Pulsed Vapor-Liquid-Solid Growth of Antimony Selenide and Antimony Sulfide Nanowires

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The vapor-liquid-solid (VLS) growth of nanostructures from gaseous precursor molecules, a catalyzed chemical vapor deposition, enjoys the status of gold standard in the preparation of semiconductor wires of the group IV elements (Si, Ge), the III–V compounds (GaN, GaP, GaAs, InP, InAs), as well as some oxides.[1–7] The situation is drastically different for V–VI semiconductors (A2B3 with A = As, Sb, Bi, and B = S, Se, Te), for which VLS growth has been documented from molecular precursors in only one case,[8] in addition to two examples of catalytic physical vapor deposition (one from heated elements, the other from heated powder).[9,10]

Among the salient characteristics of these chalcogenides, the wide range of chemical compositions x of A2B3, over which the compound A2B3 coexists in a solid solution with excess amounts of either A (x < 0) or B (x > 0) allows one to continuously tune their bandgap and crystal lattice constant, and thereby for their electrical and optical properties (orthorhombic Sb2S3 and Sb2Se3; bandgap 1.0 to 2.5 eV).[11–14] Their fast and reversible switching between crystalline and amorphous states can be exploited for data storage applications.[15,16] Finally, the V–VI materials (mostly (Sb, Bi)2(Se, Te)3) have provided the most efficient room-temperature thermoelectrics to date, and as such appear in Peltier cooling devices, thermoelectric power converters, and infrared sensors.

Nanostructuring is expected to affect the thermal, optical, and thermoelectric properties of a bulk material, and in particular improve its thermoelectric performance.[17–20] Despite the preparation of a number of antimony and bismuth chalcogenide nanostructures by electrochemical and wet chemical methods,[21–55] however, no clear improvement in the thermodynamic properties of this interesting class of semiconductors. Our first forays into this field are presented below. We were able to prepare antimony sulfide and antimony selenide nanowires in a pulsed VLS mode (Fig. 1, left). Because VLS is a type of chemical vapor deposition (CVD), it is traditionally performed in a continuous flow of one or several molecular precursors for yielding elemental or compound nanowires, respectively. For binary compounds A2B3, however, moving from the continuous delivery mode to a pulsed one can deliver a better control over the reaction. Indeed, introducing the precursors for A and B in alternating pulses instead of continuously mixing the vapors prevents them from reacting directly with one another in the gas phase and thereby avoids the deposition of unwanted particles.[60–65] Additionally, depending on the thermodynamics of the system (described by the relevant phase diagrams), the amount of A or B dissolved in the catalyst droplet at each cycle is limited. In this fashion, the growth rate could be limited by the chemical dissolution process in the catalyst, in a way analogous to what happens in atomic layer deposition (ALD). This property predisposes a pulsed VLS process to be applied to the fabrication of multisegmented wires. We were able to prove the concept in the Sb2Se3/Sb2S3 system with the simplest case, namely, wires consisting of two segments.

Exposure of Au nanoparticles prepared on the thermal oxide of a Si substrate to 300 to 400 alternating pulses of Sb(NMe3)3 and Et2Se2 vapors at 350 °C results in the growth of one-dimensional structures, as evidenced by scanning electron microscopy (SEM, Fig. 1, right). The nanowires are straight and terminated by spherical nanoparticles. In each sample, a distribution of wire diameters is observed between 40 and 200 nm, which correspond to the diameters of the capping spheres. Similar wires are obtained at the same process temperature with Sb(NMe3)3 and H2S as precursor gases (Fig. 1, center). The diameter distribution is somewhat shifted upwards with respect to the Sb/Se system (140 to 600 nm), with a tendency to a slight conical distortion of the ideal cylindrical shape.

