# Reflection absorption infrared spectroscopy analysis of the evolution of ErSb on InSb

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## ARTICLE INFO

## ABSTRACT

We discuss an ex-situ monitoring technique based on glancing-angle infrared-absorption used to determine small amounts of erbium antimonide (ErSb) deposited on an indium antimonide (InSb) layer epitaxially grown on an InSb (100) substrate by low pressure metal organic chemical vapor deposition (MOCVD). Infrared absorption from the indium–hydrogen (In–H) stretching mode at 1754.5 cm$^{-1}$ associated with a top most surface of an epitaxial InSb layer was used to compare varying levels of surface coverage with ErSb. Among four samples of varying coverage of ErSb deposition (7.2 to 21.5 monolayers), detected infrared absorption peaks distinct to In–H weakened as ErSb surface coverage increased. In the early stage of ErSb deposition, our study suggests that outermost indium atoms in the InSb buffer layer are replaced by Er resulting in increase in absorption associated with the In–H mode. Using this simple ex-situ technique, we show that it is possible to calibrate the amount of ErSb deposited atop each individual InSb substrate for depositions of few to tens of monolayers.

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## 1. Introduction

Combining nanometer-scale materials of particular chemical composition within a bulk host material of differing chemical composition often leads to unique modifications of the bulk host material's physical properties [1–3]. This phenomenon has been especially studied to optimize the thermoelectric figure-of-merit *ZT* – an indicator of thermoelectric material performance – of a bulk thermoelectric material. A material's *ZT* can be enhanced with an increase in electrical conductivity or Seebeck coefficient, or with a decrease in thermal conductivity at a given temperature. Thermoelectric properties of ternary group III–V compound semiconductor host materials such as indium gallium antimonide (InGaSb) and indium antimony arsenide (InSbAs) are expected to be largely improved by embedding nanometer-scale semi-metallic particles such as erbium antimonide (ErSb) nanoparticles into the aforementioned host materials [2]. The inclusion of these semi-metallic nanoparticles with an appropriate diameter creates desirable scattering centers for mid-wavelength phonons and provides additional charge carriers to the host material [3]. Therefore, the host material's thermoelectric figure-of-merit *ZT* is enhanced because of decreased thermal conductivity by

the reduced contribution from lattice thermal conductivity and increased electrical conductivity at a given doping concentration by supplying additional charge carriers available for conduction. In addition, the Schottky barriers created at the interface between a host material and embedded semi-metallic nanoparticles can be tuned to alter the electron energy distribution around the Fermi level, which can result in an increased Seebeck coefficient [4].

It is predicted that an optimal nanoparticle size and volume density exist where thermal conductivity is minimized and electrical conduction properties of the host material are improved [1]. This prediction illuminates the need for accurate control of the size and volume density of ErSb nanoparticles deposited and formed atop an InSb surface. Unlike molecular beam epitaxy equipped with an in-situ growth monitoring system (e.g., reflection high-energy electron diffraction) that works in ultra-high vacuum, an in-situ growth monitoring system capable of estimating the presence of a small amount of a material on a growth front is not generally available in metal organic chemical vapor deposition (MOCVD). Yet, the great success in growing high-quality III–V compound semiconductors by MOCVD is indisputable. Therefore, we explore an ex-situ calibration technique, reflection absorption infrared spectroscopy (RAIRS), based on glancing-angle infrared-absorption used to collect information on vibrational modes of chemical species that make up a surface and to obtain the amount of a small quantity of ErSb delivered onto InSb surfaces. RAIRS has proven to be a particularly useful technique in catalyst surface characterization for its ability to evaluate surface vibrational modes and resolve closely positioned absorption peaks due to
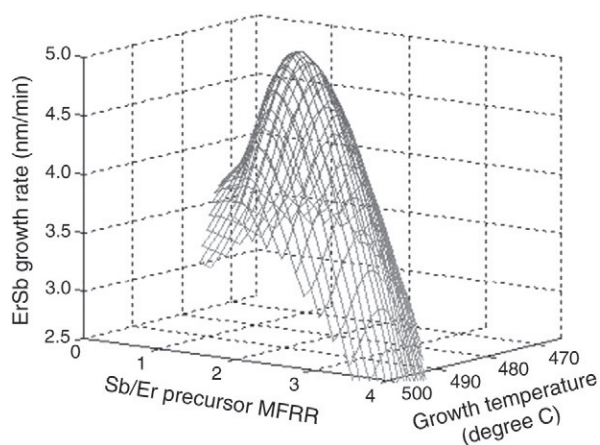
Fig. 1. The deposition rate of ErSb on InSb(100) surfaces plotted as a function of deposition temperature and the Sb/Er precursor molar flow rate ratio (MFRR). A peak deposition rate of 4.9 nm/min was obtained at 485 °C and molar flow rate ratio at 2.25.
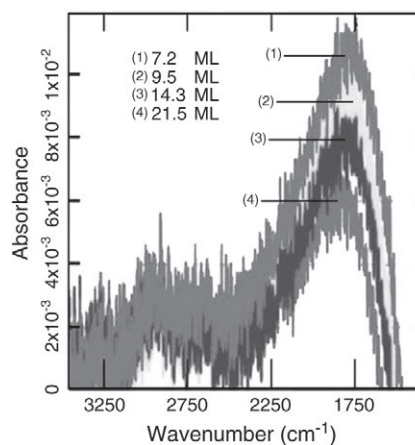


