SINGLE CRYSTAL INDIUM ANTIMONY NANOWIRES: SYNTHESIS, CHARACTERIZATION, PROPERTIES AND APPLICATIONS

Laura Qi Ye[*,1,2], Raymond H. Scheffler[1,2], Toshishige Yamada[1], and Hongbing Liu[2]*
[1]Center for Advanced Aerospace Materials and Devices, NASA Ames Research Center, Moffett Field, California 94035, U.S.A.
[2]ELORET, 465 S. Mathilda Ave., Suite 103, Sunnyvale, CA 94086
**Corresponding author: qye@mail.arc.nasa.gov*

Abstract

We report the first large-scale synthesis of single crystal InSb nanowires using self-catalyzed vapor-liquid-solid (VLS) transport process. Narrow growth window for achieving single crystal InSb nanowires has been discovered. Our batch fabricated InSb nanowires are 50-180 nm in diameter and 10-30 μm in length. Materials composition analysis by Energy-Dispersive X-ray Spectroscopy (EDAX) reveals that the as-grown InSb nanowires are pure single crystals of InSb. Structural analysis by High Resolution Transmission Electron Microscopy (HRTEM) and Selected Area Electron Diffraction (SAED) reveals that InSb nanowires have cubic crystal structures. The nanowire growth direction is found to be [001], 45 degrees toward the lattice planes in cubic structure.

Introduction

One-dimensional III-V compound semiconductor nanowires are an important class of nanomaterials that possess unique structures, remarkable properties, and great potential in a wide variety of applications. Ultra small sensors, detectors, power sources, cooling devices, communication and navigation systems with very low mass, volume, and power consumption are possible with this class of nanomaterials. While there are a number of reports in literature on large band-gap III-V semiconductor nanowires (i.e., GaAs, GaN, InP, InAs nanowires), studies on small band-gap III-V nanowires are very rare. InSb represents the smallest band-gap III-V compound semiconductor, and has its own unique physical properties. The band-gap of InSb is very narrow in the infrared region (E_g = 0.17 eV at 300 K and 0.23 eV at 0 K). InSb has extremely high carrier mobility (electron mobility = 80000 cm^2/Vs and hole mobility = 1250 cm^2/Vs), small effective mass ($m^* = 0.013m_e$), large lattice parameter (a = 6.45 Å), very big g-factor for Zeeman splitting ($g \approx 50$), and large heterostructure band offsets. These physical properties of InSb make it a promising material for infrared optical detectors and emitters, high-speed electronic devices and magnetic field sensors. InSb is the material of choice for infrared optical detectors and emitters in the 1.3-1.55 μm range of interest for long distance communication systems using non-SiO_2 fibers and for infrared imaging applications [1, 2]. As its one-dimensional counterpart, InSb nanowires have attracted great interest recently in building nanowire IR lasers. Recently, a theoretical calculation from our group suggested that InSb nanowires with nanometer scale diameters could have a thermoelectric figure of merit much higher than 1 at room temperature when compared with other III-V semiconductor nanowires that had been investigated [3]. Therefore, InSb nanowires could be promising thermoelectric material for cooling and power generation applications. This was our motivation of studying the growth, characterization, and properties of InSb nanowires.

Experimental Details

InSb nanowires have been successfully grown in our lab in a Lindberg tube furnace using self-catalyzed vapor-liquid-solid (VLS) transport process. A 24” quartz tube (20 mm ID $\times$ 25 mm OD) was first annealed on the Lindberg tube furnace in 200 sccm H_2 flow at 1000°C for 1 hr. Then the source material 99.999% (metals basis) InSb powder (purchased from Alfa Aesar) was loaded in the middle compartment of a three-compartment quartz boat (19 mm OD) 2/3 full. The substrates were quartz wafer pieces or 0.5 μm silicon dioxide/silicon (100) wafer pieces deposited with 400 nm indium layers by thermal evaporation. The substrates were loaded on top of the quartz boat (middle compartment) with the indium layer facing down (toward the source material). The furnace was flushed with Ar/H_2 gas (50 sccm Ar and 50 sccm H_2) for 15 min, and then gradually ramped to 300°C in 15 min in 100 sccm H_2 flow. The substrates were pretreated at 300°C for 15 min. They were then heated to 528°C in 10 min to start the growth of InSb nanowires. Normally, in order to achieve 10-20 μm long InSb nanowires, a growth time of three to four hours was needed. The InSb nanowires were grown self-catalyzed from indium particles in H_2 reducing gas environment at atmospheric pressure. The growth temperature window was found to be between 528°C and 535°C. After growth, the as-grown InSb nanowire samples were cooled down slowly to room temperature in 100 sccm H_2 flow in about a few hours.

