Growth and Characterization of Single Crystalline InSb Nanowires for Thermoelectric Applications

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ABSTRACT

We report here the first large-scale synthesis of single crystalline InSb nanowires via a self-catalyzed vapor-solid-liquid (VLS) growth method. Narrow growth window for achieving high quality single crystal InSb nanowires has been found at growth temperature of 650°C and chamber pressure of 350 torr. Our batch fabricated InSb nanowires are 20-100 nm in diameter and 10-50 micron in length. Materials composition analysis by Energy-Dispersive X-ray Spectroscopy (EDS) reveals that the as-grown InSb nanowires are pure single crystals of InSb. The native oxide layer along the nanowires is only 3 nm thick. Structural analysis by X-ray diffraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM), and Selected Area Electron Diffraction (SAED) reveals that InSb nanowires have Face-Centered Cubic (FCC) unit cell structure with a = 6.55 Å. The nanowire growth direction is found to be along [001] direction. We have measured thermoelectric transport properties of these nanowires. We are currently investigating these single crystalline InSb nanowires for thermoelectric device integration in energy efficient solid-state refrigeration and power generation applications. Preliminary prototype thermoelectric nano coolers and nano power generators device design are presented here.

Keywords: InSb (indium antimonite), nanowires, thermoelectric, single crystal, large-scale synthesis

1 INTRODUCTION

One-dimensional III-V compound semiconductor nanowires are an important class of nanomaterials that possess unique structures, remarkable properties, and great potential in various 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. Small band-gap III-V compound semiconductors are extremely important for long-wavelength optoelectronic device and thermoelectric device applications. 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 300K and 0.23 eV at 0K). InSb has very high carrier mobility (electron mobility=78000 cm^2/Vs and hole mobility=1250 cm^2/Vs at room temperature), small electron effective mass ($m^*=0.013m_e$), large lattice parameter (a=6.45 Å), big g-factor for Zeeman splitting (g≈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 Galvan magnetic, and high-speed magnetic field sensors. InSb is important 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]. InSb also has a very high power factor at 723K [3, 4], it becomes the material of choice for thermoelectric applications in the intermediate temperature range of 650-750K. 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 wires with nanometer scale diameters are good candidate material for thermoelectric applications [5]. It has a thermoelectric figure of merit much higher than 1 at room temperature when compared with other III-V semiconductor nanowires that had been investigated. InSb nanowires could be promising thermoelectric material for cooling and power generation. This was our motivation for studying the growth, characterization, and properties of InSb nanowires.

2 EXPERIMENTAL DETAILS

InSb nanowires have been successfully grown in our lab in a Lindberg tube furnace using vapor-liquid-solid (VLS) transport process. A 24” quartz tube (20mm ID × 25mm 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 (19mm 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 100 sccm H_2) for 15 min, and then gradually ramped to 300°C in 15 min in 100 sccm H_2 and 50 sccm Ar gas flow. The substrates were pretreated at 300°C for 15 min. They were then heated to 650°C in 10 min at a tube pressure of 350 torr to start the growth of InSb nanowires. In order to achieve 10-50 µm long InSb nanowires, a growth time of two to three hours was needed. The InSb nanowires were grown self-catalyzed from indium particles in H_2 reducing gas environment at sub-atmospheric pressure. The growth temperature window was found to be between 650°C and 700°C at a pressure of 200-350 torr. After growth, the as-grown InSb nanowire samples were cooled down slowly to room temperature in 100 sccm H_2 and 50 sccm Ar flows 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), X-ray diffraction (PANalytical (Philips Analytical) X'Pert PRO X-ray diffraction system), High-Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAED) pattern analysis (Philips CM200 FEG-TEM), and Energy-Dispersive X-ray Spectroscopy (EDS) (Nanoprobe-EDS). The nanowires were characterized either as grown on the substrates or after being dispersed in IPA and then cropped on TEM copper grids.

3 DISCUSSION

3.1 SEM analysis

Figure 1 shows the SEM images of the as-grown InSb nanowires on quartz substrate. Typically, they formed dense mesh-like straight and long InSb nanowires (Figure 1(a)). We were able to grow this density of InSb nanowires over 2 cm^2 areas on substrate. The high magnification SEM image (Figure 1(b)) clearly reveals that these nanowires are high quality single crystals with clear cubic crystalline facets formed at the tip of the nanowires. The nanowires are slightly tapered, with the diameter varied from 100 nm at the base to 60 nm at the tip.

