Effects of \( \text{As}_2 \) versus \( \text{As}_4 \) on InAs/GaSb heterostructures: As-for-Sb exchange and film stability

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(Received 21 March 2001; accepted 26 May 2001)

We have used cross-sectional scanning tunneling microscopy and x-ray diffraction to characterize and compare the effects of \( \text{As}_2 \) versus \( \text{As}_4 \) on the growth of InAs/GaSb heterostructures by molecular beam epitaxy. When GaSb surfaces are exposed to an \( \text{As}_2 \) flux, the As exchanges with the surface Sb in an anion exchange reaction that creates layers of GaAs. In contrast, when GaSb surfaces are exposed to \( \text{As}_4 \) fluxes, there is no evidence of the As-for-Sb exchange reaction. When comparing the use of \( \text{As}_2 \) and \( \text{As}_4 \) in periodic InAs/GaSb superlattices, the differences in the As incorporation rate into GaSb is further evident in x-ray diffraction spectra as a shift in the average lattice constant of the epilayer due to GaAs bond formation. Although inhibiting the exchange reaction would be useful in the minimization of the cross incorporation of As in the GaSb layers, the growth of InAs/GaSb heterostructures using \( \text{As}_4 \) can be complicated by the introduction of film instabilities that have not been observed in growths using \( \text{As}_2 \).

I. INTRODUCTION

The epitaxial growth of III–V semiconductor heterostructures containing both arsenides and antimonides has generated much interest due to the variety of band alignments that are possible while still maintaining a near-lattice match. The “6.1 Å” family of semiconductors, namely, InAs, GaSb, AlSb, and their related alloys, can be combined in heterostructures to fabricate a variety of devices including field-effect transistors, resonant tunneling structures, infrared structures to fabricate a variety of devices including field-effect transistors, resonant tunneling structures, infrared lasers, and infrared detectors. A challenging aspect of mixed arsenide and antimonide growth is controlling the composition of the interfaces as well as of the individual material layers. In InAs/GaSb superlattices, these issues arise in the determination of interfacial bond types (InSb-or GaAs-like) and in the cross incorporation of group-V atoms (As in GaSb layers and Sb in InAs layers). Related work with InAs/AlSb structures has demonstrated how compositional variations, particularly at the interfaces, can dramatically affect the transport and optical properties of the heterostructure.

Although interfacial composition can be controlled effectively and reproducibly using migration-enhanced epitaxy (MEE), it is difficult to limit the amount of cross incorporation of group-V atoms during growth. For instance, the growth of As- and Sb-based heterostructures can be complicated by the potential reaction of As with antimonide surfaces. It has been proposed that As is reactive towards GaSb and AlSb surfaces because the formation of GaAs or AlAs bonds in GaSb and AlSb layers would be thermodynamically favorable (based on the formation energies of the bonds). Additionally, it has been shown in various studies that different group-V species—i.e., tetramer, dimer, or monomer—react and incorporate differently on semiconductor surfaces. Although exactly how devices are influenced by the type of group-V species is not clear, there is some evidence that device performance depends on the type used during growth.

It has been widely reported that when \( \text{As}_2 \) is incident on an antimonide surface, an anion exchange reaction occurs, with As displacing surface Sb. Kaspi reported that this reaction readily occurs at temperatures above 400 °C, and that with prolonged exposure to \( \text{As}_2 \), eventually causes a spotty reflection high-energy electron diffraction (RHEED) pattern. The RHEED transition was attributed to a marked roughening, or islanding, of the surface that ultimately allowed for the continued displacement of Sb. In contrast, other studies have reported that under similar conditions the As-for-Sb exchange proceeds to about 0.85 ML up to temperatures of 450 °C, indicating a minimal amount of surface roughening, and that only the top-layer Sb is displaced. However, at higher temperatures, there was again evidence of surface roughening and increased desorption of Sb.

