Title: MOCVD growth process and characterization of rare earth nanocomposite embedded in the indium gallium antimonide matrix

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ABSTRACT

In the continuing quest for more efficient and environmentally friendly electrical power generation, new concept of solid-state thermoelectric devices are among the technological frontiers where applications of nanotechnology are expected to bringdramatic improvements in their overall performance. We propose the new design concept of thermoelectric devices based on a high-quality semiconductor host that contains semimetallic nanoparticles, referred to as "nanocomposite". Two materials, Zn-doped InGaSb and ErSb are used as a host semiconductor and semimetallic nanoparticles, respectively. We use low-pressure metal organic chemical vapor deposition to grow ErSb nanoparticles embedded in Zn-doped InGaSb. Grown materials are structurally and electrically characterized to assess their potentials for thermoelectric devices.

INTRODUCTION

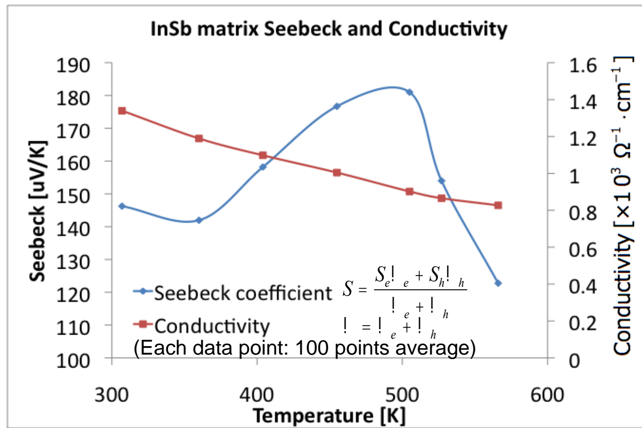
According to statistics, in 2005 the population of the world is 6.5 billion and the worldwide energy consumption is 8 billion tons equivalent to oil. However, only 35 % of consumed energy is used as energy source while the other 65 % is dumped as heat. Thus, high efficiency and environment friendly energy sources are strongly required to satisfy such a tight growing energy demand. Thermoelectrics is one of the expected candidates because of its durability due to no internal mechanical system and energy conversion from discarded heat. The requirement of thermoelectrics materials to the energy source application are 10 % conversion efficiency and 2.0 or more dimension less figure of merit. One of the most promising avenues for designing high-efficiency thermoelectric devices is to combine a bulk semiconductor host with semimetallic nanoparticles, referred to as nanocomposite. Nanocomposites are expected to exhibit three advantageous features; (1) high electrical conductivity owing to the high-quality host semiconductor and excess free carries supplied by semimetallic nanoparticles, (2) low thermal conductivity owing to embedded semimetallic nanoparticles that scatter long-wavelength phonons, and (3) high Seebeck coefficient realized by energy filtering at the interface between the semimetallic nanoparticles and the host semiconductor. Tuning these three features independently would lead us to a high ZT, thermoelectric figure of merit that cannot be obtained easily by traditional thermoelectric devices based on bulk semiconductors [1]. In general, semiconductors suitable for thermoelectric host materials have; small band gap and high carrier mobility. In our experiment described below, the host semiconductor is either InSb, one of group III-V compound semiconductor binary alloys, or InGaSb, one of group III-V compound

semiconductor ternary alloys. InSb has a band gap of 0.17 eV (300 K), electron and hole mobilities 80000 and 1250 cm^2/Vs (300 K), respectively, and bulk ZT of InSb is 0.058 (300 K [2]). InGaSb has a band gap of 0.17 eV (300 K), electron and hole mobilities 5000 ~ 80000 and 850 ~ 1250 cm^2/Vs (300 K), respectively, and bulk ZT of InGaSb is 0.058 ~ 0.024 (300 K [2]). ErSb is chosen as a material for nanoparticles that are embedded in either InSb or InGaSb host. To enhance the thermoelectrics properties of the host materials InSb, III-V semiconductor, ErSb rare earth metal-V, is chosen for co-doped nanoparticles due to the chemical affinity. Palmstrøm et al. reported the lattice matching between InSb host material and ErSb achieved while the rare earth-V binary system offer a very large range of lattice parameters, 4.51 – 6.58 A which corresponds to lattice matched to InGaSb [3]. Free hole concentration in the host material is carefully tuned to optimize electrical conductivity minimizing degrading thermal conductivity .