(a) (b)

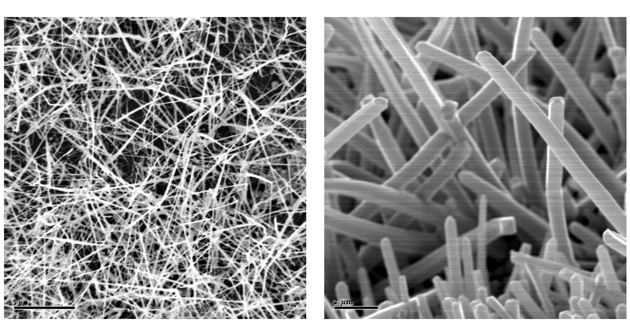


Figure 1. SEM images of the as-grown InSb nanowires. (a) Dense mesh-like straight and long InSb nanowires. (b) High magnification SEM view of cubic crystalline nanowires.

3.2 X-ray diffraction analysis

Figure 2 is the X-ray diffraction pattern of the as-grown InSb nanowires on quartz substrate. All of the strong intensity peaks can be indexed to the zinc blende (FCC) structure of InSb. The 2θ peak at 23.6° is a clear indication of InSb(111) peak. No other crystalline impurities, such as In_2O_3, were detected in the XRD pattern. This proves that the as-grown nanowire sample is indeed pure crystals of InSb.

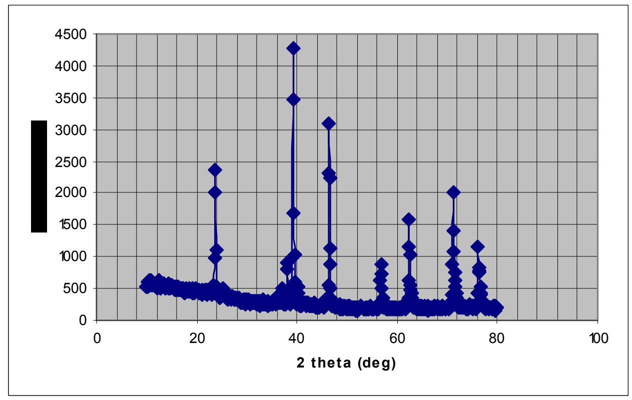


Figure 2. X-ray diffraction pattern of the as-grown InSb nanowires on quartz substrate.

3.3 HRTEM analysis

Figure 3 shows the HRTEM image of a single InSb nanowire cropped on TEM copper grid from IPA solution. These images are 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 4.6 Å. The lattice fringes are at 45 degrees toward the growth direction of the nanowire. The most dense lattice plane is along [01-1] direction and the growth direction is found to be [001]. We also can clearly see that the native oxide layer thickness along the InSb nanowire is 3 nm. Current tunneling to the nanowires during electrical measurement is therefore possible.

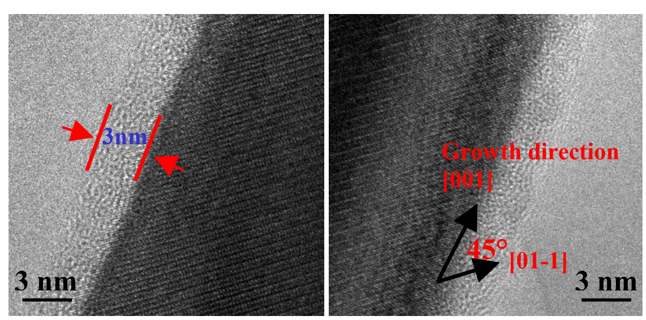


Figure 3. HRTEM images of InSb nanowires at 1140 K magnification. The scale bar on the image is 3 nm.