Fig. 3. RAIRS spectra of the four samples with varying coverage of ErSb on In–H terminated InSb surfaces. Detected infrared absorption peaks distinct to the In–H stretching mode at 1754.5 cm$^{-1}$ weakened as ErSb surface coverage increased.

high spectral resolution [5]. Metal nanoparticles such as Au supported by $Al_2O_3$, $SiO_2$, FeO (111), $CeO_2$, and $TiO_2$ thin films have been extensively studied with great success using RAIRS [6]. In addition to RAIRS, atomic force microscopy (AFM) is also used to further evaluate the surface morphology and concentration of ErSb nanoparticles formed on the InSb surface.

## 2. Experiment

When exposed to vapor phase chemicals, solid surfaces can serve as a growth platform for crystal formation. ErSb deposited atop an InSb surface forms ErSb nanoparticles largely due to thermodynamic differences in the enthalpy of formation between the two materials [7]. Four samples with four different amounts of ErSb deposited on InSb surfaces were made on InSb (100) substrates by low-pressure MOCVD [8,9]. Prior to ErSb deposition, a 500 nm unintentionally doped InSb buffer layer was grown on an InSb(100) substrate, creating a smooth surface that served as a growth platform for ErSb deposition. Tris(isopropyl-cyclopentadienyl) erbium and trimethyl-antimony were used for the growth of ErSb on the InSb buffer layer. Shown in Fig. 1 is a deposition rate of ErSb plotted against temperature and molar flow rate ratio between Sb and Er precursors. The figure shows a deposition rate peak of 4.9 nm/min at a temperature of 485 °C and precursor molar flow rate ratio of 2.25. Fig. 1 clearly shows that the ErSb deposition rate is

very sensitivity to both temperature and molar flow rate ratio. The peak deposition rate shown in Fig. 1 was used for each of the four samples hosting different amounts of ErSb deposited on the InSb buffer layer. By varying the ErSb growth time, each sample yielded a specific amount of deposited ErSb ranging from 7.2 to 21.5 monolayers (ML).

Fig. 2 illustrates the configuration of our RAIRS measurement. An infrared beam is collimated onto the surface of the sample at an approximate incident angle of 8°. A portion of the emitted infrared beam is absorbed by the vibrational modes associated with In–H bonds present on InSb surfaces partially covered by ErSb deposition. The remaining unabsorbed incident infrared light is reflected and collected by a detector. Detection of the reflected infrared spectrum reveals absorption peaks characteristic to the stretching mode of exposed In–H bonds present on the surface of the InSb buffer layer. In our RAIRS measurement, absorption spectra were obtained with respect to a reference sample that provided a surface of an InSb buffer layer without ErSb, therefore the RAIRS spectrum collected from the 0 ML sample shows no spectroscopic features associated with In–H bonds.