EXPERIMENT

In the following section we will describe the MOCVD growth of ErSb nanocomposites in the zinc doped InGa(As)Sb host materials. We took the three step strategy; (1) begin with the homoepitaxy growth of InSb host material on the n-type InSb (100) substrate and semi-insulated (SI) GaAs (100) substrate, (2) try ErSb thin film growth on the n-type InSb (100) substrate, finally (3) challenge the growth of ErSb nanocomposites embedded in the host materials on the n-type InSb (100) substrate. The lattice constant of the host material is adjusted gallium (Ga) dope into the InSb film and hole density is tuned by zinc (Zn) dope. Since the band gap of InSb is fairly small (0.17 eV) and Zn has high diffusion rate in the host materials, the grown films are separated from n-type InSb (100) substrate with 200 nm SI-InSb buffer layers. In the each stage, we conducted fundamental characterization on the grown samples to obtain the optimum growth conditions.

The target in the first step is to demonstrate the InSb host material MOCVD homoepitaxial growth with precursors Trimethylindium (In) and, Triethylantimony (Sb) on semi-insulated GaAs (100) or n-type InSb substrate. The growth are conducted at 485 C, 2 minutes duration time. As shown in Fig. 1, the grown InSb film on SI-GaAs substrate have the temperature dependencies of Seebeck coefficient showing (1) the local minimum at 353 C, (2) monotonically increases to the local maximum at 495 C because of the increase of the hole density, and (3) drop due to the contribution of thermally excited electron in the SI-GaAs substrate in high temperature region. The electrical conductivity shows monotonically decrease as temperature increase due to carrier scattering by thermally created phonons. The similar thermoelectrics properties were measured in the InSb film grown by MBE indicating the MOCVD grown InSb thin film has the potential of application to the thermoelectrics host material.



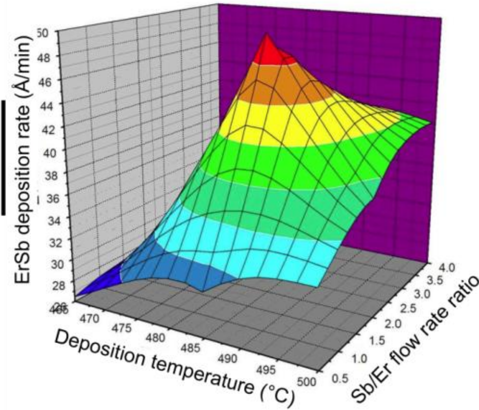


Fig. 1 Seebeck coefficient shows the local minimum at 353 C, monotonically increase until 495 C, and drops due to the contribution of the thermally excited electrons in the SI-GaAs substrate in high temperature region. The electric conductivity monotonically decreases as temperature rises due to the scattering by thermally created phonons. (The each blue and red data points are average of 600 times measurement) Fig. 2 ErSb thin film growth rate as a function of the deposition temperature and Sb/Er precursor flow rate ratio. The thin film growth ratio has maximum at 485 C and the flow rate ratio at 2.25.

In the second step, the vert first challenge of MOCVD ErSb thin film growth is conducted. The target here is to establish single crystal ErSb thin film growth condition. We find the ErSb film growth has the maximum rate 47 angstrom/min at growth temperature 485 C and Sb and Er precursor flow rate ratio 2.25 as shown in Fig 2. The grown ErSb thin film with the maximum growth rate shows smooth surface feature and EDX spectra on the surface indicates co-existence of In, Sb and Er in the film. XRD scan spectra on the film shows co-existence of ErSb (422) and ErSb (511) atomic planes indicating single crystal growth in the film. The similar rare earth (RE) - group V MBE grown film on III-V substrate was reported indicating co-existence of {l00}<011>RE-V//{100}<011>III-V and rotated {l10}<011>RE-V//{100}<011>III-V [3]. Since ErSb (422) and ErSb (511) atomic planes work as diffraction gratings which have different lateral grating pitches on the film surface, some ErSb peaks, i.e. ErSb (400) might be weakened as being hidden behind the XRD background spectra.

