

# Reflection Absorption Infrared Spectroscopy Study on the Spontaneous Formation of Erbium Monoantimonide Nanoparticles on Indium Antimonide Surfaces

Takehiro Onishi<sup>1</sup>, Andrew J. Lohn<sup>1,2</sup>, Elane Coleman<sup>3</sup>, Gary S. Tompa<sup>3</sup> and Nobuhiko P. Kobayashi<sup>1,2</sup>;

<sup>1</sup>Baskin School of Engineering, University of California Santa Cruz, Santa Cruz, California;

<sup>2</sup>Nanostructured Energy Conversion Technology and Research (NECTAR), Advanced Studies Laboratories NASA Ames Research Center, Moffett Field, California; <sup>3</sup>Structured Materials Industries, Piscataway, New Jersey.

## ABSTRACT

We describe an ex-situ monitoring technique for a small amount (~30 mono-layers) of erbium monoantimonide (ErSb) deposited on an indium antimonide (InSb) epitaxial layer prepared on InSb (100) substrates by metal organic chemical vapor deposition (MOCVD). Our objective is to improve thermoelectrics properties of nanocomposites that employ nanometer size semi-metallic ErSb particles (ErSb nanoparticles) embedded in ternary group III-V compound semiconductor host materials such as indium gallium antimonide (InGaSb) and indium antimonide arsenide (InSbAs). The formation of ErSb nanoparticles embedded in a host material is spontaneous and needs to be carefully controlled to tune the size and volume density of the ErSb nanoparticles. We used an ex-situ monitoring technique based on glancing-angle infrared-absorption, reflection absorption infra-red spectroscopy (RAIRS), to study the formation of ErSb nanoparticles to correlate the amount of delivered ErSb and surface morphology of the surface of InSb covered with ErSb.

## INTRODUCTION

In the quest of developing a route to optimize physical properties such as Seebeck coefficient, electrical conductivity, and thermal conductivity of bulk group III-V compound semiconductors with the view toward efficient thermoelectric power generation devices, we have been developing “nanocomposites” in which semi-metallic rare-earth compound (e.g., erbium monoantimonide) in the form of nanometer-scale particles are embedded in a ternary group III-V compound semiconductor host. Combining dissimilar materials at nanometer-scale within a bulk material often leads to unique modifications in physical properties of the resulting bulk material. The formation of semiconductor quantum dots such as indium arsenide within a gallium arsenide host is driven by atomistic surface processes under the influence of mechanical stress caused by mismatch strain between two dissimilar materials (i.e., the Stranski-Krastanov mechanism [1]). A solid surface acts as a growth front where it meets a liquid or vapor phase. The process of crystal growth is catalyzed by physical and chemical characteristics of a surface on which various atomistic processes progress simultaneously.

Our goal is to grow semi-metallic ErSb nanoparticles embedded within ternary group III-V compound semiconductor host materials such as indium gallium antimonides (InGaSb) and indium antimonide arsenide (InSbAs). This unique combination of two dissimilar materials is a new approach for synthesizing nanocomposites, a structure consisting of semi-metallic nanoparticles embedded in a bulk semiconductor host, which could exhibit peculiar physical properties not available in ordinary isotropic bulk semiconductors. Unlike InAs islands on a

GaAs surface, the formation of ErSb nanoparticles on an indium antimonide (InSb) surface is largely driven by thermodynamic difference in the enthalpy of formation between the two materials [2], however, the growth mechanism of ErSb nanoparticles on an InSb surface can be still assessed by studying atomistic processes that occur on a surface. Ideally the formation of ErSb nanoparticles should be monitored in-situ during the deposition, however, a vapor phase epitaxial growth technique we use is proceeds at process pressure not suitable for surface analytical techniques such as reflection high energy electron diffraction, therefore it is highly desirable to develop an ex-situ diagnostic technique by which signatures of various atomistic surface processes can be collected on a grown surface, and we seek an ex-situ technique to evaluate a small amount of Er deposition onto InSb surfaces. In this paper, we applied an ex-situ diagnostic technique based on infra-red spectroscopy with a glancing angle arrangement, reflection absorption infra-red spectroscopy (RAIRS), to characterize surfaces of InSb covered with various very small amounts of ErSb to investigate growth mechanisms that govern the formation of the ErSb nanoparticles. Atomic force microscopy (AFM) is also used as a complementary technique to the RAIRS measurement.