The body of the wires consists of the desired V–VI compound, as indicated by X-ray spectroscopy (EDX) in the beam of a transmission electron microscope (the results are displayed for the Sb/Se system in Fig. 2). Quantification of the Sb L line, Se K

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of the as-prepared wires is confirmed on the ensemble scale by X-ray diffraction (XRD, Fig. 3): All maxima match the reference for orthorhombic Sb$_2$Se$_3$ (JCPDS 15-0861) except for the peak at 2θ = 38.2°, attributed to diffraction from the [111] lattice planes of gold (cubic space group Fm$ar{3}$m, JCPDS Card 04-0784) in the catalyst particles. Similar observations can be made in the case of the sulfide wires: the purity of the wire body and of the catalyst particle is shown by EDX (see Supporting Information), the crystallinity appears in the HRTEM of a selected area (lattice spacings 0.28 nm) and the XRD of the ensembles (all peaks indexed to the orthorhombic phase of antimony sulfide, space group Pbnm, JCPDS Card 06-0474).

 Taken together, the data strongly suggest that the pulsed growth proceeds via a VLS mechanism; the shape of the wires, their crystallinity, and the presence of a gold sphere at the tip are good indicators for it. The absence of growth (except for small numbers of massive crystals) in regions of the Si substrate that do not bear Au nanoparticles corroborates this. The growth temperature of the novel pulsed VLS process corresponds to that of the eutectic in the Sb–Au phase diagram (35% Sb),[66] and is slightly lower than that reported for the uncatalyzed chemical vapor deposition of Sb compounds from Sb(NMe$_2$)$_3$.[67] This is compatible with the scheme delineated above (Fig. 1, left) for self-limited growth of wires in pulsed VLS mode.[68] The slightly conical shape of the Sb$_2$S$_3$ wires suggests that a non-catalytic (and therefore isotropic) CVD process contributes to the growth to a minor extent. Indeed, we have observed the uncatalyzed formation of films in ALD mode in the reaction between Sb(NMe$_2$)$_3$ and H$_2$S at much lower
temperature, as expected from the acid-base chemistry of those two molecules. In contrast to this, Sb(NMe₂)₃ and Et₂Se₂ are inert to each other up to the onset of thermal decomposition, which precludes isotropic CVD of Sb₂Se₃.

The VLS growth of Sb₂S₃ and Sb₂Se₃ wires at a common temperature is particularly advantageous for the preparation of segmented heterostructures. The principle is proven by the two-segmented wires displayed in Figure 4. When Sb₂S₃ wires characterized by SEM (Fig. 4a) are submitted to the conditions of Sb₂Se₃ VLS deposition, the Au droplet carries out its catalytic function despite the interruption and each wire resumes its growth without alterations to the first segment (Fig. 4b). That the material of the second segment (Sb₂Se₃) is different from the first is evidenced by a slight chemical contrast in the SEM, by the shape dissimilarity, as well as by EDX analysis (segment 1: 39% Sb, 57% S, 5% Se; segment 2: 35% Sb, 9% S, 56% Se). The EDX analysis is confirmed when carried out as element mappings and as a line scan across the boundary between consecutive segments, as presented in the Supporting Information. The Sb₂S₃ segment exhibits a conical shape in Figure 4 as already observed for pure Sb₂S₃ wires (Fig. 1).

The changes of growth direction observed within the second segment could be related to several effects: epitaxial strain originating at the sulfide/selenide interface, sulfide remnants in the gold droplet being incorporated into the selenide segment, or differences between the two materials in the relative surface energies of the crystal faces. Similar phenomena are often observed for VLS-grown wires of various materials, even in the absence of chemically distinct segments, and are very sensitive to experimental parameters such as temperature, impurities, and catalyst diameter. For example, the preferred growth direction may change abruptly upon small variations in wire diameter, growth temperature, or chemical composition, if the energies of different crystal surfaces are close to one another. When three growth periods (Sb₂S₃/Sb₂Se₃/Sb₂S₃) are carried out consecutively, the selenide segment is contaminated with significant amounts of sulfur (EDX: 33% Sb, 16% S, 51% Se). The sulfide segments, however, remain pure (EDX: 40% Sb, 58% S, 2% Se), which precludes interdiffusion of the chalcogenides. Instead, these observations are consistent with the deposition of small amounts of Sb₂S₃ in the isotropic CVD mode noted above. This undesirable phenomenon should result during the third VLS step in the formation of a cylindrical Sb₂S₃ sheath on the whole length of the segmented structures.

