A series of two-layer InAsSb films were grown with molecular beam epitaxy (MBE). We report the effect of substrate temperature on the composition of InAsSb grown with and without a Bi surfactant and find that the Sb incorporation is suppressed as the substrate temperature increases, and that it is also further suppressed by the presence of Bi at all temperatures. We examine the data with a kinetic model, which gives insights into the composition of mixed anion alloys using straightforward rate equations for each process that occurs during growth. It was shown that the reduction in Sb composition is due to the preferential removal of Bi by As, and that removal.

SUBJECT TERMS
Bi surfactant, Sb incorporation, InAsSb, semiconducting III-V materials, molecular beam epitaxy
ABSTRACT
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Suggested Reviewers: Joshua Zide PhD
Associate Professor, Materials Science and Engineering, University of Delaware
zide@udel.edu
Dr. Zide is an organizer of international Bismuth conferences and has solid expertise in MBE

Anthony Krier PhD
Professor, Physics, Lancaster University
a.krier@lancaster.ac.uk
Dr. Krier has expertise in analogous materials systems and MBE

Stephen Sweeney PhD
Professor, Physics, University of Surrey
s.sweeney@surrey.ac.uk
Dr. Sweeney is an expert in III-V growths with Bi
The influence of growth temperature on Sb incorporation in InAsSb, and the temperature-dependent impact of Bi surfactants

W.L. Sarney a,1, S.P. Svensson a, E.M. Anderson b, A.M. Lundquist b, C. Pearson c, J. M. Millunchick b

a. US Army Research Laboratory, 2800 Powder Mill Road, Adelphi MD, 20783 USA
b. Department of Materials Science and Engineering, University of Michigan, Ann Arbor MI, 48109 USA
c. Department of Computer Science, Engineering, and Physics, University of Michigan–Flint, Flint MI 48502

a. This manuscript is our original work and we are submitting it to the Journal of Crystal Growth only.
b. All authors have checked the manuscript and have agreed to the submission.

1 Corresponding author: W.L. Sarney, wendy.l.sarney.civ@mail.mil, 1-301-394-5761
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W.L. Sarney\textsuperscript{a,1}, S.P. Svensson\textsuperscript{a}, E.M. Anderson\textsuperscript{b}, A.M. Lundquist\textsuperscript{b}, C. Pearson\textsuperscript{c}, J. M. Millunchick\textsuperscript{b}

\textsuperscript{a.} US Army Research Laboratory, 2800 Powder Mill Road, Adelphi MD, 20783 USA
\textsuperscript{b.} Department of Materials Science and Engineering, University of Michigan, Ann Arbor MI, 48109 USA
\textsuperscript{c.} Department of Computer Science, Engineering, and Physics, University of Michigan–Flint, Flint MI 48502

Highlights

We report the effect of substrate temperature on the composition of InAsSb grown with and without a Bi surfactant and find that the Sb incorporation is suppressed as the substrate temperature increases, and that it is also further suppressed by the presence of Bi at all temperatures.

We examine the data with a kinetic model, which gives insights into the composition of mixed anion alloys using straightforward rate equations for each process that occurs during growth.

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\textsuperscript{1} Corresponding author: W.L. Sarney, wendy.l.sarney.civ@mail.mil, 1-301-394-5761
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W.L. Sarney\textsuperscript{a,1}, S.P. Svensson\textsuperscript{a}, E.M. Anderson\textsuperscript{b}, A.M. Lundquist\textsuperscript{b}, C. Pearson\textsuperscript{c}, J. M. Millunchick\textsuperscript{b}

\textit{a. US Army Research Laboratory, 2800 Powder Mill Road, Adelphi MD, 20783 USA}
\textit{b. Department of Materials Science and Engineering, University of Michigan, Ann Arbor MI, 48109 USA}
\textit{c. Department of Computer Science, Engineering, and Physics, University of Michigan–Flint, Flint MI 48502}

Key words: B2 Semiconducting III-V materials, A3 molecular beam epitaxy

Abstract

A series of two-layer InAsSb films were grown with molecular beam epitaxy (MBE). We report the effect of substrate temperature on the composition of InAsSb grown with and without a Bi surfactant and find that the Sb incorporation is suppressed as the substrate temperature increases, and that it is also further suppressed by the presence of Bi at all temperatures. We examine the data with a kinetic model, which gives insights into the composition of mixed anion alloys using straightforward rate equations for each process that occurs during growth. It was shown that the reduction in Sb composition is due to the preferential removal of Bi by As, and that removal rate obeys an Arrhenius dependence with an activation energy of 1.35 eV.