Materials and structural characterization of the as-grown InSb nanowires were performed using Scanning Electron Microscopy (SEM) (Hitachi S-4000), Transmission Electron Microscopy (TEM), High-Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAED) pattern analysis (Philips CM200 FEG-TEM), and Energy-Dispersive X-ray Spectroscopy (EDAX) (Nanoprobe-EDS). The nanowires were characterized either as-is on the substrates or being dissolved in IPA solutions and then cropped on TEM copper grids.

Discussion

SEM analysis

Figure 1 shows the SEM images of the as-grown InSb nanowires on quartz substrate. Typically, they formed dense mash-like straight and long InSb nanowires (Figure 1(a)). We were able to grow this density of InSb nanowires over 2 cm^2 areas. Occasionally, we observed large InSb nanowire flowers (Figure 1(b)). The zoomed-in SEM image (Figure 1(c)) clearly reveals that these nanowires are high quality single crystals with clear crystalline facets formed at the top. Near the edge of the sample, we observed that InSb nanowires changed crystal growth directions (Figure 1(d)) probably due to temperature and gas flow fluctuation at the edge of the sample. The crystals twisted 90 degrees to continue grow along another direction perpendicular to the one before. This observation indicates a cubic InSb nanowire crystalline structure.

TEM analysis

Figure 2 shows the TEM image of a single InSb nanowire cropped on TEM copper grid from IPA solution. It reveals that the nanowire is tapered, with the diameter varied from 150 nm at the base to 70 nm at the tip. The InSb nanowire was further characterized by HRTEM. Figure 3 shows the HRTEM images of InSb nanowires at 1140 K magnification (the scale bar on the image is 3 nm). We can clearly see that two sets of lattice fringes are visible. The lattice fringes inter-planar distance is 6.8 Å. The lattice fringes are at 45 degrees toward the growth direction of the nanowire. The native oxide layer thickness along the InSb nanowire is 3 nm (current tunneling to the nanowires is therefore possible). In both SEM and TEM images, we don't observe any obvious indium droplets at the tip of the nanowire. However, we believe indium is the species present at the very tip of the nanowire. The nanowires were formed by a self-catalyzed nucleation process in which indium beads formed during the pre-annealing step acted as the initial catalyst. The antimony vapor from the source materials then saturated in these indium droplets and pushed the InSb crystal out to form the 1D nanowire structure. Since indium is a low melting point (m.p. 156.6°C) metal and it is very easy to be vaporized during growth process, the indium vapor released from the InSb powder source became the constant supplier of indium to from InSb 1D crystals on substrate.