The apparent discrepancy in what growth conditions lead to surface roughening due to the As-for-Sb exchange is presumably due to differences in the calibrations of the reported temperatures and fluxes. Our objective in this study is to focus on the extent of the As-for-Sb exchange under conditions of minimal islanding or roughening. Whereas substrate temperature and \( \text{As}_2 \) flux have been shown to be key factors in the As-for-Sb exchange reaction, it has also been observed that \( \text{As}_2 \) and \( \text{As}_4 \) react differently with GaSb surfaces; specifically, that \( \text{As}_4 \) does not readily displace surface Sb. In this work, we examine the nature of the As-for-Sb exchange reaction by comparing the effects of exposing GaSb surfaces with \( \text{As}_2 \) and \( \text{As}_4 \) as revealed by cross-sectional scanning tunneling microscopy (XSTM). Our results confirm that \( \text{As}_4 \) is less reactive than \( \text{As}_2 \) to GaSb surfaces, resulting in a lower As incorporation rate into GaSb layers. While studying...
| 1. REPORT DATE | MAR 2001 |
| 2. REPORT TYPE | |
| 3. DATES COVERED | 00-00-2001 to 00-00-2001 |
| 4. TITLE AND SUBTITLE | Effects of As2 versus As4 on InAs/GaSb heterostructures: As-for-Sb exchange and film stability |
| 5a. CONTRACT NUMBER | |
| 5b. GRANT NUMBER | |
| 5c. PROGRAM ELEMENT NUMBER | |
| 5d. PROJECT NUMBER | |
| 5e. TASK NUMBER | |
| 5f. WORK UNIT NUMBER | |
| 6. AUTHOR(S) | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) | Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC, 20375 |
| 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | |
| 10. SPONSOR/MONITOR’S ACRONYM(S) | |
| 11. SPONSOR/MONITOR’S REPORT NUMBER(S) | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT | Approved for public release; distribution unlimited |
| 13. SUPPLEMENTARY NOTES | |
| 14. ABSTRACT | |
| 15. SUBJECT TERMS | |
| 16. SECURITY CLASSIFICATION OF: | a. REPORT b. ABSTRACT c. THIS PAGE |
| unclassified | unclassified | unclassified |
| 17. LIMITATION OF ABSTRACT | Same as Report (SAR) |
| 18. NUMBER OF PAGES | 5 |
| 19a. NAME OF RESPONSIBLE PERSON | |
the interaction of $\text{As}_4$ with GaSb surfaces, we have also discovered that the use of $\text{As}_4$ for the growth of InAs/GaSb heterostructures can lead to unexpected film instabilities.

II. EXPERIMENT

All samples were grown on nominally flat and undoped GaSb(001) ‘‘epiready’’ substrates in a III–V solid-source molecular beam epitaxy (MBE) system equipped with RHEED. The growth rates were determined by RHEED oscillations and were set to be 0.5 ML/s for both InAs and GaSb. The group-V fluxes were calibrated by determining several points in which growth became group-V limited, as judged from RHEED oscillations. At these points we are measuring the effective ‘‘incorporation rate’’ of group-V species. Hence, ‘‘1 ML/s’’ of Sb$_4$ flux is the flux just sufficient to sustain 1 ML/s of GaSb film growth.

For this study we have grown two different structures. The first structure was designed to examine the effects of As exposure time on GaSb surfaces. Samples with this structure were prepared with many periods of 13 ML of InAs alternating with 14 ML of GaSb. GaAs bonds were formed at each GaSb-on-InAs interface by MEE; i.e., after terminating the InAs with As, 1 ML of Ga was first deposited prior to the GaSb film growth. At each InAs-on-GaSb interface, the GaSb was exposed to As at various substrate temperatures and for different exposure times and As$_x$ species. Both the As$_2$ and As$_4$ fluxes were at 1 ML/s. The second structure we prepared was a type-II superlattice of the type used in our infrared detector studies, composed of 140 periods of (InAs)$_{13}$/ (GaSb)$_{13}$ with InSb bonds formed by MEE at each interface. The first 90 periods were doped $p$ type (Be$\times 3 \times 10^{15}$), and the last 50 periods doped $n$ type (Si$\times 10^{18}$). (Because Si is a $p$-type dopant in GaSb, only the InAs layers were doped within the $n$-type section of the superlattice.) The growth temperature for this superlattice was 390 °C, calibrated by the $(1 \times 5)$-to-$(1 \times 3)$ phase transition at $\sim 415$ °C.

The XSTM measurements were performed in an ultrahigh-vacuum surface-analysis chamber with a base pressure $<1 \times 10^{-10}$ Torr. After being loaded into the chamber, the samples were out-gassed at $\sim 100$ °C for about 45 min. The samples were then both scribed and cleaved in situ to expose either a $(110)$ or $(\overline{1}10)$ surface depending on the mounting orientation. All gray-scale images shown are for filled electronics states (showing the As/Sb sublattice). The InAs/GaSb superlattice samples were also characterized by double-crystal x-ray diffraction (XRD) using a Cu Ka source, a GaSb reference crystal, and the (004) reflection.

