J|A|C|S
COMMUNICATIONS

Published on Web 02/28/2003

Synthesis of InP Nanotubes

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One-dimensional structures, such as semiconductor nanowires or carbon nanotubes, are attractive building blocks for nanoelectronics. In contrast to organic molecules and quantum dots, they can relatively easily be manipulated and contacted to form functional circuits.[1] The electronic structure of semiconducting nanowires is determined by the chemical composition and the diameter and additionally these wires can be n-type or p-type doped.[2] Moreover, atomically abrupt heterojunctions have been synthesized in a nanowire,[3] and strong quantization effects in a one-dimensional nanowire were established by the incorporation of a quantum dot in the wire.[4] However, the confinement for nanowires with a homogeneous composition, which still have macroscopic dimensions in one direction, is clearly less than for quantum dots. The confinement effect in one-dimensional structures can be enhanced by the formation of tubes instead of wires. Recently the synthesis of transition-metal chalcogenide nanotubes has been reported.[5] They have a pseudographitic morphology, and the electronic properties are determined by the diameter and the chirality of the tubes, in analogy to carbon NTs.[6] Therefore, it is difficult to predetermine the electronic properties of tubes of these material classes.

In this contribution the synthesis of crystalline and optically active InP nanotubes is reported. The InP tubes have the zinc blende structure and therefore represent a new class of tube materials. The tubes are grown via the VLS (vapor−liquid−solid) laser ablation method, analogous to nanowire growth.[7] The synthesis was carried out without the use of a template. The ablation setup and synthesis conditions are similar to those reported in ref 8. The beam of an ArF laser (λ = 193 nm, 100 mJ/pulse, 10 Hz) is focused on a pressed InP target (density 65%). A silicon sample with a native oxide layer covered with an equivalent of a 2−20 Å Au film was used as the substrate. The substrate was placed on an Al_2O_3 block at the downstream end of the tube oven, and the temperature was measured 1 mm below the substrate with the use of a thermocouple. The substrate temperature was well stabilized before the ablation was started. After synthesis the sample was studied with electron microscopy. For TEM a Cu grid provided with a film of amorphous carbon was wiped over the substrate.

When the substrate temperature was in the range 430−500 °C and an undoped InP (6N) target was used, single-crystalline InP nanowires were formed, which were grown in the [111] direction as has been reported by others.[8] However, when higher temperatures (>500 °C) were applied, InP nanotubes were formed. Figure 1a shows a top view SEM (Philips XL40FEG) image of a substrate after growth at a substrate temperature of 515 °C; over 95% of the deposited material consisted of wire-like structures. A closer examination by TEM (TECNAI TF30ST), presented in Figures 1, b−e, showed that hollow tubes were formed. Judging from the contrast from both bright-field TEM and HAADF (high-angle annular dark field) imaging it was clear that there was no material present in the core of the tubes. The tubes were terminated by a particle (Figure 1c) which contained gold; this indicates that the

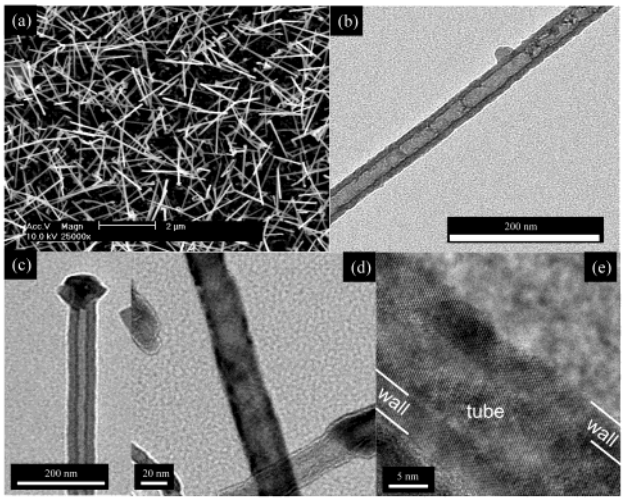

Figure 1. (a) SEM image of InP tubes grown at 515 °C on a silicon substrate provided with a 10-Å Au film. (b,c) TEM images of InP tubes from the same sample. (c) Particle at the termination of a tube. (d,e) TEM images of tubes grown at 520 °C on a substrate covered with an equivalent of a 2-Å Au film by using an InP target doped with 0.1 mol % Zn.

tubes grow from the liquid InP−Au phase via the VLS mechanism.[7] The diameter of the tubes was uniform along their length. The darker regions in Figure 1d correspond to the walls of the tube and are due to diffraction originating from the crystalline nature of this tube. Upon tilting the sample with respect to the electron beam, diffraction fringes can be seen to move over the entire width of the tubes, implying a cylindrical shape of the crystals. The observation that the diffraction contrast is most pronounced in the walls again confirms the hollow nature of the tubes. The thickness of the wall of the nanotube shown in the HRTEM image in Figure 1e was approximately 4 nm. From electron diffraction and X-ray diffraction measurements it was clear that the crystal lattice corresponded to the InP zinc blende lattice. The tubes did not oxidize upon exposure to ambient air for over a month. Preliminary photoluminescence experiments showed emission at 590 nm upon excition at 514 nm for tubes having a wall thickness of approximately 2 nm and a diameter of 27 nm, whereas InP wires with a similar diameter emit at 880 nm. This increased blue-shift demonstrates that the quantum confinement effect is stronger in these tubular structures than in solid nanowires.

