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Molecular beam epitaxy using bismuth as a constituent in InAs and a surfactant in InAs/InAsSb superlattices

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Alloying bismuth with InAs provides a ternary material system near the 6.1 Å lattice constant, which covers the technologically important mid- and long-wavelength infrared region. One challenge for this material system is that it is not straightforward to incorporate bismuth into the bulk InAs lattice, since bismuth has a tendency to surface-segregate and form droplets during growth. In this work, the conditions for InAsBi growth using molecular beam epitaxy are explored. A growth window is identified (temperatures $\approx 270^\circ\text{C}$, V/III flux ratios $0.98 \leq \text{As/In} \leq 1.02$, and $\text{Bi/In} \approx 0.065$) for droplet-free, high-quality crystalline material, where InAsBi layers with compositions of up to 5.8% bismuth (nearly lattice-matched to GaSb) are attained. The structural quality of InAsBi bulk and quantum well samples is evaluated using x-ray diffraction and transmission electron microscopy. The optical quality is assessed using photoluminescence, which is observed from quantum well structures up to room temperature and from thick, low Bi-content bulk layers at low temperatures. Bismuth is also used as a surfactant during the growth of InAs/InAsSb superlattices at 430°C where it is observed that a small bismuth flux changes the surface reconstruction of InAs from (2×1) to (1×3) , reduces the sticking coefficient of antimony, results in a slight increase in photoluminescence intensity, does not significantly incorporate, and does not alter the surface morphology. © 2014 American Vacuum Society.

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I. INTRODUCTION

Alloying semiconductor materials provides additional degrees of freedom to engineer the bandgap energy and band offsets for electronic and optoelectronic device applications. Specifically, alloying host materials with heavier elements typically reduces the bandgap energy. For instance, when Bi is alloyed with GaAs or InAs, the bandgap reduction comes primarily from the upward shift of the heavy and light hole bands, while the split-off hole band and conduction band are only weakly affected.¹ The bandgap reduction associated with Bi-alloying is significantly larger than for In (12 meV/%)² or Sb (17 meV/%)² alloying in GaAs or Sb (7.2 meV/%)² alloying in InAs. Large bandgap reduction rates that vary with mole fraction are reported for $\text{GaAs}_{1-x}\text{Bi}_x$ with 90 meV per % Bi at $x = 0.01$, 57 meV per % Bi at $x = 0.05$, and 43 meV per % Bi at $x = 0.10$;³ 83 meV/% Bi for $x = 0-0.036$;⁴ and 62 meV/% Bi for $x = 0.02-0.08$.⁵ Since the strain introduced by incorporation of Bi is not correspondingly larger, a greater bandgap reduction is achieved with less strain using Bi compared to In or Sb.

A bound state will split off from the host band structure when the on-site energy of an isoelectronic impurity atom, such as Bi, is sufficiently different from the energy of the host orbitals. Otherwise, the impurity atom, which has similar electronic properties as the host, simply distorts the host band structure. Although the potential of one Bi atom may not be enough to pull a localized state out of the band continuum, two next-nearest neighbor Bi atoms or larger Bi-clusters may be sufficient. This phenomenon introduces a distribution of localized states in the vicinity of the valence band.^{6,7} This behavior is a unique feature in the electronic band structure of III-V-Bi semiconductors.

The smallest reported room temperature bandgap of bulk $\text{InAs}_{1-x}\text{Sb}_x$ is 100 meV,⁸ which occurs at a composition of $x = 0.65$ and is not lattice-matched to any conventional substrate. For small bandgap materials near the lattice constant of GaSb, InAs can be alloyed with modest amounts of Bi. The band anticrossing model accurately predicts the bandgap of GaAsSb (Ref. 9) and reasonably predicts the bandgap of GaAsBi (Ref. 9) for Bi mole fractions up to 4%. When applied to InAsBi, this model predicts a bandgap reduction of 58 meV/% Bi, which is consistent with the reported value of 55 meV/% Bi in samples grown by metalorganic vapor

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Fig. 1. Room temperature bandgap energy vs lattice constant of selected III-V ternaries. The bandgap of InAsBi decreases by 58 meV per percent Bi and has a type-I band alignment to InAs (see inset). InAs_{0.94}Bi_{0.06} is lattice-matched to GaSb and becomes semimetallic at 7.3% Bi.

phase epitaxy.¹⁰ The room temperature bandgaps of InAsBi and InAsSb are compared in Fig. 1; the inset shows the band offsets of InAs and InAsBi with 4, 5, and 6% Bi. The bandgap of InAsBi lattice-matched to GaSb is 53 meV at 6.0% Bi and becomes semimetallic at 7.3% Bi. Furthermore, its type-I band alignment provides strong wavefunction overlap between electrons and holes in InAs/InAsBi heterostructures, making them strong absorbers and good candidates for high performance far-infrared optoelectronic materials.

Surfactant species are widely used during molecular beam epitaxy growth due to their beneficial effects on surface morphology and material quality. In particular, the use of reactive¹¹ surfactants, such as Te, have been reported to delay relaxation in highly strained InAs (Ref. 12) or InGaAs;¹³ while the use of nonreactive¹¹ surfactants have been reported to increase photoluminescence (PL) intensity and carrier mobility while decreasing surface roughness in n-AlGaAs using Sb,^{14,15} and improving N-incorporation, photoluminescence intensity, and surface morphology in GaAsN using Bi.^{16,17} Both Sb and Bi are suitable surfactants for arsenides as the typical growth temperatures are sufficiently high that little Sb or Bi incorporates, and the trace amounts that do are isoelectronic with As. Likewise, Bi is a suitable surfactant for antimonides such as InAs/InAsSb superlattices.

This work presents a detailed investigation of the molecular beam epitaxy growth and the structural and optical properties of InAsBi alloys on GaSb substrates, and the effects of Bi as a surfactant during the growth of InAs/InAsSb superlattices on GaSb substrates.

II. GROWTH OF InAsBi

Bismuth is a difficult element to incorporate into III-V alloys during molecular beam epitaxy growth because it surface segregates and evaporates from the surface at the typical

III-V growth temperatures of 400–700 °C, and it forms surface droplets when the growth temperature is reduced below 400 °C. Significant Bi incorporation occurs when near-stoichiometric group-V fluxes and low growth temperatures (~300 °C) are utilized. In this work, