Effects of As_2 versus As_4 on InAs/GaSb heterostructures: As-for-Sb exchange and film stability

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We have used cross-sectional scanning tunneling microscopy and x-ray diffraction to characterize and compare the effects of As_2 versus As_4 on the growth of InAs/GaSb heterostructures by molecular beam epitaxy. When GaSb surfaces are exposed to an 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 As_4 fluxes, there is no evidence of the As-for-Sb exchange reaction. When comparing the use of As_2 and 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 As_4 can be complicated by the introduction of film instabilities that have not been observed in growths using As_2. [DOI: 10.1116/1.1386377]

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,[1] resonant tunneling structures,[2,3] infrared lasers,[4] and infrared detectors.[5] 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.[6–8]

Although interfacial composition can be controlled effectively and reproducibly using migration-enhanced epitaxy (MEE),[8,9] 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).[10] 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.[11–13] 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.[14]

It has been widely reported that when As_x is incident on an antimonide surface, an anion exchange reaction occurs, with As displacing surface Sb.[12,15–17] Kaspi reported that this reaction readily occurs at temperatures above 400 °C, and that with prolonged exposure to As_2, eventually causes a spotty reflection high-energy electron diffraction (RHEED) pattern.[15] 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.[16,17] 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 As_2 flux have been shown to be key factors in the As-for-Sb exchange reaction, it has also been observed that As_2 and As_4 react differently with GaSb surfaces; specifically, that As_4 does not readily displace surface Sb.[12] In this work, we examine the nature of the As-for-Sb exchange reaction by comparing the effects of exposing GaSb surfaces with As_2 and As_4 as revealed by cross-sectional scanning tunneling microscopy (XSTM). Our results confirm that As_4 is less reactive than As_2 to GaSb surfaces, resulting in a lower As incorporation rate into GaSb layers. While studying

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the interaction of As_4 with GaSb surfaces, we have also discovered that the use of 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$\sim 3\times 10^{15}$), and the last 50 periods doped *n* type (Si$\sim 10^{18}$). (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 (1×5)-to-(1×3) phase transition at $\sim$415 °C.[18]

The XSTM measurements were performed in an ultra-high-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 $(\bar{1}10)$ 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 $K\alpha$ 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.[19,20] 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.[21]

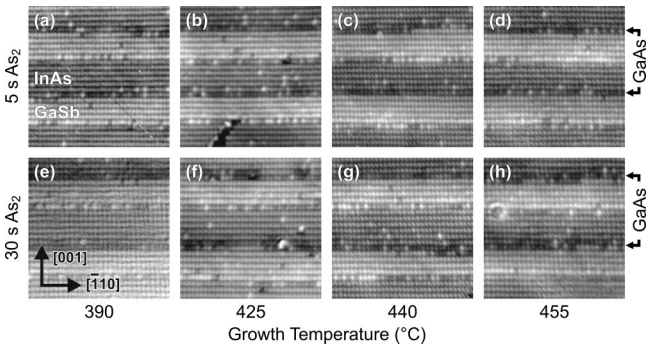

FIG. 1. Set of filled-state XSTM images, 15 nm×15 nm, of InAs/GaSb heterostructures grown over a range of temperatures and with each GaSb layer exposed to As_2 for either 5 or 30 s prior to InAs growth. All images are of the (110) cleavage surface. The dark features along each InAs-on-GaSb interface are evidence of GaAs interfacial bonds.

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.[19] 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.[19]

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-

ited. Perhaps at higher temperatures the surface roughens more during the exchange reaction, so that the reaction goes further before the surface is fully terminated with GaAs.[15]

Interestingly, for all temperatures and exposure times, some Sb appears to remain within the GaAs interfacial region, indicating that not all of the surface Sb is displaced by As. This incomplete displacement is also supported by the observation of the Sb within the InAs layers (the ''bright atoms''). The origin of these substitutional Sb atoms is not from background Sb randomly incorporating into the InAs, but rather from multilayer Sb inherent to the GaSb surface reconstruction which floats up into the next InAs layer.[22] Given the As_2 flux of ~1 ML/s, a 30 s exposure should be an ample supply of As to provide complete exchange of surface Sb. The residual Sb that has been left on the surface during the exposure might have come from the GaSb layer as the surface roughened during GaAs formation.[15] However, at lower temperatures and shorter exposures, where nearly a full layer of GaAs is visible and roughening appears minimal, Sb can still be seen in the InAs layer. This result suggests another possibility: that As may not completely displace Sb from the surface, but rather may coexist on the surface with Sb in local equilibrium. Thus, some Sb remains at or near the surface throughout the exchange reaction, eventually being incorporated into the subsequent InAs layer. This scenario would explain why the amount of Sb reported to be displaced in similar experiments, ~0.85 ML,[16,17] is substantially less than the terminal Sb coverage on the GaSb(001)-$\beta(4\times3)$ surface reconstruction, $1\frac{7}{12}$ ML.[23]

Previous work has demonstrated that the type of group-V species can affect anion exchange for both antimony and arsenic.[12] Generally, the anion exchange reactions occur more readily with cracked species (As_2 and Sb_2) than with uncracked ones (As_4 and Sb_4). Given these differences, it is worth examining the interaction of As_4 with GaSb surfaces for comparison. In Fig. 2 we display images of a heterostructure grown at 425 °C with the same nominal structure as that shown in Figs. 1(b) and 1(f), but with As_4 instead of As_2. For both the exposure times, there is little evidence of the formation of GaAs interfacial bonds.