In the presence of dopants a different morphology, i.e. nanotubes partly filled with InP crystallites, was also observed. The morphology depended on the dopants added to the InP target and on the substrate temperature. Figure 2 shows a TEM image of a partially hollow tube formed by using an InP target doped with 1 mol % Se at a substrate temperature of 513 °C. From high-resolution studies it was clear that the dark regions correspond to crystalline InP, and bright- and dark-field TEM imaging showed that there was no material present at the lighter regions in the core. Table 1 shows

10.1021/ja0299102 CCC: $25.00

Figure 2. (a) TEM image of a partially filled nanotube, grown at 513 °C on a substrate covered with an equivalent of a 5-Å Au film by using an InP target doped with 1 mol % Se.

Table 1. Obtained Morphology in the Indicated Substrate Temperature Range When a Dopant Was Added to the InP Target[1]

dopant	solid wire	partly filled	hollow tube
no dope	T < 500 °C	–	T > 500 °C
S	–	460 < T <480°C	T > 480 °C
Se	T < 485 °C	485 < T <530°C	T > 530 °C
Te	T < 500 °C	no data	no data
Zn	T < 480 °C	480 < T <515°C	T > 515 °C

the morphology obtained when dopants (0.1 or 1 mol %) were added to the target at a given temperature. With static SIMS and XPS it was shown that dopant atoms were transferred from the target into the wires. When a target dopant concentration of 1.0 mol % with respect to InP was used, an estimated concentration of 10^{20} atoms/cm^3 was present in the wires. These macroscopic chemical analyses were done on a large number of wires and therefore do not give information about the dopant distribution in the nanostructures. The target dopant concentration had no influence on the resulting morphology. At the higher temperatures tubes were formed, and at the lower temperatures, solid wires. At intermediate temperatures the partly filled tubes were observed.

A simple model for the growth dynamics is proposed. At relatively low temperature the growth rate is controlled by the crystal growth rate at the liquid−solid interface (kinetically limited). Rate of the diffusion of atoms in the droplet is then relatively fast with respect to that of crystal growth, and the concentration is uniform throughout the droplet (Figure 3a). Growth takes place at the entire liquid−solid junction, giving rise to solid wires. At elevated temperatures the growth rate has increased with respect to the rate of diffusion; the concentration of atoms in the droplet has been depleted, and the growth becomes diffusion-limited. At the liquid−solid interface the nucleation front is ring-shaped, giving rise to the growth of tubes (Figure 3b). An analogous growth mechanism was proposed for the growth of hollow and solid carbon nanofibers.[9]

To explain the formation of partially filled tubes the effect of the presence of a dopant on the growth should be considered. Three different steps in the VLS synthesis can be distinguished:[10] the absorption of species at the gas−liquid interface, the diffusion of species through the droplet, and the crystal growth at the liquid−solid interface. It is known that dopant atoms can affect all three steps. It is not clear from these experiments which process is affected the most. It has been reported that metal atoms can induce

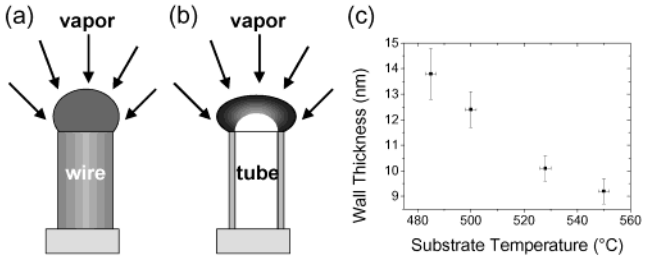

Figure 3. Schematic presentation of the formation of (a) solid nanowires by a kinetically limited process at relatively low temperatures, (b) hollow nanotubes by a diffusion-limited process at higher temperatures. The transition temperature is typically 500 °C, but dopants added to the InP target influence this temperature. The InP concentration in the droplet is indicated by the gray scale. (c) Wall thickness versus substrate temperature. An InP target with 0.1 mol % sulfur was used, leading to the formation of tubes in the applied temperature range.

or suppress a periodic instability in the VLS wire growth by changing the wetting properties at the liquid−solid interface.[11]

According to our proposed model the thickness of the mantle is expected to depend on the applied temperature. At increasing temperatures, the growth rate increases with respect to the diffusion rate; the species have a decreasing amount of time to migrate through the droplet. In Figure 3c the mantle thickness of the tubes is plotted versus the applied temperature. For this experiment an InP target with 0.1 mol % S was used, leading to the formation of tubes in the applied temperature range. The wall thickness was measured by using TEM. Obviously, the wall thickness decreased for higher temperatures as expected.

In summary, we have synthesized crystalline InP tubes by using the VLS growth mechanism. The wall thickness can be tuned by the temperature. Since nanowires of most of the III−V compound semiconductors have been grown,[12] we believe that tubes consisting of these materials can also be synthesized. This gives the opportunity to tune the electronic properties of these tubular one-dimensional structures in an even wider range.

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JA0299102