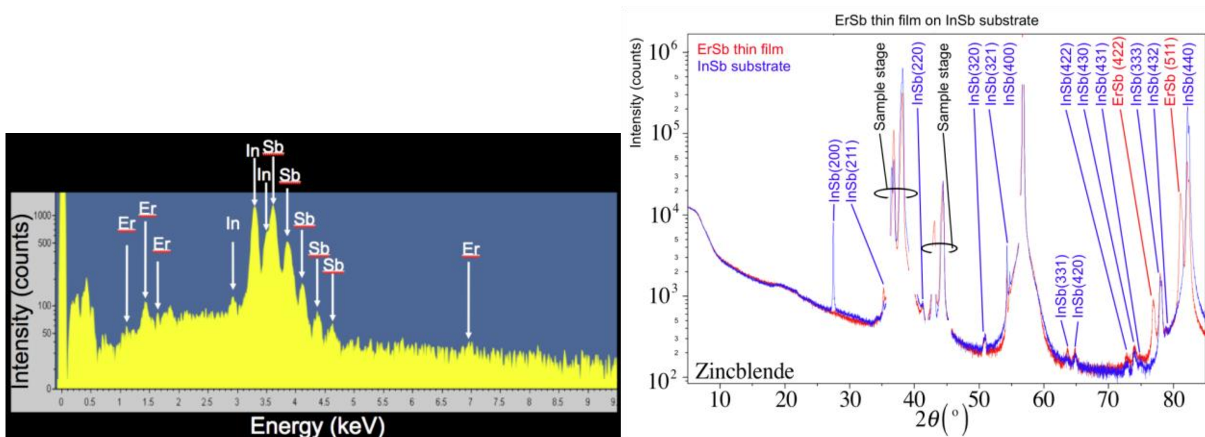
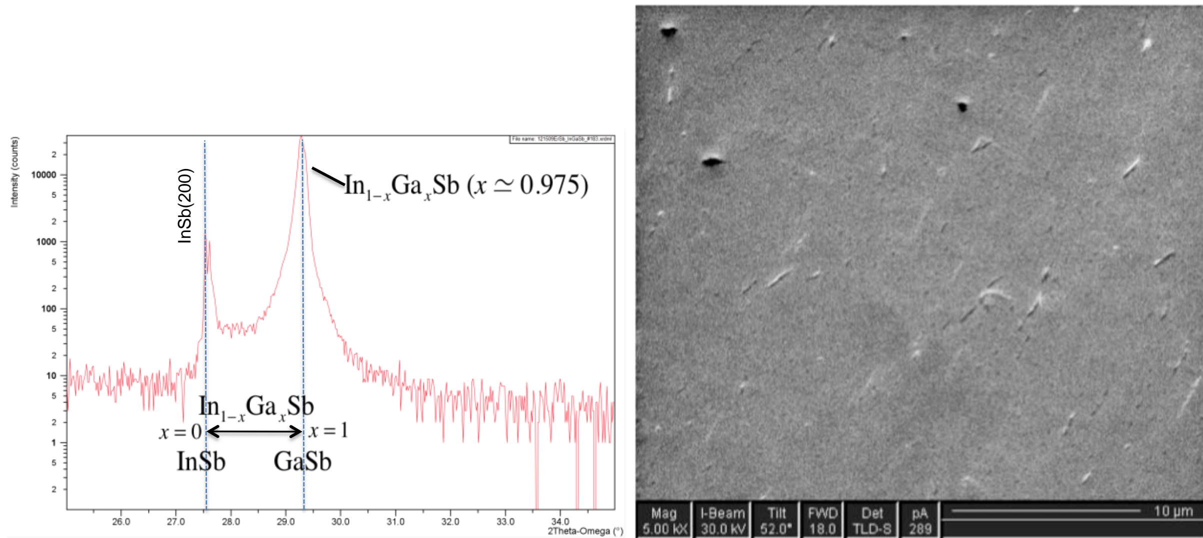


Fig. 3 (Left) EDS on ErSb film shows all composite elements in the grown film. Fig. 4 (Right) XRD on ErSb film indicates ErSb single crystal structure showing ErSb (422) and ErSb (511) peaks. The other peaks might be weakned due to the lateral diffaction grating effect by ErSb (422) and ErSb (511) crystal structure on the film surface.