3.4 SAED pattern analysis

The crystalline structure of the lattice and the crystal planes can be derived from SAED patterns. Figure 4 shows the diffraction pattern with [1-10] beam direction. A clear rectangle diffraction pattern is observed. After detailed crystal structure analysis examining practically all possible crystal lattices and beam directions, we conclude that the InSb nanowires have Face-Centered-Cubic (FCC) unit cell structure. From beam direction [1-10], the diffraction dots are identified as planes shown in Figure 4. Since $r = g * L * \lambda$, where r is the measured dot distance on the diffraction pattern film, $g = (h^2+k^2+l^2)^{1/2} / a$ (hkl is the plane indices and a is the cubic unit cell length of the crystal structure), L is the distance of the nanowire to the projected film on TEM, λ is the wavelength of the TEM electron beam, we can calculate the cubic unit cell length based on the measurement of the diffraction pattern films. From these measurements, we find that the unit cell length of the InSb nanowire crystal structure is 6.55 Å.

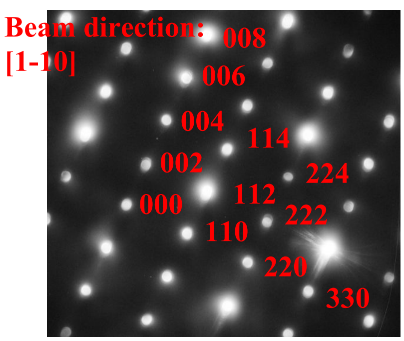


Figure 4. Selected area electron diffraction pattern of InSb nanowires with [1-10] beam direction.

In a FCC lattice, the densest planes are {01-1}. The distance between the most dense plane is $a/\sqrt{2}$, where a is the cubic unit cell length. In our case, a is derived to be 6.55 Å, which gives the distance between the most dense plane 4.63 Å. This number is fairly close to the measured real space lattice fringe distance of 4.6 Å as can be derived from the HRTEM images in Figure 3.

3.5 EDS analysis

EDS measurements confirm that the material compositions of the nanowire are indeed In and Sb. Figure 5 shows the EDS spectrum of the InSb nanowire. Spatially resolved elemental analysis by EDS clearly proves that In and Sb are 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 are from the TEM Cu grid, we only observe a very weak peak at 0.55 KeV. This is attributed to the trace amount of oxygen from the native oxide layer along the InSb nanowire. From the clear EDS spectrum, we conclude that our nanowire is single crystal, pure InSb nanowire.

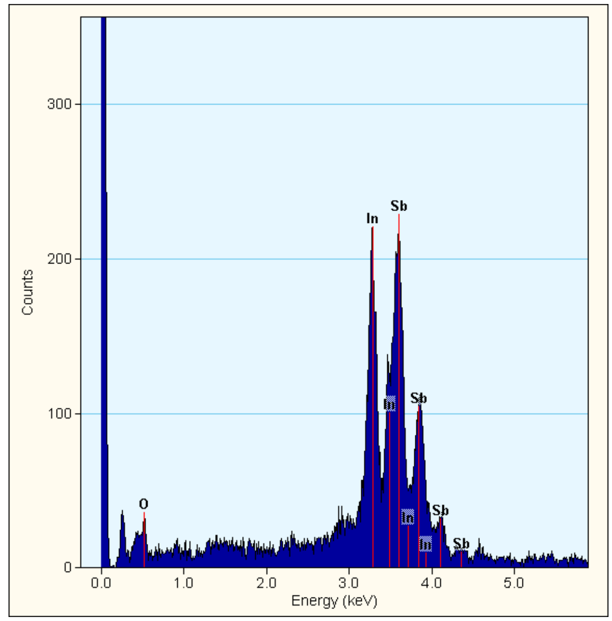


Figure 5. Energy-dispersive X-ray spectroscopy spectrum of InSb nanowire.