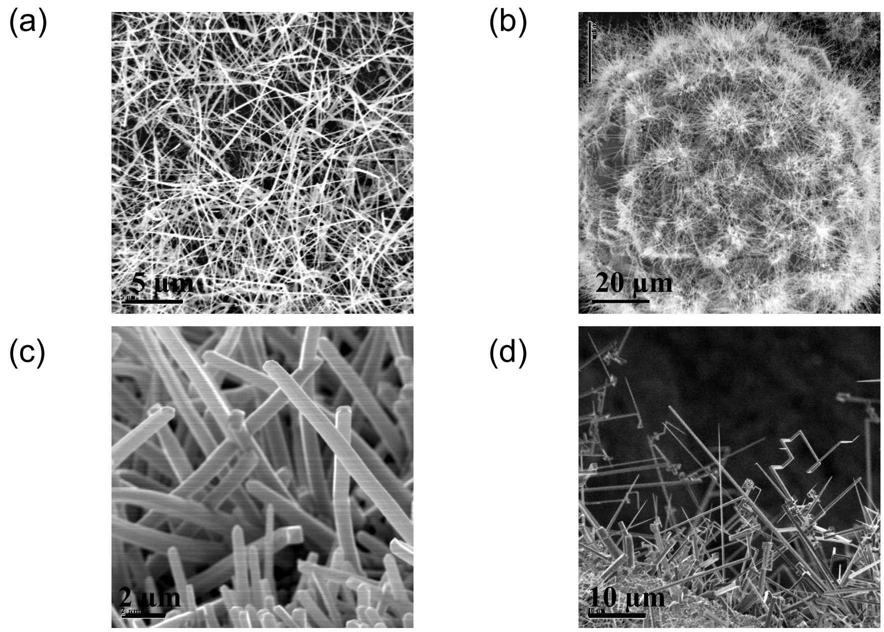

Figure 1. SEM images of the as-grown InSb nanowires. (a) Dense mash-like straight and long InSb nanowires. (b) InSb nanowire flowers. (c) zoomed-in SEM view. (d) InSb nanowires twist 90 degrees to continue grow.

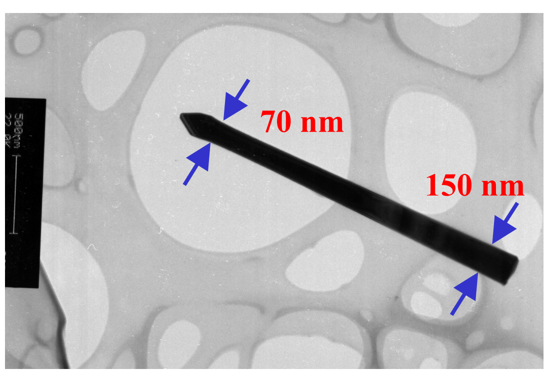

Figure 2. TEM image of a single InSb nanowire.

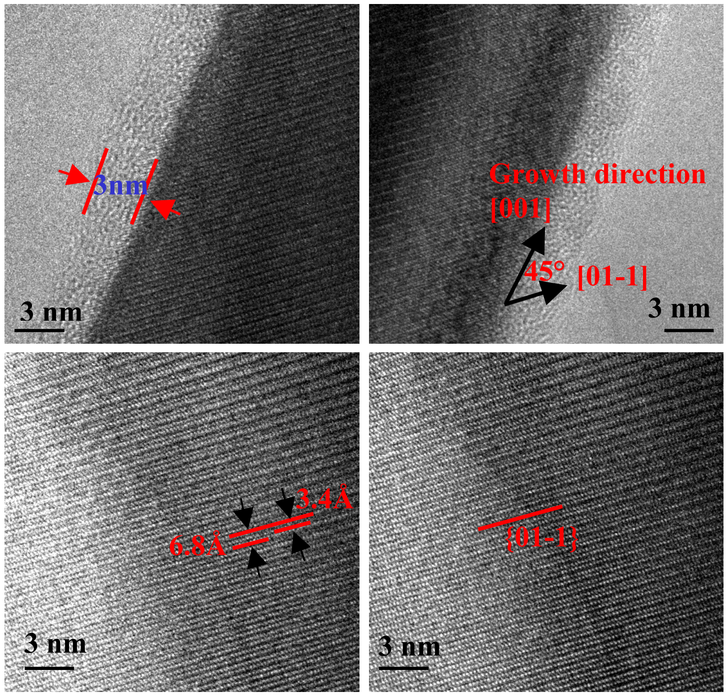

Figure 3. HRTEM images of InSb nanowires at 1140 K magnification.