III. RESULTS AND DISCUSSION

The sources of interfacial contrast and identification of GaAs bonds in XSTM images of InAs/GaSb heterostructures have been discussed previously in detail. Briefly, the contrast of GaAs bonds at InAs–GaSb interfaces is primarily related to structural effects. The GaAs bonds, which are strained to the larger GaSb lattice constant, can relax slightly inward on the free $(110)$ cleavage surface. When the resulting interfacial bonds are aligned ‘‘in plane,’’ the relaxation occurs primarily parallel to the surface and is difficult to detect in XSTM. However, when the interfacial bonds are aligned ‘‘out of plane,’’ the relaxation has an observable displacement perpendicular to the surface, appearing as depressed (or darker) ‘‘atoms’’ in filled-state XSTM images. These structural effects have also been predicted in first-principles calculations.

To study As$_x$ exposures on GaSb with XSTM, it is necessary to cleave the samples to expose the $(110)$ surface so that the GaAs interfacial bonds at the InAs-on-GaSb interfaces will be observable. Figure 1 shows a set of XSTM images of the $(110)$ plane through InAs/GaSb layers in which the GaSb surfaces were exposed to As$_2$ for either 5 s [Figs. 1(a)–1(d)] or 30 s [Figs. 1(e)–1(h)] at various substrate temperatures. The darker rows that are evident at the InAs-on-GaSb interfaces correspond to the GaAs bonds that have formed via As-for-Sb exchange. Before discussing the images in more detail, it is important to recall that only every other growth layer within the film is seen in XSTM images [because of the structure of the $(110)$ crystal face]. Thus, for example, two layers of GaAs-like material would be observed as one GaAs-like layer in an XSTM image. A more comprehensive discussion of the interpretation of XSTM images has been published elsewhere.

At 390 °C, the GaAs layer that has formed appears to be confined to the first 1–2 ML of the interface for either 5 and 30 s exposures [Figs. 1(a) and 1(e)]. For the 5 s As$_2$ exposure, there appears to be parts of the interface where minimal GaAs formation has occurred [Fig. 1(a)]. For growth temperatures of 425 °C and higher, the As–Sb exchange occurs over 2–3 ML, with the reaction being more complete for the 30 s exposures. Generally, as the temperature and exposure time increases, the number of monolayers over which GaAs bonds can be observed increases up to a value of about 3 ML. Comparing Figs. 1(g) and 1(h), it appears that the anion exchange may be self-limiting once a complete GaAs layer forms. It is possible that once the surface is essentially terminated with GaAs bonds, the exchange reaction is inhib-
And 28!

Fig. 2. InAs/GaSb heterostructures grown at 425 °C using As₄. The GaSb layers were exposed to an As₄ flux at the InAs-on-GaSb interfaces for (a) 5 s and (b) 30 s (images 15 nm × 15 nm). There is little evidence of GaAs interfacial bonds at the InAs-on-GaSb interfaces. (c) A larger-scale image, 18 nm × 60 nm, of the heterostructure shown in (b).

![Image](https://example.com/image.png)

Fig. 3. X-ray diffraction (XRD) spectra for the two different InAs/GaSb superlattices imaged in Fig. 3, with Bragg angles defined relative to the position of the GaSb substrate peak. In both spectra, sharp satellite peaks occur at the angles expected from the superlattice period (~8 nm). In each case, the position of the epilayer peak (the one adjacent to the substrate peak) reveals that the overall mismatch of the superlattice to the substrate is <0.2%. In general, we find that the average lattice constant for As₄ growths is relatively independent of growth conditions, but for As₂ growths ranges between 0% and 0.2% smaller than the substrate depending on the growth conditions. We attribute this variation to the increased propensity of background As₂ to

![Diagram](https://example.com/diagram.png)

Fig. 4. Comparison of the x-ray diffraction (XRD) spectra for the two different InAs/GaSb superlattices imaged in Fig. 3, with Bragg angles defined relative to the position of the GaSb substrate peak. In both spectra, sharp satellite peaks occur at the angles expected from the superlattice period (~8 nm). In each case, the position of the epilayer peak (the one adjacent to the substrate peak) reveals that the overall mismatch of the superlattice to the substrate is <0.2%. In general, we find that the average lattice constant for As₄ growths is relatively independent of growth conditions, but for As₂ growths ranges between 0% and 0.2% smaller than the substrate depending on the growth conditions. We attribute this variation to the increased propensity of background As₂ to

![Graph](https://example.com/graph.png)
incorporate into the GaSb layers and thereby create (smaller) GaAs bonds, decreasing the average lattice constant.

