hydrogen sulfide was supplied by a pressurized canister regulated at 0.3–0.7 bar. The ALD process consisted of alternating and separate introductions of Zn(C$_2$H$_5$)$_2$ and H$_2$S into the reaction chamber. For each precursor, the pump was first disconnected from the chamber and the vapor was allowed to enter into it (‘pulse’). The precursor vapor was then left to react in the chamber with the AAO substrate (‘exposure’), after which the chamber was evacuated (‘purge’). The three steps were carried out for the second precursor, and the whole process was repeated in a cyclic manner (see figure 1). The precursors were kept at room temperature. The pulse, exposure and purging durations were, respectively, 50 ms, 20 s and 40 s for both precursors. Within each cycle, the reactant gases were taken in and out of the chamber by a 40 cm$^3$ min$^{-1}$ flow of argon carrier gas. During the purging steps, the chamber was pumped down to a vacuum pressure better than 0.5 mbar. The deposition temperature (temperature of the AAO template) was set by regulating the heating power through the hot plate of the ALD chamber. Figure 2 shows variation of the radial growth rate of the nanotubes with the temperature. Here, first a series of 300 ALD cycles at $T = 75$, 100, 120, 150 and 180°C were performed to obtain tubes with wall thicknesses of about 40 nm or larger. The precise thickness of each set

**Figure 1.** A snapshot of the ALD cycles. The pulse, exposure and purge periods for both the precursors diethylzinc and hydrogen sulfide, were 50 ms, 20 s and 40 s, respectively. Within the each purging step, the reaction chamber was pumped down to a pressure of about 0.4 mbar.

**Figure 2.** Growth rates of the ALD process determined by an FE-SEM (open squares) and by a TEM (open triangles) at $T = 75$, 100, 120, 150 and 180°C. The solid lines are guides to the eye. Note that, as the temperature rises, the films become rougher.
of depositions was then estimated both by a field-emission scanning electron microscope (FE-SEM) and by a transmission electron microscope (TEM). The obtained nanotubes with lengths as long as 50 μm did not exhibit any traceable variation in their wall thickness distribution along the tube axes. This fact is an indication of the good diffusivity of the precursor molecules along the long pore channels of the AAO templates and points at the feasibility of fabrication of nanotubes with even larger aspect ratios than those achieved in the present study, ~300. Still, while the depositions at temperatures up to 150 °C resulted in very smooth and conformal film surfaces, the one at 180 °C gave rise to the formation of rough and somewhat granular films. Figures 3 and 4, taken by an FE-SEM, exhibit examples of the nanotubes formed by atomic layer deposition of ZnS thin films onto the pore walls of host templates with various pore sizes at different temperatures. The relatively large growth rates here, about 1.4–2.0 Å/cycle, and the deposition temperatures, as low 75 °C, have to be compared to those reported for the ALD of ZnS thin films onto glass substrates earlier [23] (less than 0.9 Å/cycle at 200–300 °C, and a very strong dependence of the growth rate on $T$), and to the lattice constants of crystalline ZnS in its zinc-blende and wurtzite phases, 5.41 Å and 3.82 Å, respectively [3].

To facilitate further studies on the physical properties of the synthesized tubes, it is of crucial importance to be able to detach them from the template host. To get a solution of single ZnS nanotubes, a small piece, ~10 mm² in size, of embedding AAO matrix was dissolved in 1 ml of a one molar NaOH solution and was subsequently purified to neutrality in distilled water. (The pore density of the AAO templates is in the range 10⁶–10⁸ mm⁻².) It is worth mentioning that the density of nanotubes in such a suspension would be large enough to allow for, for instance, optical measurements on the samples. Figure 5 shows an image of the tubes dispersed on an SiOₓ/Si substrate taken by an FE-SEM. The inset is a transmission electron microscope micrograph taken from a mixture of tubes with different diameters.

Elemental composition of the samples was determined by an energy dispersive x-ray (EDX) spectrometer integrated into an SEM. The ratio of measured stoichiometric quantities, 30.93% zinc and 33.81% sulfur, is close to the expected

4 We are currently working on the optical characterization of the nanotube solutions. Based on our preliminary results, the tubes are semiconducting and their energy bandgaps are comparable to those of ZnS in its bulk phases.
Figure 5. Dispersed ZnS nanotubes on an SiO$_2$/Si substrate. The numbers are lithographically fabricated marks for addressing individual tubes. The upper inset is a TEM image taken from a mixture of NTs with different diameters. The deposited wall thickness, $\sim$17 nm, is a result of 100 ALD cycles at 120°C. The lower inset depicts a bundle of ZnS nanotubes with lengths in excess of 50 $\mu$m deposited at 75°C.

Table 1. Elemental analysis of the films deposited onto Si substrates. Shortly prior to the deposition, the substrate surface was cleaned in a full RCA (Radio Corporation America) process. Note that the detected mass percentages of zinc and sulfur further confirm the desired 1:1 stoichiometric value for ZnS (cf figure 6). For details, see the text.

| Element | $T = 120^\circ$C | $T = 180^\circ$C | Used technique |
|---------|-----------------|-----------------|----------------|
| C       | <6 ppm          | 48 ppm          | CHNOS (burning) |
| Zn      | 1203 ppm (0.12%)| 1481 ppm (0.14%)| AAS            |
| S       | 587 ppm (0.06%) | 585 ppm (0.06%) | CHNOS          |
| P       | <1 ppm          | <1 ppm          | ICP            |
| Si      | 99.61%          | 99.47%          | Photometry     |
| Al      | <1 ppm          | <1 ppm          | ICP            |
| O       | 912 ppm (0.09%) | 1365 ppm (0.14%)| CHNOS          |

The detected large amount of carbon, instead, has a less certain origin. To clarify whether it is an artifact of the EDX set-up (typically encountered in the detection of light elements) or it originates from the incomplete reaction of the precursors, the samples were further analyzed by alternative complementary techniques [24]. These included CHNOS analysis (burning of the samples and analyzing of the product gases) for the determination of carbon, sulfur and oxygen content, atomic absorption spectroscopy (AAS) for the detection of zinc, inductively coupled plasma (ICP) technique for the verification of phosphorus and aluminum, as well as photometry for the determination of silicon content. Table 1 summarizes the outcomes of these analyses. Evidently, the stoichiometric ratios of zinc and sulfide are correct and there is only a negligible trace of carbon or other impurities present. Interestingly, and somewhat counter-intuitively, the film deposited at 120°C has better quality (in terms of both the stoichiometry and the lesser amount of impurity carbon) than that grown at 180°C.

Figure 6. EDX data of the nanotubes dispersed on an SiO$_2$/Si substrate. The detected elements and their respective proportions are given on the graph. The high mass percentage of carbon is due to the typical uncertainties of the EDX technique in detection of light elements (see table 1). The ratio Zn:S is in good agreement with the ideal 1:1 stoichiometric value.
To summarize, we have fabricated ZnS nanotubes by low-temperature atomic layer deposition (ALD). The tubes had a very smooth wall surface and their diameter (30–200 nm), wall thickness (10–60 nm) and length (up to several tens of μm) were precisely tailored by a combination of electrochemical and ALD techniques. In addition, the effect of the deposition temperature on the growth rate of the films, chemical composition of the samples, as well as their crystal structure, were addressed.

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