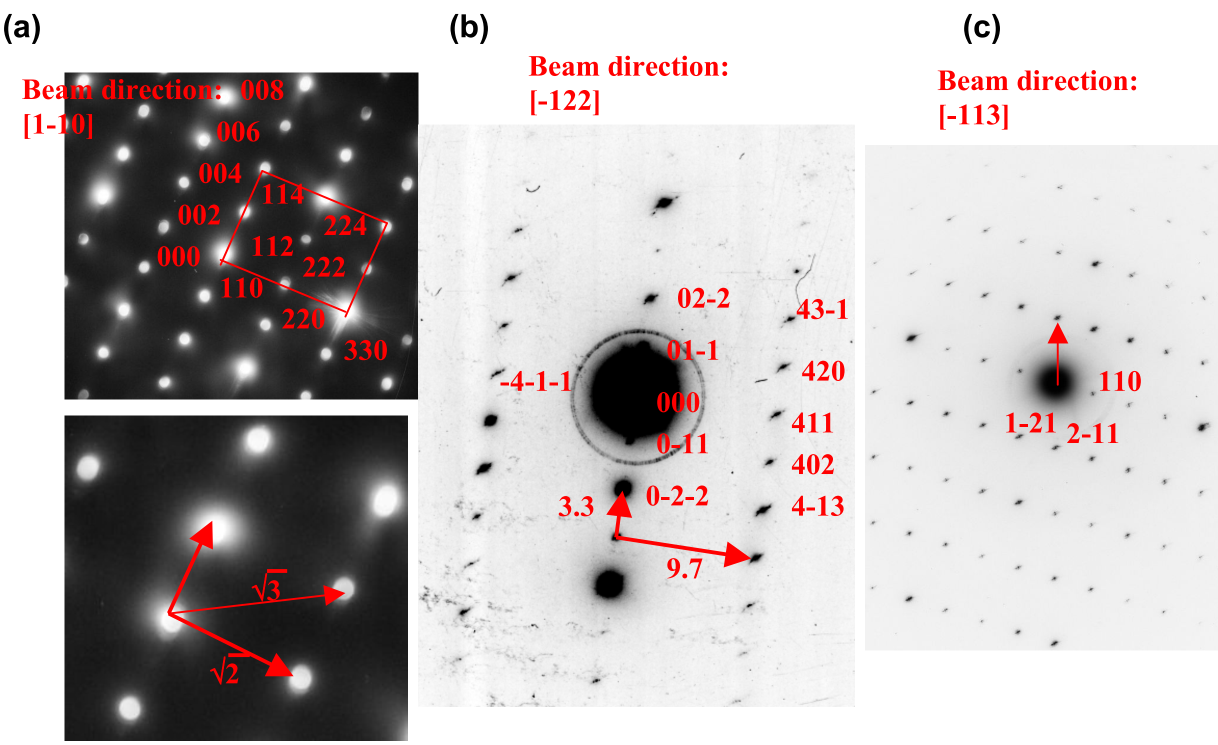

Figure 4. SAED patterns of InSb nanowires. (a) Diffraction pattern with [1-10] beam direction. (b) Diffraction pattern with [-122] beam direction. (b) Diffraction pattern with [-113] beam direction. The diffraction dots for each beam direction are identified as planes shown in the figures.

SAED pattern analysis

The crystalline structure of the lattice and the crystal planes can be derived from SAED patterns. Figure 4 (a) shows the diffraction pattern with [1-10] beam direction. A clear rectangle diffraction pattern with the side ratio of 1:√2 is observed. Figure 4 (b) shows the diffraction pattern with [-122] beam direction. A clear rectangle diffraction pattern with the side ratio of 1:3 is observed. When we tilted the same InSb nanowire as in (b), we observed a clear hexagonal diffraction pattern with [-113] beam direction. After detailed crystal structure analysis examining practically all possible crystal lattices and beam directions, we conclude that the InSb nanowires have clearly cubic unit cell structure with diffraction dots for each beam direction identified as planes shown in the figures.