Although As_4 does not appear to induce the As-for-Sb exchange reaction, it can have a surprising and dramatic effect on the film stability. As seen in the larger-scale XSTM image in Fig. 2(c), the As_4 causes large variations in the thickness of the individual epilayers to emerge, particularly in the InAs layers. Film instabilities such as these are phenomena in strained-layer growth that was first described analytically by Srolovitz using a linear stability analysis.[24] Since then, further discussions and analyses of strained-layer film growth have followed,[25,26] including experimental observations in several material systems such as SiGe/Si(001) (Refs. 27 and 28) and GaSb/InAs.[29] These film instabilities are manifested as highly anisotropic surface and interface modulations that are primarily one-dimensional in nature—i.e., the modulations generally occur along one crystallographic direction and then simply repeat in the growth direction, resulting in a surface morphology resembling uniformly spaced ripples.

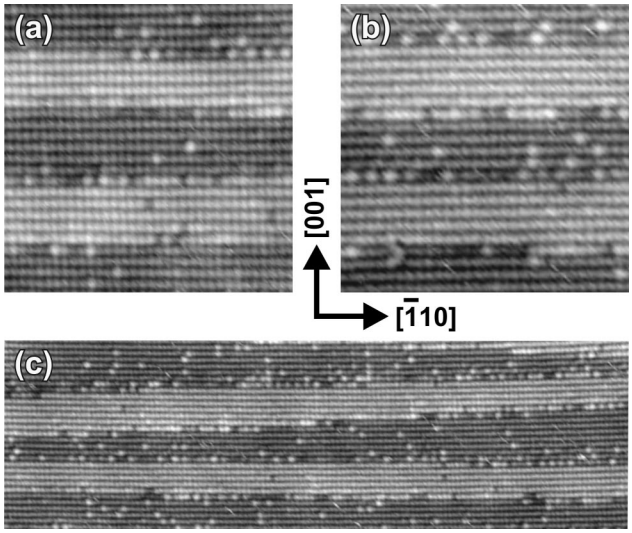

FIG. 2. InAs/GaSb heterostructures grown at 425 °C using As_4. The GaSb layers were exposed to an As_4 flux at the InAs-on-GaSb interfaces for (a) 5 s and (b) 30 s (images 15 nm×15 nm). There is little evidence of GaAs interfacial bonds at the InAs-on-GaSb interfaces. (c) A larger-scale image, 18 nm×60 nm, of the heterostructure shown in (b).

To further study the onset of these undulations in InAs/GaSb superlattices, we fabricated our second test structures, the type-II superlattices, with a more periodic structure (i.e., no changes in growth temperature or As exposures during the growth). A typical XSTM image of such a superlattice grown with As_2 is shown in Fig. 3(a). The thickness of all the layers is uniform and the interfaces are relatively abrupt. As discussed above, the bright ''dots'' in the InAs layers are excess Sb atoms from the GaSb interfacial surface.[22] Similarly, the dark ''dots'' in the GaSb layers are associated with As atoms in Sb sites; however, in this case, the As is uniformly distributed throughout the GaSb layers as a result of incorporation from background As.[30] An XSTM image of an identical InAs/GaSb superlattice grown with As_4 is shown in Fig. 3(b). Although there appears to be a similar amount of Sb cross incorporation in the InAs layers, there does not appear to be as much As in the GaSb. This difference is consistent with the earlier observation that As_4 does not react as readily as As_2 with GaSb.

In Fig. 4, we compare 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 As_4 growths is relatively independent of growth conditions, but for As_2 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 As_2 to