## 3. Results and discussion

Considerable amounts of hydrogen and hydrogen radicals are present in our low-pressure MOCVD growth environment. This is, in
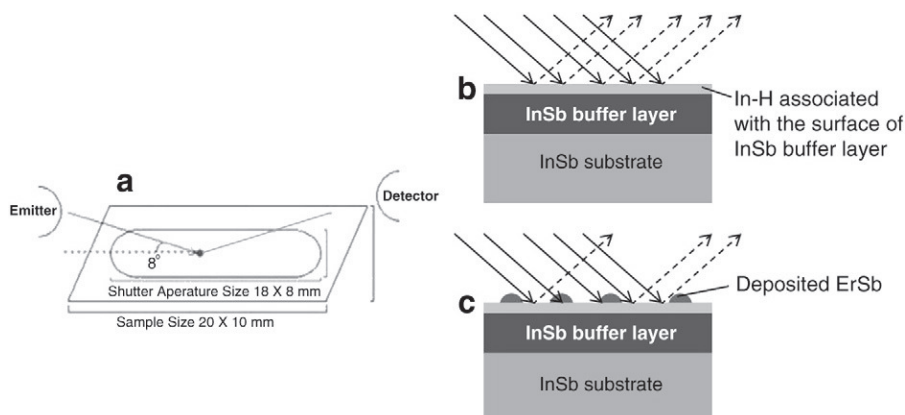


Fig. 2. (a) Reflection absorption infra-red spectroscopy (RAIRS) configuration. (b) and (c) Schematics showing that an increase in surface coverage of ErSb results in a decrease in the number of detected In–H bonds exposed on the InSb buffer layer surface.
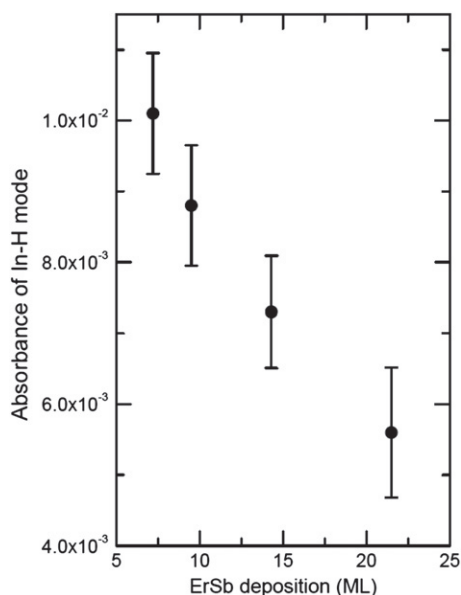
**Fig. 4.** Peak absorbance at 1754.5 cm$^{-1}$ of In–H vibrational mode plotted as a function of ErSb deposition.

particular, expected because we use rather low V/III ratio, 15/1, for the growth of InSb in contrast to typical growth conditions for group III-arsenide and –phosphide for which much higher V/III ratio is used. Prior to ErSb deposition, In–H surface bonds are formed and characterized by their distinct vibrational modes. These vibrational modes are capable of infrared absorption in the 1660–1682 cm$^{-1}$ range reported for hydrogen-terminated indium phosphide (InP) surfaces [10] and 1754.5 cm$^{-1}$ range reported for the In–H stretching mode of InH$_3$ [11]. Based on this information, we studied chemical and morphological evolution of the surface of the InSb buffer layers upon ErSb deposition.

Fig. 3 shows RAIRS spectra obtained from the four samples with different growth times at a given deposition rate as calibrated in Fig. 2. Each sample is covered with a specific amount of ErSb ranging from 7.2 to 21.5 ML. In Fig. 4, the peak absorption intensity is plotted as a function of ErSb deposition showing linear correlation between these two quantities based on the trend seen in the range of ErSb deposition of 7.2–21.5 ML. It is apparent in Fig. 3 that as the amount