\textsuperscript{1} Corresponding author: W.L. Sarney, wendy.Lsarney.civ@mail.mil, 1-301-394-5761
1.0 Introduction

Compositional control of the mixed group V alloys is complicated because incorporation is not directly analogous to the ratio of the group V fluxes. Such control, however, is essential for the performance of semiconductor devices based on group V alloys. For instance, InAsSb is a direct bandgap semiconductor that is capable of reaching the narrow bandgaps needed for long wavelength infrared (LWIR) detector applications. We previously reported the growth of unstrained, unrelaxed, InAsSb free of bandgap-reducing ordering, and reported bandgaps that were sufficient for detection in the LWIR band [1]. The composition must be precisely controlled in order to produce the strain-free condition [2], and also to obtain devices that operate at specific wavelengths. Optimization of the materials quality also requires controlled variations of the group V/III ratio and substrate temperature. In addition, one can consider using surfactants to further improve the material. In each case it is critical to maintain the lattice constant and therefore the composition so that strain effects are avoided.

Group V/III flux ratios, substrate temperature, and the use of surfactants such as Bi are known to influence group V incorporation. Young, et al, studied Bi surfactant growth of GaN$_x$As$_{1-x}$ by molecular beam epitaxy (MBE), and found that the surfactant increased the nitrogen incorporation by as much as 60% [3]. Tixier, et al, also studied surfactant enhanced growth of GaNAs and InGaNAs using bismuth and report the same trend [4]. They assert that Bi reduces the incorporation of defects and/or impurities in the dilute GaNAs based alloys, as evidenced by higher photoluminescence peak intensities. Anderson, et al, found that the presence of Bi decreases the Sb incorporation in InAsSb films that were grown under conditions that have been otherwise optimized for InAsSb lattice matched to GaSb substrates [5]. The decrease in
incorporated Sb is proportional to the Bi flux and attributed to the preferential replacement of Bi by As.

In this paper, we report the effect of substrate temperature on the composition of InAsSb grown with and without Bi surfactant, and obtain an activation energy for the replacement of Bi by As of 1.35 eV. We find that Sb incorporation is suppressed up to ~40% as the substrate temperature increases from 400 to 490 C. Sb incorporation is further suppressed by as much as 35% by the presence of Bi at all temperatures. The suppressing effect of Bi decreases, but does not disappear, for increasing growth temperatures up to 490 C.

2.0 Experiment

We grew a series of two-layer InAsSb films at substrate temperatures ranging from 400-490 C. The material was grown in a Gen II Veeco solid-source MBE system equipped with As and Sb valved cracker sources and solid sources for In, Ga, and Bi. The films were grown on epi-ready, exact-oriented (001) GaSb-substrates from WaferTech LLC.

In all cases, the first 0.6 um layer was grown with the Bi shutter closed, followed immediately by the growth of the second 0.3 um layer with the Bi shutter open. The Bi source was a Veeco, 200 g, low-temperature, SUMO cell, with an integral shutter placed in an auxiliary port below the main source flange [6]. There is a very steep incidence angle between the molecular beam and the substrate normal. In order to read realistic values, the beam flux monitor (BFM) is rotated down to the 240 degree position. At the normal 180 degree position most of the Bi flux is shadowed by the protective cup around the BFM. The Bi cell temperature was set to give a beam equivalent pressure (BEP) of 4.8x10^{-7} Torr, as measured in this configuration.
We have shown in prior experiments that Bi is not expected to incorporate under these conditions [5]. The Sb/As ratio was constant in all growths for all layers, and corresponds to the value needed to grow lattice matched InAsSb on GaSb without using Bi surfactant at 415 C. The In growth rate was 1 \( \mu \)m/hr. The Sb BEP was \( 1.2 \times 10^{-7} \) Torr and the As BEP was \( 5.71 \times 10^{-7} \) Torr. The absolute flux of all the constituents and the V/III ratios were kept constant for both layers of each sample across the temperature series, therefore we can compare the compositions of the layers grown with or without Bi. Since the first layer was grown without the presence of Bi for each temperature, we also directly observe the influence of substrate temperature on Sb incorporation, and the second layer allows a direct observation of the influence of the Bi surfactant on the composition. Triple axis (004), (444), and (115) high-resolution X-ray diffraction (XRD) were collected for all samples, and reciprocal space maps (RSMs) were collected from selected samples. The complete data set was analyzed with a kinetic model of anion incorporation.