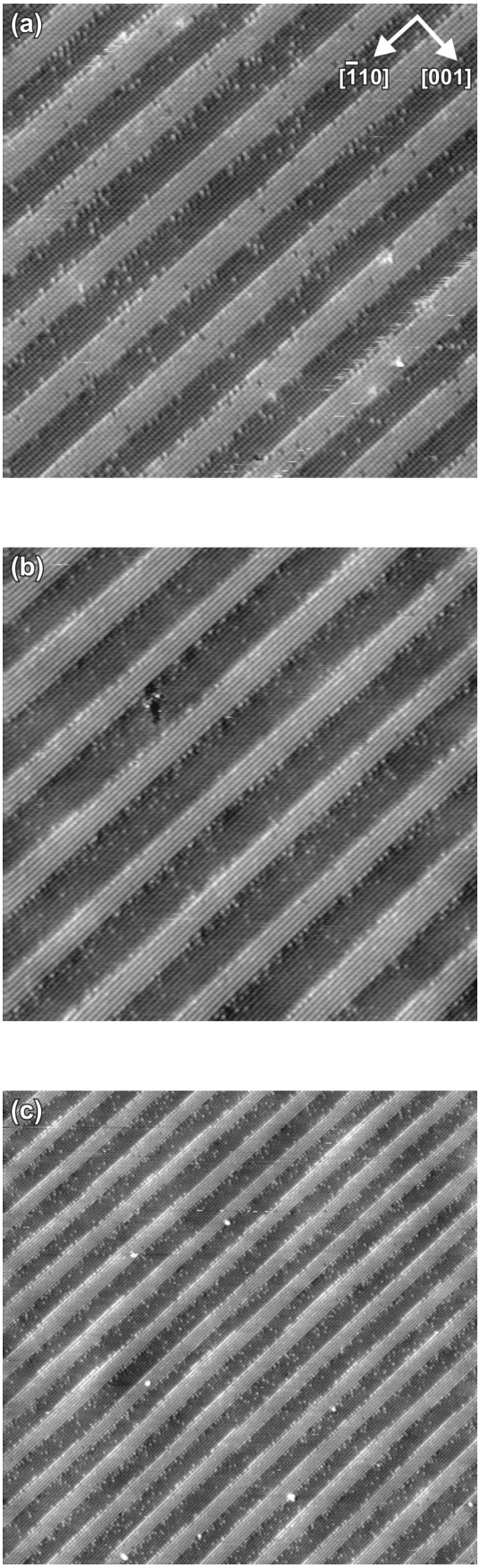

FIG. 3. InAs/GaSb superlattices grown at 390 °C using (a) As_2 and (b), (c) As_4 with an As_4:In flux ratio of 2.0:1. The images in (a) and (b) are 55 nm×55 nm, and in (c) 110 nm×110 nm.

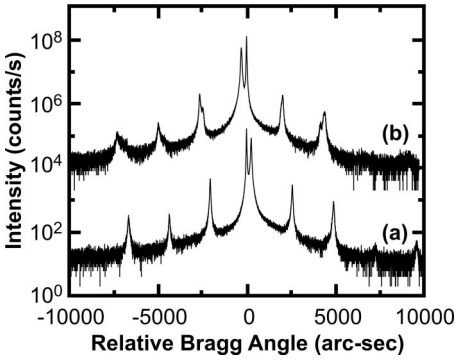

FIG. 4. XRD spectra of InAs/GaSb superlattices, $[(InAs)_{13}/(GaSb)_{13}]_{140}$, grown at 390 °C using (a) As_2 and (b) As_4. The spectra are plotted relative to the Bragg angle for bulk GaSb. In (a) the epilayer peak (the peak just off zero) is at a larger Bragg angle than the GaSb substrate peak, indicating that the average lattice constant of the superlattice is smaller than that of GaSb. Conversely, in (b), the position of the epilayer peak indicates a lattice constant smaller than the substrate.

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.

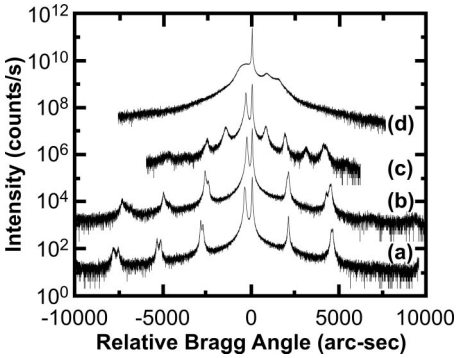

FIG. 5. XRD spectra of InAs/GaSb superlattices grown at 390 °C as a function of As_4:In flux ratios: (a) 1.6:1; (b) 2.0:1; (c) 2.7:1; (d) 4.0:1. The spectra are plotted relative to the Bragg angle for bulk GaSb.

Interestingly, XSTM images (not shown) of superlattices grown at an As_4:In flux ratio of ~2.7:1 reveal that the film instability leads to periodic modulations that are ordered both laterally and vertically in the structure. These self-organized modulations form an array of quantum-wire-like structures that are similar to growth structures recently described theoretically for strain-balanced superlattices.[31–33] (A more comprehensive study of the film instability we observe in InAs/GaSb superlattices will be the focus of a separate publication.) Although the origins of the observed growth instability are not yet understood, our results demonstrate that growth with As_4—even at relatively modest fluxes—can adversely affect the superlattice structure.

IV. CONCLUSIONS

We have used XSTM and XRD to characterize and compare the effects of As_2 vs As_4 on the growth of InAs/GaSb heterostructures by MBE. When GaSb surfaces are exposed to As_2 fluxes, the surface Sb is displaced in an anion exchange 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 As_4 results in little, if any, GaAs formation. Although growing with As_4 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 onset of the instability, inhomogeneities in the superlattice can be observed in XSTM images even when there is little notable change in the XRD spectra. Although the decreased reactivity of As_4 with antimonide surfaces could be advantageous 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 As_4.

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