EDAX analysis

EDAX measurements confirm the material compositions of the nanowire are indeed indium and antimony. Figure 5 shows the EDAX spectrum of the InSb nanowire. Spatially resolved elemental analysis by EDAX clearly proved that In and Sb were present as evidenced by the strong In L peak at 3.285 KeV and strong Sb L peak at 3.604 KeV. Besides the weak Cu L peak at 0.932 KeV and the strong Cu K peak at 8.038 KeV (not shown in this spectrum) that were from the TEM Cu grid, we observed a very week peak at 0.55 KeV. This was attributed to the trace amount of oxygen from the native oxide layer along the InSb nanowire. From the clear EDAX spectrum, we conclude that our nanowire is single crystal pure InSb nanowire.

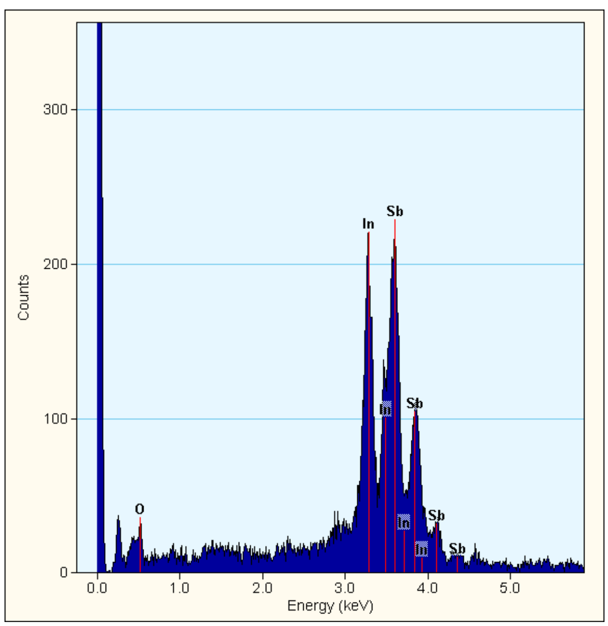

Figure 5. EDAX spectrum of InSb nanowire.

We also did hot probe measurements and found that our as-grown InSb nanowires exhibited characteristics of n-type semiconductors. We therefore conclude that the un-intentionally doped InSb nanowire is intrinsically n-type. We suspect it could due to oxygen substitutions in the nanowires or trace amount of Te presenting (it is known that Te and Sb are very difficult to separate from each other). This experimental finding provides valuable information for future computer simulations and property predictions of InSb nanowire-based devices and sensors. We are currently investigating this type of single crystal InSb nanowires for their potential applications as thermoelectric nanomaterials in energy efficient solid-state refrigeration and power generation applications.

Conclusions

We have successfully synthesized single crystal InSb nanowires using self-catalyzed VLS transport process. Our InSb nanowires are typically 50-180 nm in diameter and 10-30 μm in length with high crystalline quality. Structural analysis by TEM, HRTEM, and SAED reveals that our as-grown InSb nanowires have cubic crystalline structure. EDAX measurements prove that the nanowire is in deed InSb. The InSb nanowires are grown along [001] direction, 45 degrees toward the lattice planes in cubic crystalline structure.

Acknowledgments

This work is supported under NASA contracts No. NNA05BE36C (BAA extramural award) to Eloret and No. NAS2-03144 to the University of California, Santa Cruz, University Affiliated Research Center (UARC). The authors thank Hidenori Yamada for assisting InSb nanowire synthesis. QY thanks National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory (LBL) for proposal award to use the DOE facility there. We thank Dr. Harry Partridge, Dr. Chris Dateo, and Terry Buffum for management support.

References

1. D. C. Tran, G. H. Siegel, and B. Bendow, *J. Lightwave Technol*. LT-2, 536 (1984).
2. M. E. Lines, *Science* 226, 663 (1984).
3. N. Mingo, *Appl. Phys. Lett*. 84, 2652 (2004).
4. S. Yamaguchi, T. Matsumoto, J. Yamazaki, N. Kaiwa, and A. Yamamoto, *Appl. Phys. Lett*. 87, 201902 (2005).