3.0 Results and Discussion

Figure 1 shows the (004) triple axis XRD scans for all of the films grown in this study. In each case, the film peak on the left corresponds to the first InAsSb layer grown with the Bi closed and the peak to the right corresponds to the second layer grown with the Bi open. A series of (004) and (444) reciprocal space maps with a phi rotation of 90 degrees have also been collected for selected samples, with a representative subset shown in Figure 2-3. For the samples grown at 415 and 430 C (shown in Figure 2), the small lattice mismatch is accommodated by tetragonal distortion, where the lateral lattice constant is mostly unchanged for the two film layers relative to the substrate but there is a clear expansion in the film’s vertical lattice constant. The samples grown at 475 C and 490 C show complete relaxation, accommodated by
dislocations, as evident by the change in the lateral lattice constant as illustrated in the (004) RSM map for the sample grown at 475 C (Figure 3). The (004) and (444) scans also showed an absence of Pendellosung fringes for these two samples, which indicates that the top surfaces are not flat. In this set of experiments it is not possible to assess the effect of the Bi surfactant on the film quality, since it affects the composition and thus the lattice mismatch of the films.

The compositions for each film were calculated using two (004) triple axis scans with a 180 degree rotation in phi, and two (115) scans in glancing incidence and exit also with a 180 degree rotation in phi. Figure 4 shows the Sb incorporation with and without a Bi surfactant as a function of substrate temperature. The Sb composition grown with or without Bi, monotonically decreases with increasing growth temperature. The effect of the Bi surfactant decreases with increasing growth temperature, as indicated by the decreased separation between (004) peaks corresponding to the two layers, but it still had some effect even at the highest experimental growth temperature of 490 C.

The composition of mixed anion alloys can be modeled using straightforward rate equations for each process that occurs during growth. While there are several examples of such models for binary mixed anion alloys in the literature, Anderson, et al [5] recently developed a model that can account for up to three anions. The impinging flux is the primary term that determines the net growth flux of each component, but it is diminished by desorption and surface segregation. Another process known to occur in mixed anion systems is the removal of one anion species in place of another [7]. For instance, As preferentially displaces Sb in both GaAsSb [6] and InAsSb [8]. The net flux for each anion is as follows:

\[
J_i = F_i - \theta_i P_i^{\text{dec}} \pm \theta_i P_i^{\text{rem}} \pm x_j \theta_j P_j^{\text{reg}} \mp x_k \theta_k P_k^{\text{reg}}
\]  

(1)
The first term on the right hand side represents the amount of impinging ith anion, $F_i$. The second term represents the reduction in the net flux due to desorption, which is the product of the rate of desorption and the surface coverage of the ith anion, $\theta_i$. The third and fourth terms increase or decrease (depending on the anion in question) the net flux via the preferential removal of one anion for another, and depend on the product of the coverage the removed anion and the rate of removal, $P^{\text{rem}}$. In the case of mixed As-Sb alloys, As preferentially displaces Sb [7] and recently it was shown that As displaces Bi as well [5]. The fifth and sixth terms increase or decrease the net flux due to surface segregation, that is, the exchange of subsurface with surface anions. These terms are the product of the concentration of the segregating anion in the subsurface layer (assumed to be the same as that of the bulk) $x$, the surface coverage of the surface anion, and the rate of segregation. In general, the bulk composition is proportional to the surface concentration via the equilibrium partition coefficient $K$, and can range from 0 (for a pure surfactant) to 1 (for complete incorporation) [9]. All of the rates take the standard Arrhenius form

$$P = \frac{(N \nu)^2}{F_{\text{In}}} \exp \left[ -\frac{2E_j}{kT} \right],$$

where $N$ is the density of atomic surface sites, $\nu$ is the attempt frequency ($10^{12}$ s$^{-1}$), $E_j$ is the activation energy of the jth process, $k$ is Boltzmann’s constant, and $T$ is the temperature. $F_{\text{In}}$ is the impinging In flux, which acts to limit the process. Anderson, et al, showed that at these growth temperatures, there is no Bi incorporation into the InAsSb films such that the net Bi flux $J_{\text{Bi}}$ is zero [5]. Thus, the coverage of the Bi can be written as Langmuir isotherm modified to include the Bi removal by As term:

$$\theta_{\text{Bi}} = \frac{F_{\text{Bi}}}{N\nu} \left( \exp \left( \frac{E_{\text{Bi}}^{\text{des}}}{kT} \right) + \exp \left( \frac{E_{\text{Bi}}^{\text{rem}}}{kT} \right) \right) \frac{1}{1 + \frac{F_{\text{Bi}}}{N\nu} \left( \exp \left( \frac{E_{\text{Bi}}^{\text{des}}}{kT} \right) + \exp \left( \frac{E_{\text{Bi}}^{\text{rem}}}{kT} \right) \right)}. $$ (2)
This series of equations may be solved for the composition of Sb as a function of the deposition flux of each element and temperature, assuming that the surface is always terminated in a single layer of anions, and the film is stochiometric. Most of the activation energies for the various processes can be obtained in the literature. For instance, the energies used in this work are 2.4 eV for As desorption from InAs [10], 2.7 eV for Sb desorption from InSb [11], 1.3 eV for the removal of Sb by As from InAsSb [10], and 1.2 eV for the Sb segregation of Sb in InAsSb [12]. The desorption of Bi and the removal of Bi by As on InAsSbBi are not known, so the known energy for Bi desorption from GaAsBi (1.8eV ) [3] and Sb removal by As on InAsSb (1.3eV) were used as initial inputs and varied to obtain the best fit for the data. The In, As, and Sb fluxes were calculated by starving the growth surface of anions until we observed a decrease in the growth rate by RHEED oscillations. Under these conditions, V/III=1, thus the anion flux is equal to the cation flux. The Bi fluxes were not measured directly, but were calculated from BEP measurements and published methods for calculating the ion gauge sensitivity to various elemental vapors [13-14]. The solid lines in Figure 4a are fits using the model. The values of the energies for Bi desorption and the removal of Bi by As on InAsSbBi that best fit the data were $E_{\text{des Bi}}^{\text{des}}=1.7$ eV and $E_{\text{rem As→Bi}}^{\text{rem}}=1.35$eV. The segregation factor was previously found to be 0.4 for InAsSb [7], but that value had to be lowered to 0.27 to fit this data. The need for this reduction suggests that Bi on the surface reduces the equilibrium segregation parameter. The decrease in the concentration as a function of temperature regardless of whether a surfactant is present arises as a result of the removal of Sb by As, which lowers the overall surface coverage of Sb. The model also predicts that the Sb concentration of the InAsSb films decreases with increasing Bi flux, as should in agreement with prior reports [5]. As more Bi occupies the surface, there is a higher probability that those Bi atoms will be replaced by As.
Both Bi desorption and Bi removal terms are necessary to fit the experimental data, demonstrating that the Bi surfactant doesn't act as a steric barrier for Sb incorporation, but alters the chemistry of incorporation. If only Bi desorption is considered, the Sb concentration is predicted to be the same with and without the Bi surfactant. It is the catalytic effect of the Bi on the As incorporation that drives this change in Sb concentration. The origin of this effect is likely due to the fact that the In-As bond is stronger than the In-Sb or predicted In-Bi bonds [15]. This hypothesis is consistent with the observed enhanced N incorporation in the presence of a Bi surfactant for GaNAs [3]. In that case, the Ga-N bond is stronger than the Ga-As or predicted Ga-Bi bonds [13], resulting in faster removal of Bi by N than by As. The Bi-induced reduction in concentration is eliminated at higher temperatures, most likely because the Bi coverage, and this the enhanced As incorporation, goes to zero.

4.0 Conclusion

We report the effect of substrate temperature on the composition of InAsSb grown with and a without Bi surfactant. We find that Sb incorporation is suppressed up to \( \sim 40\% \) as the substrate temperature increases from 400 to 490 C. Sb incorporation is further suppressed by as much as 35\% by the presence of Bi at all temperatures. The suppressing effect of Bi decreases, but does not disappear, for increasing growth temperatures up to 490 C. Kinetic modeling allows a predication of the composition of mixed anion alloys using straightforward rate equations for each process that occurs during growth. The decrease in the Sb concentration as a function of temperature is due to the removal of Sb by As, which lowers the overall surface coverage of Sb. The reduction in Sb composition results from the preferential removal of Bi by As, and that removal rate obeys an Arrhenius dependence with an activation energy of 1.35 eV. This work enables future experiments of the dependence of the crystalline quality of InAsSb on Bi
surfactants by design of growth conditions (substrate temperature and fluxes) that would result in InAsSb films with constant composition, e.g. lattice matched to a GaSb substrate.

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References


Figure Captions

Figure 1. Triple axis x-ray diffraction from the bi-layered InAsSb structures grown on GaSb at different substrate temperatures, $T_{\text{sub}}$. The peaks at the highest angles originate from the layers exposed to Bi.

Figure 2(a) (004) and (b) (444) reciprocal space maps of the film grown at 430 C.

Figure 3. (004) reciprocal space map of sample grown at 475 C.

Figure 4. Sb concentration in InAsSb as a function of substrate temperature for layers grown with and without Bi exposure. The lines represent the model fit.
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