## EXPERIMENT and DISCUSSION

ErSb samples studied by RAIRS were grown by low-pressure metal organic chemical vapor deposition (MOCVD) with tris(isopropylcyclopentadienyl) erbium and trimethylantimony at the growth temperature of 485 °C and the growth pressure of 120 torr. Prior to the deposition of ErSb, a 500 nm unintentionally doped InSb buffer layer was grown on InSb (100) substrates to obtain smooth surface of InSb on which ErSb was deposited. Fig. 1 shows the deposition rate of ErSb plotted as a function of the deposition temperature and the molar-flow rate ratio of the Sb precursor to that of the Er precursor. The ErSb deposition rate was obtained by growing a thick ErSb (300 nm) for a given growth time. The ErSb deposition rate shows a peak at 49 Å/min when the deposition temperature and the precursor molar-flow rate ratio are 485 °C and 2.25, respectively. It is apparent that the ErSb deposition rate is very sensitive to both the deposition temperature and the precursor molar-flow rate ratio. The ErSb deposition rate is expected to critically influence the formation of ErSb nanoparticles during the MOCVD co-deposition (e.g., depositing both ErSb and InSb simultaneously) process. Furthermore, the total amount of Er delivered onto a growing surface is equally important to control the size and volume density of the ErSb nanoparticles.

Four samples were prepared with four different growth times at a given deposition rate, as a result the four samples of InSb surfaces covered with different total amount of ErSb were studied by RAIRS. In the RAIRS measurement, a monochromatic infra-red beam was directed onto the surface of InSb at a shallow incident angle ( $\sim 8^\circ$ ) with respect to the surface of InSb as depicted in Fig. 2. Vibrational modes associated with the bond between indium and hydrogen (In-H) are used to diagnose the surface characteristics related to the growth conditions under which Er and Sb precursors are delivered onto the InSb surfaces. Absorption associated with In-H bonds is expected to appear in the range reported for In-H stretching mode of  $\text{InH}_3$  ( $1754.5 \text{ cm}^{-1}$ ) [3] and hydrogen-terminated InP surfaces ( $1660 - 1682 \text{ cm}^{-1}$ ) [4].

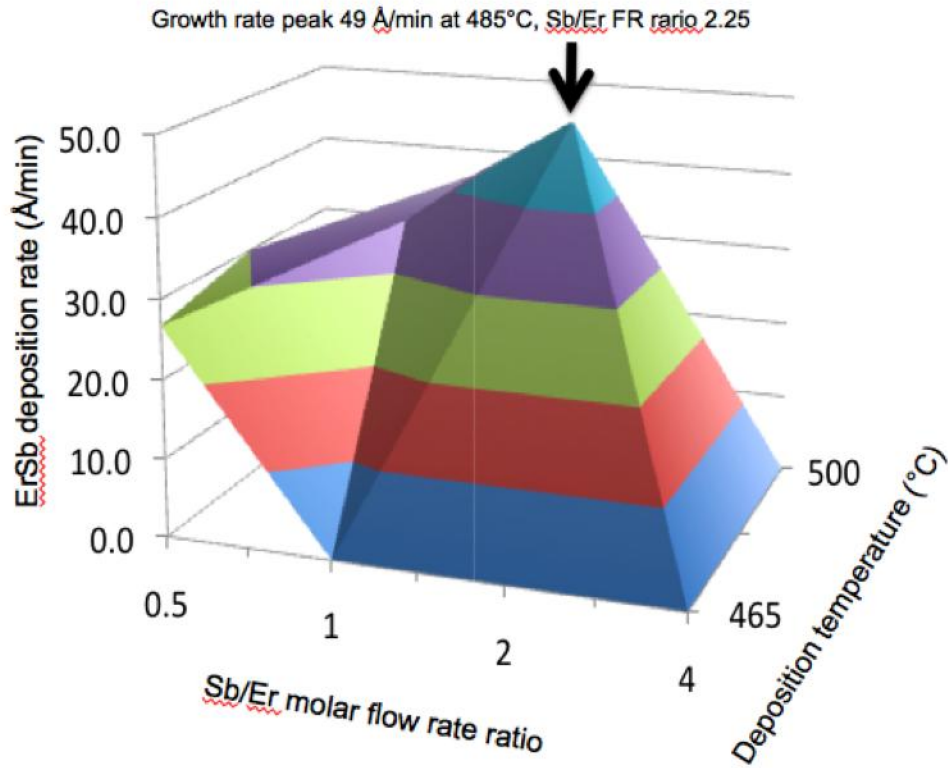


Fig. 1: ErSb deposition rate on InSb (100) substrate has strong sensitivity to the deposition temperature and the Sb/Er precursor flow rate ratio. The peak deposition rate 49 Å/min was obtained at 485 °C and the Sr/Er flow rate ratio of 2.25.