of deposited ErSb increases and covers the InSb surface, the RAIRS absorption peaks associated with the In–H bonds decrease. This simple picture, however, does not appear to describe the evolution from 0 ML (i.e., the reference sample) to 7.2 ML ErSb sample. As mentioned earlier, our RAIRS measurement is a comparative measurement done on the four InSb surfaces covered with different amounts of ErSb using an InSb surface with 0 ML ErSb deposition (i.e., the reference sample). If we assume that the surface of the reference sample was completely occupied by In–H bonds, the In–H absorption on the 7.2 ML ErSb sample would have shown reduced absorption, in other words, in our RAIRS measurement, the absorption of the 7.2 ML ErSb sample should have been recorded as "negative" absorption. Therefore, the positive absorption of the 7.2 ML ErSb sample seen in Fig. 3 suggests that the number of In–H bonds on the 7.2 ML ErSb sample is indeed larger than that on the reference sample. Qualitative description for the evolution from 0 ML to 7.2 ML ErSb sample is as follows; under our specific growth conditions, the surface of the InSb buffer layer (i.e., the reference sample with 0 ML ErSb) is covered predominantly with antimony. It is also highly likely that a small number of In–H bonds coexist. The heat of formation of Er–Sb and In–Sb is −286.8 kJ/mol and −34.1 kJ/mol, respectively [12,13], thus, upon the deposition of 7.2 ML ErSb, at least during the early stage of ErSb deposition, there is a strong thermodynamic driving force for indium atoms in the InSb buffer layer being replaced by Er to form ErSb. This replacement process creates more free indium atoms available to form additional In–H bonds on the 7.2 ML ErSb sample leading to the "positive" absorption as seen in Fig. 3. Further deposition of ErSb results in complete coverage of the InSb buffer layer and the number of In–H bonds that participate in the absorption decreases as nominal thickness of ErSb increases. Also notable in Fig. 3 is the capability of RAIRS to clearly distinguish a 2.3 ML difference of deposition between a 9.5 ML ErSb sample and 7.2 ML ErSb sample.

To further assess the small amount of ErSb deposition profiled by the RAIRS experiments, we evaluated the samples by atomic force microscopy (AFM). The two samples representing the upper and the lower bounds of ErSb deposition range we studied; 7.2 ML (a) and 21.5 ML (b) are shown in Fig. 5. Clearly seen are ErSb islands covering the surfaces of the InSb buffer layers. Surface coverage of ErSb was also obtained by AFM and plotted in Fig. 6. Extrapolating to 0 ML does not seem to traverse 0%, which may indicate the significance of the replacement process occurring between erbium and indium as described earlier. The 7.2 ML sample surface is approximately 29% covered and the 21.5 ML sample surface is approximately 55% covered. These AFM results are qualitatively consistent with the RAIRS
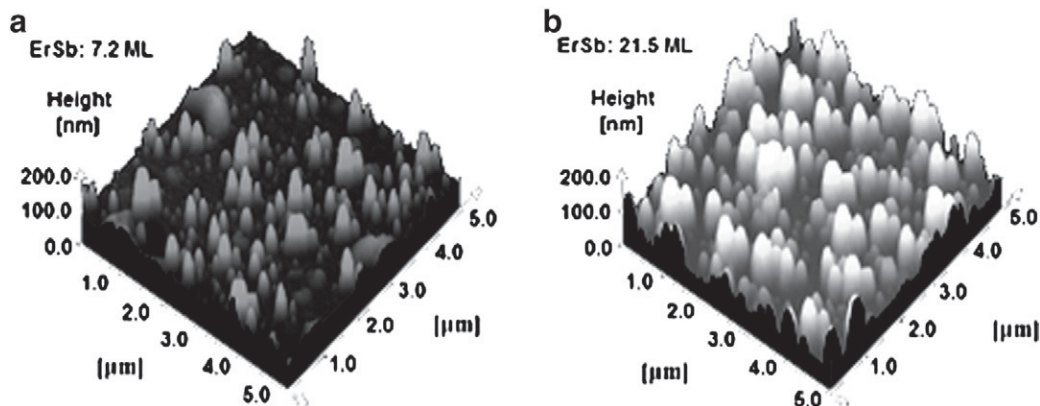