The XRD spectra for all InAs/GaSb superlattices we have grown using a wide range of As$_2$ fluxes and substrate temperatures are all qualitatively similar to the spectrum shown in Fig. 4(a), with only the position of the epilayer peak varying because of differing degrees of As cross incorporation. XSTM images of such samples always reveal a very periodic structure of uniform layer widths with abrupt interfaces, as expected. In contrast, things get more complicated when the superlattices are grown with As$_4$. As described earlier in our discussion of Fig. 2(c), we have discovered that using As$_4$ for the growth of InAs/GaSb heterostructures can lead to significant film instabilities during growth. The onset of this instability can be discerned by close inspection of Fig. 3(b), from a superlattice grown with an As$_4$ :In flux ratio of 2.0:1. The material layers vary slightly from period to period, and the thickness of each layer also varies within the range of the image. These variations are somewhat easier to observe over larger scales, as shown in Fig. 3(c), and are evidence of some type of instability during the film growth.

Although the instability is subtle for InAs/GaSb superlattices grown with an As$_4$ :In flux ratio of 2.0:1, any such instability that disrupts the structural uniformity of the material is obviously undesirable for device growth and optimization. In order to observe the effect of the As$_4$ flux on the overall superlattice structure, we have performed XRD as a function of the As$_4$ :In flux ratio (Fig. 5). At an As$_4$ :In flux ratio of 2.7:1, the satellite peaks have a much smaller intensity, and additional peaks emerge, indicative of a new periodicity within the material. At 4.0:1, it is difficult to observe any periodicity in the spectra, further indicating that the growth has become unstable. Note that at this time it is not clear whether the critical parameter is the As$_4$ :In flux ratio or the magnitude of the As$_4$ flux. Furthermore, we suspect that the dependence on As$_4$ is also a function of the growth temperature, which will affect both the growth and cross-incorporation kinetics.
Interestingly, XSTM images (not shown) of superlattices grown at an As₄:In flux ratio of ~2.7:1 reveal that the film instability leads to periodic modulations that are ordered in an anion e-xheterostructures by MBE. When GaSb surfaces are exposed to As₂ fluxes, the surface Sb is displaced in an anion ex-position increases with both higher growth temperatures and we generally find that the width of the GaAs interfacial re-gion increases with both higher growth temperatures and

IV. CONCLUSIONS

We have used XSTM and XRD to characterize and com-pare the effects of As₂ vs As₄ on the growth of InAs/GaSb heterostructures by MBE. When GaSb surfaces are exposed to As₂ fluxes, the surface Sb is displaced in an anion ex-change that appears to be self-limiting once a ~3-ML-thick GaAs layer forms. Although it is difficult to determine the exact amount of Sb that has been displaced from the surface, we generally find that the width of the GaAs interfacial region increases with both higher growth temperatures and longer exposure times. In contrast, exposure with As₄ results in little, if any, GaAs formation. Although growing with As₄ appears to reduce the cross incorporation of As into GaSb, we have discovered that its use leads to an unexpected growth instability for InAs/GaSb heterostructures. At the on-set of the instability, inhomogeneities in the superlattice can be observed in XSTM images even when there is little no-talbe change in the XRD spectra. Although the decreased reactiv of As₄ with antimonide surfaces could be advanta-
geous during growth, a better understanding of how and why this film instability occurs must be achieved to address whether or not they can be avoided during the otherwise beneficial growth with As₄.

FIG. 5. XRD spectra of InAs/GaSb superlattices grown at 390 °C as a func-tion of As₂:In flux ratios: (a) 1.6:1; (b) 2.0:1; (c) 2.7:1; (d) 4.0:1. The spectra are plotted relative to the Bragg angle for bulk GaSb.

ACKNOWLEDGMENTS

This work was supported of the Office of Naval Research, the Defense Advanced Research Projects Agency, and a NRL–NRC Postdoctoral Research Associateship for one of the authors (B.Z.N.).