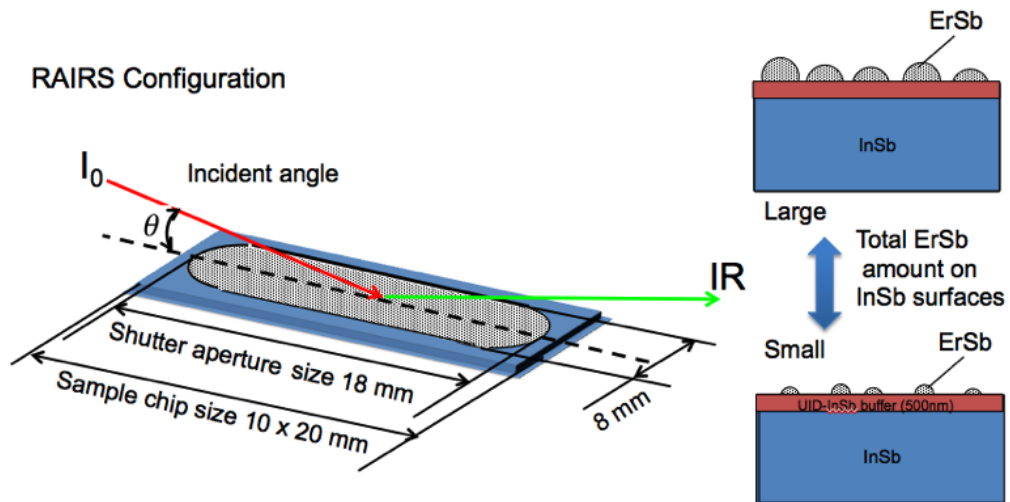


Fig. 2: Reflection absorption infra-red spectroscopy (RAIRS) configuration and expected ErSb cover growth features on 500 nm thickness unintentionally doped InSb buffer layer prepared on n-type InSb (100) substrate.

Unlike ultra-high vacuum deposition processes such as molecular beam epitaxy, a larger amount of hydrogen and hydrogen radicals are present in our MOCVD growth

environment. Accordingly, a growing InSb surface is expected to be terminated by hydrogen, which results in an InSb surface terminated with In-H bonds even after exposed to ambient. Therefore, in the RAIRS measurement, we focus on infra-red absorption associated with vibrational modes of In-H bonds that exist on InSb surfaces. As schematically shown in Fig. 2 (right), the infra-red absorption associated with In-H bonds is expected to weaken as the surface of InSb is covered by ErSb, which provides us a signature of ErSb deposition that progresses on the InSb surface.