In the third step, the enhancement of thermoelectrics properties of the host material InSb is conducted applying InGa_xSb_1-x (0< x <1) tarnally crystal structure and the co-doped ErSb nanoparticles. The purpose of the InGa_xSb_1-x (0< x <1) tarnally crystal structure is to offer the scattering source of long wavelength phonons as Sb atoms in the InSb binary crystal are randomly replaced with Ga atoms. On the other hand, the co-doping of ErSb nanoparticles work as both long wavelength phonon scattering source and low energy electron filter in the host material. As a result, it is expected that the thermal conductivity of host materials are reduced and power factor, (Seebeck coefficient)^2 x (electrical conductivity), stay fairly identical level. The growth of ErSb embedded in InGa(As)Sb:Zn host material is conducted at temperature 485 C with 2 sec Er precursor injection during 2min MOCVD process. The precursors in the growth are Trimethylindium (In), Triethylantimony (Sb), and Tri(isopropylcylopentadienyl)Erbium (Er) respectively. SEM surface imaging in Fig. 6 shows smooth surface. XRD spectra shows peaks shift of InSb (200) and InSb (400) due to Ga fraction increase in the InSb host material. Enhanced XRD scan at InSb (200) peak has the peak shift corresponding to Ga fraction x = 0.975 indicating the full range of Ga fraction tuning in the host material film, GaSb (6.095 A) < ErSb (6.11 A) < InSb (6.458 A).



[Fig. 5 (Left) XRD scan result on InGaSb matrix shows the peak shift due to Ga fraction against. Fig. 6 (Right) SEM images on InGaSb:ErSb shows smooth morphology]

TEM cross section imaging indicate uniformly distributed 20 ~ 35 nm diameter ErSb nanocolum grown vertically in InGaSb:Zn host material (Fig. 7) and uniformly distributed 20 ~ 30 nm diameter ErSb nanoparticles in InAsSb:Zn host material (Fig. 8) in the grown samples. Where TEM image in Fig. 7 and 8 are taken with electron acceleration voltage at 200 kV. The sample lamellas are processed by Ga iron beam FIB acceleration voltage at 30 kV using vertical curving technique. (1) The processed area is covered by Pt barrier layer, (2) 4 um depth vertical trenches

are created in the both side of the lamella, (3) The underneath cut and the left and right slits are created, (4) The both surface of the lamella are polished by the iron beam into 50 ~ 60 nm thickness, (5) The lamella is scraped off and transferred by tipped glass capillary micro-manipulator onto a copper TEM grid.