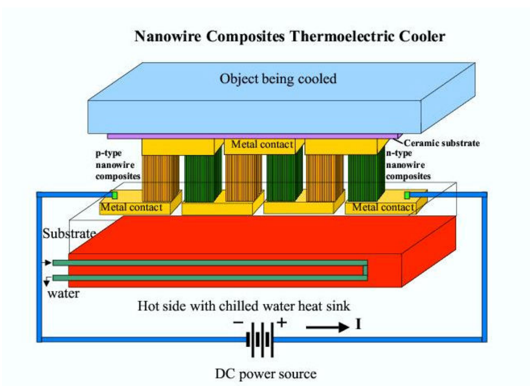
We also have performed hot probe measurements and found that our as-grown InSb nanowires exhibited characteristics of n-type semiconductors. We therefore conclude that the un-intentionally doped InSb nanowire is intrinsically n-type. We suspect that it could be due to oxygen substitutions in the nanowires or trace amount of Te present (it is known that Te and Sb are very difficult to separate from each other). We have measured thermoelectric transport properties of these as-grown InSb nanowires, and have reported them in journals recently [6,7].

We are currently synthesizing $In_xGa_{1-x}Sb$ based p-type nanowires based on a similar VLS method. With the successful synthesis of both n- and p-type single crystalline InSb nanowires, we will investigate the integration method for fabricating InSb nanowire based thermoelectric devices and their potential applications in energy efficient solid-state refrigeration and power generation applications.

Figure 6 shows two schematic diagrams of the basic thermoelectric nano cells for (a) cooling and (b) power generation. The p-type and n-type nanowire array legs can be patterned and grown separately on the same set of substrate wafers. The p-type and n-type nanowire micron zones can be defined and registered through standard photolithographic steps. After nanowire growth, a layer of p- or n-type thermoelectric thin film materials can be CVD deposited into the p- or n- type nanowire array micron zones, respectively. These films are used to support the nanowires and to form p- or n-type nanowire composites. The composite legs can then be interconnected in series through lithographic patterning and metalization processes. In cooling configuration (a), one side of the nanowire composites is in contact with a hot side with chilled water heat sink. The other side is in contact with the object that is being cooled through a ceramic substrate. The DC current is flowing from the n- nanowire to the p-nanowire in series. The carriers in p-nanowires ("holes") and n-nanowires (electrons) move the heat from the cold side to the hot side, and therefore cool the object on the cold side. In power generation configuration (b), one side of the nanowire composites is in contact with a hot side with heater. The other side is in contact with a cold side with chilled water heat sink. Heat flows from the hot side to the cold side through p- and n- nanowire composites. The holes in p-type nanowires and the electrons in n-type nanowires move accordingly in series, and therefore form electric current. This DC current can be drawn from the device through the metal contact pads at the edge.

These prototype thermoelectric nano cells can be designed as a universal chip format where electrical contact pads are aligned at the edges of a standard square chip. They can be easily stacked together and assembled into multi-stage modules to make a thermoelectric device of any size desired.

(a)



(b)

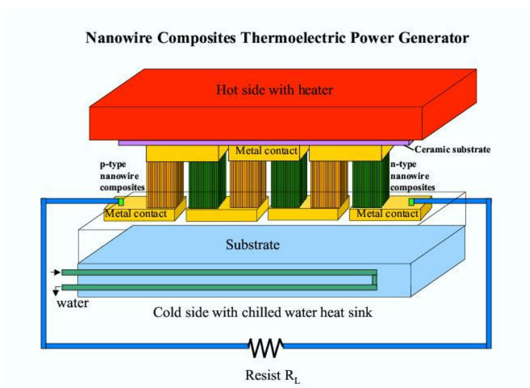


Figure 6. Schematic diagrams of (a) a prototype thermoelectric nano cooler; and (b) a prototype nano power generator.

4 CONCLUSIONS

Through a detailed investigation of various growth conditions, we have identified a narrow growth window for producing high crystalline quality InSb nanowires in large scales. The single crystalline InSb nanowires have been successfully synthesized at 650°C under chamber pressure of 350 torr using a self-catalyzed VLS transport process. Our batch produced InSb nanowires are typically 20-100 nm in diameter and 10-50 μm in length with high crystalline quality. Structural analysis by SEM, XRD, HRTEM, and SAED reveals that our as-grown InSb nanowires have FCC crystalline structure with cubic unit cell length of 6.55 Å. EDS measurements prove that the nanowire is in deed InSb. The InSb nanowires are grown along [001] direction, 45 degrees toward the most dense lattice planes in FCC structure. Prototype thermoelectric nano coolers and nano power generators based on single crystalline p- and n-type InSb nanowires and their composites have been designed.

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