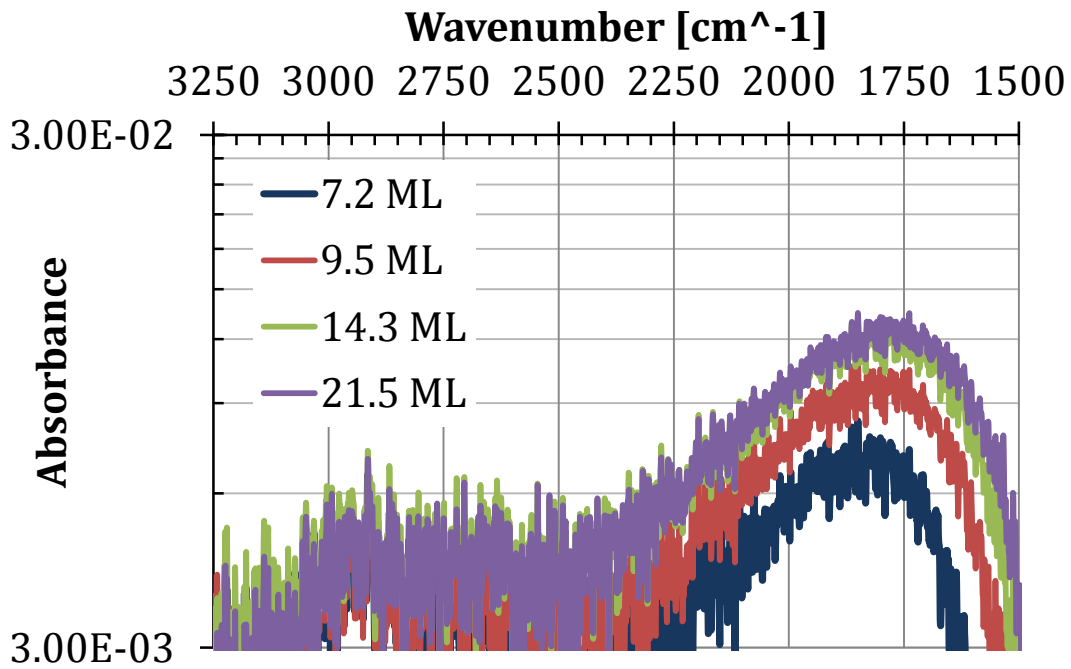


Fig. 3: RAIRS spectra collected from the four ErSb samples with various total ErSb coverage (7.2-21.5 ML) on hydrogen terminated InSb surfaces.

Fig. 3 shows RAIRS spectra collected from the four ErSb samples with various nominal ErSb coverage (7.2 ML-21.5 ML) on hydrogen terminated InSb surfaces. As clearly seen, the absorption associated with the In-H bonds decreases as the amount of ErSb on the InSb surfaces increases. The smallest increment of 2.3 ML from 7.2 ML to 9.5 ML can be distinguished, which suggests that RAIRS is a capable ex-situ tool for calibrating a small amount of ErSb on InSb when the surface of InSb is saturated with hydrogen. The peaks correspond to those reported for In-H stretching modes [3][4].

Fig. 4 shows AFM images collected on two of the ErSb samples with ErSb 7.2 ML (left) and 21.5 ML (right).. The images clearly show that the surface of the InSb buffer layer is covered by a numerous ErSb islands with surface coverage of 65.3 % for the 7.2 ML ErSb sample and 81.5 % for the 21.5 ML ErSb sample., which is consistent with the RAIRS results that the incident infra-red is absorbed by In-H bonds present on the exposed InSb buffer layer partially covered by ErSb islands.

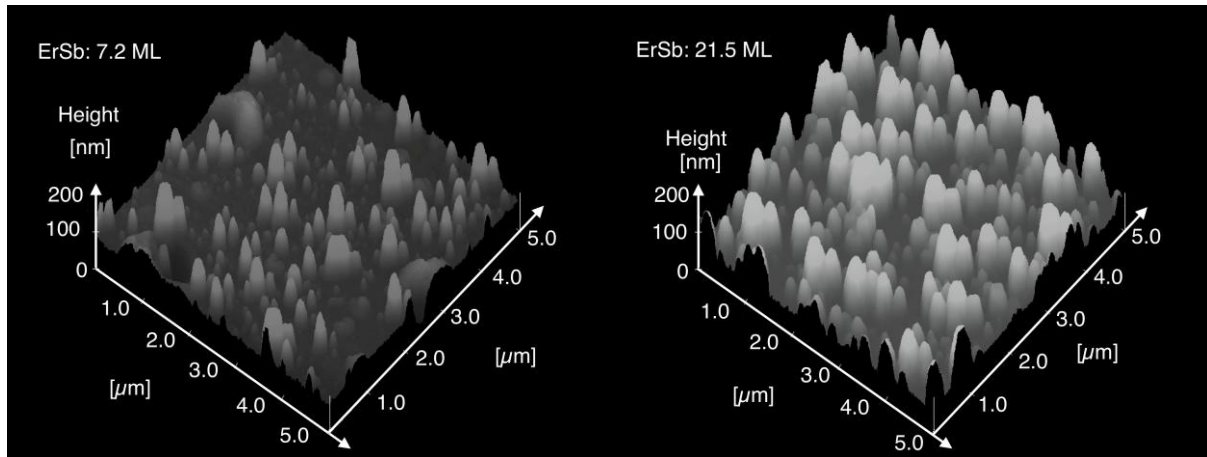


Fig. 4: AFM images of two distinctive ErSb coverage on the surface of InSb buffer layer ce. (left) ErSb surface coverage of 65.3 % for the ErSb 7.2 ML sample. (right) ErSb surface coverage of 81.5 % for the ErSb 21.5 ML sample.

## SUMMARY

Our study suggests that the RAIRS is capable of evaluating a small amount ( $\sim 2.3$  ML) of ErSb that partially covers InSb surfaces terminated with In-H bonds. THE RAIRS results, combined with the AFM images, indicates that ErSb deposited on InSb (100) surfaces grow into island morphology under the MOCVD growth conditions we used.

## ACKNOWLEDGMENTS

This work is funded by DARPA/DSO and ONR. We are grateful to Hewlett-Packard Laboratories for their continuous support.

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