**Fig. 5.** AFM images collected on two of the samples with varying coverage of ErSb on In–H terminated InSb surfaces. ErSb covers approximately 29% of the InSb surface for the 7.2 ML sample (a) and approximately 55% of the InSb surface for the 21.5 ML sample (b).
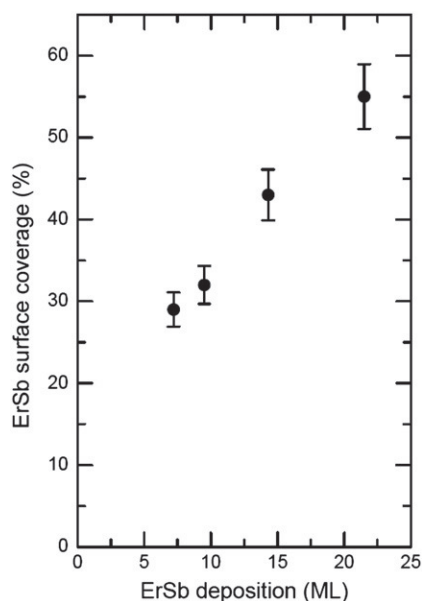
**Fig. 6.** ErSb surface coverage on the InSb buffer layer.

results and further qualify RAIRS as a competent ex-situ calibration technique for evaluating the deposition of few to tens of ML surface coverage.

RAIRS offers two main advantages over alternative characterization techniques. First, it can be performed in non-vacuum environments since it is an optical technique. Second, even at adsorption as low as 0.01%–2%, the RAIRS signals associated with the number of surface adsorbing molecules is generally recorded at relatively high resolution using modern FTIR spectrometers. Also, while the technique is not surface-specific, it can be shown theoretically that the best sensitivity for IR measurements on metallic surfaces is obtained using grazing-incidence reflection of the IR light [5]. Our studies take advantage of these benefits of RAIRS and use the reflection IR technique to measure mono-layer amounts of ErSb on In–H terminated InSb surfaces. The technique can also be used to measure mono-layer amounts of materials other than ErSb deposited on similar surfaces, making material deposition rates of differing materials easy to compare.

## 4. Summary

In developing enhanced thermoelectric materials with embedded nanoparticles, it is necessary to monitor the size and volume density of grown nanoparticles. An optimal nanoparticle size and volume density may exist where the figure-of-merit *ZT* of the host thermoelectric material is optimized. Therefore, we discuss an ex-situ monitoring technique based on glancing-angle, infrared-absorption called RAIRS used to measure the amount of ErSb nanoparticles deposited atop InSb substrates. After exposing the surface of the InSb substrates to a shallow angle infrared beam, we detected distinct absorption peaks associated with In–H surface bonds found on the substrate surface before and after ErSb deposition. The difference in the absorption peaks measured before and after ErSb deposition revealed the amount of ErSb deposited atop the substrate surface. We used AFM to visualize the surface topology of the InSb substrates with grown ErSb nanoparticles. Results from both RAIRS and AFM correlated well with one another, qualifying RAIRS as a competent ex-situ monitoring technique for evaluating the deposition of mono-layer amounts of ErSb on In–H terminated InSb surfaces.

## Acknowledgments

## References

[1] N. Mingo, et al., Nano Lett. 9 (2) (2009) 711.
[2] J.M.O. Zide, et al., Thermoelectrics 2006 ICT'06 25th International Conference (2006).
[3] M. Zebarjadi, et al., J. Electron. Mater. 38 (66) (2009).
[4] D. Vashaee, A. Shakouri, Phys. Rev. Lett. 92 (10) (2004) [106103/1-4].
[5] N. Sheppard, J. Erkelens, Appl. Spectrosc. 38 (4) (1984) 471.
[6] E. Wilson, et al., J. Phys. Chem. C 114 (15) (2010) 6879.
[7] T. Onishi, et al., Proceeding of MRS 2010 Spring Meeting Symposium DD Paper 250 Number 763327 (2010).
[8] K.J. Norris, et al., J. Electron. Mater. 41 (5) (2012) 971.
[9] K.J. Norris, et al., Proc SPIE 8106 (2011) 81060Q.
[10] K. Raghavachari, et al., J. Am. Chem. Soc. 124 (50) (2002) 15119.
[11] P. Pullumbi, et al., Chem. Phys. 185 (1994) 25.
[12] K. Yamaguchi, et al., Mater. Trans. 35 (1994) 396.
[13] B.D. Schultz, et al., Phys. Rev. B 73 (2006) 241407.