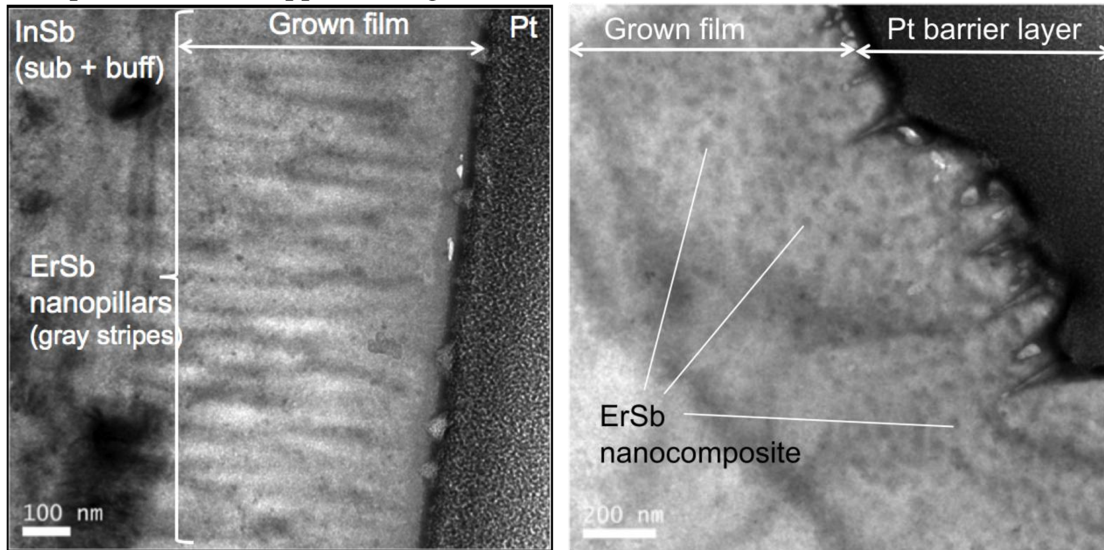


Fig. 7 (Left) TEM image of InGaSb:ErSb shows uniformly distributed 20 ~ 35 nm diameter nanocolumn in InGaAs:Zn matrix layer. Fig. 8 (Right) TEM image of InAsSb:ErSb shows uniformly distributed 20 ~ 35 nm diameter nanoparticles in InGaAs:Zn matrix layer

DISCUSSION

The InSb film growth has encouraging thermoelectrics properties as host material (Fig. 1). The first ErSb growth by MOCVD with the condition (Fig. 2) indicate single crystal strucrure (Fig. 4) and co-doped element ratio is preferable (Fig. 3). We have obtained the capability of the full range of Ga fraction tuning in InGaSb host (Fig. 5). The ErSb nanoparticle co-doped InGa(As)Sb film is demonstrated successfully and it show smooth surface (Fig. 6) and Er condensation into 20 ~ 35 nm diameter nanocolums in the InGaSb film (Fig. 7) and 20 ~ 30 nm diameter nanoparticles in the InAsSb film suggeste that we will realize nanometer size ErSb nanocomposites with tuning of Er precursor injection time.

However, due to heteroepitaxy InGa(As)Sb:ErSb film on InSb substrate, the TEM sample lamellas are strongly warpaged preventing from obtaining diffraction patterns and High Resolution TEM (HRTEM) images. To overcome the hardship, HRTEM on homoepitaxy multi InSb:ErSb layers which has variation in Er/Sb flow rate in the growth recipe is planned.

EDX on TEM samples in FIB process did not show Er sign due to the low sensitivity of EDX apparatus. Thus the line and area EDX mapping on the TEM samples will be performed in the next study with high sensitivity EDX.

For tuning carrier density in InGa(As)Sb matrix, we applied co-dope Zn. However, due to high diffusion rate of Zn along with small band gap of InSb, the InSb substrate have started to contribute into the thermoelectrics properties. To separate the substrate effect from electric properties of the grown film, larger band gap substrate (i.e. InP:Fe) [8] sample growth is planned in the next step.

Although the MOCVD growth is successfully conducted, the enhancement of ZT is depending on the other studies for the host material choice and nanocomposites. Thus, the further thermoelectrics material studies are strongly needed to achieve ZT >2.0 or more.

RESULTS

We have successfully grown InSb host material on SI-GaAs substrate being in good agreement with identical component thin films grown by MBE in the temperature dependencies of Seebeck and electric conductivity. Being independent on InSb matrix, ErSb film is deposited on the n-type InSb (100) substrate. XRD indicates ErSb (422) and ErSb (511) crystal structures in the deposited ErSb film and EDX shows co-existence of In, Sb, and Er in the ErSb layer. Following the success in the individual growth of the InSb matrix and ErSb thin film, we merge both process to grow ErSb nanocomposites in the InGa(As)Sb:Zn matrix. XRD shows InSb (200) peak shift with respect to Ga fraction and TEM images indicate ErSb nanocomposite in InGa(As)Sb:Zn matrix. The results strongly indicates MOCVD grown ErSb nanocomposites embedded InGa(As)Sb:Zn host materials are applicable to ZT enhanced thermoelectrics materials.

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