Thus, the reactions of tris(dimethylamido)antimonide with hydrogen sulfide and with diethylidiselenide, respectively, can be carried out in a pulsed VLS mode at a common temperature of 350 °C, and result in the growth of antimony sulfide and selenide wires. Both reactions yield pure, stoichiometric, and crystalline material. The gold nanocrystal that directs the growth retains its catalytic properties when the reaction is switched between sulfide and selenide. This constellation of favorable properties allows the growth of one-dimensional objects that consist of alternating Sb₂S₃ and Sb₂Se₃ segments.

A minor side-reaction between the Sb₂S₃ precursors in ALD mode causes a conical distortion of the sulfide wires and deteriorates the quality of the segmented structures. We intend to circumvent these deleterious effects by templating the growth in a suitable porous material. Templating will simultaneously enable us to control the diameter, patterning, and orientation of aligned, vertical wires of the V–VI semiconductors. Success in this endeavor should pave the way to transport measurements of relevance to thermoelectric phenomena.

**Experimental**

A Savannah 100 ALD reactor from Cambridge Nanotech Inc. in which the substrate was attached to the top heater. Argon was used as carrier gas and was allowed to flow at a rate of 40 to 60 mL min⁻¹.

**Precursors**: The antimony precursor used for both types of nanowires is tris(dimethylamido)antimonide (Sb(NMe₂)₃ from Strem). Diethylidiselenide (Et₂Se₂ from Strem) and hydrogen sulfide (H₂S from Sigma Aldrich) were used as the selenium and sulfur sources. Liquid precursors were kept in anaerobic conditions in Swagelok stainless steel bottles at room temperature, and H₂S was delivered directly from the lecture bottle. Caution: these highly toxic, volatile molecules should be handled with extreme care and in an appropriately ventilated environment!

**Substrate Preparation**: SiO₂/Si wafers were cut into pieces of approximately 1 x 1 cm² and were chemically cleaned using piranha solution (H₃O₂ + H₂SO₄), methanol and finally deionized water, then dried at 100 °C for 5 min. A thin layer of gold (5–10 nm) was sputtered onto the surface (Cressington Sputter Coater 108 Auto) and the substrates were...
Table 1. One cycle of the pulsed VLS process.

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annealed at 650 °C for 1 h in air. The gold clusters formed ranged from 50 to 250 nm in diameter (SEM images in Supporting information).

**Growth:** The pulsed VLS process consists in alternating and separate introductions of different precursors into the reaction chamber (Table 1). The pump is first disconnected from the chamber, and then the first precursor is allowed to enter into the chamber (“pulse”). The precursor vapors are then left to react in the chamber (“exposure”), after which the system is evacuated (“purge”). The three steps are carried out for the second precursor, then the whole procedure is repeated in a cyclic manner.

For the growth of antimony selenide wires, the pulse, exposure and purge durations for both Sb(NMe₂)₃ and Et₂Se₂ were set to 1.4, 15 and 20 s, respectively. The same parameters were used for antimony sulfide except for the H₂S pulse time, which was reduced to 50 ms. Both types of wires were grown by carrying out 300 to 400 reaction cycles at a substrate temperature of 350 °C.

**Physical Methods:** SEM images were captured using a JEOL 6390 while the X-ray diffraction patterns were obtained with a Philips X’ Pert MDP System using the Cu Kα radiation. TEM and HRTEM, and EDX spectra were acquired on a Philips CM20FEG operating at 200 kV. Repeated EDX analyses of neighboring wires yield a dispersion of the results of up to 5%. This value can be considered as the uncertainty on the EDX results reported in the main text.

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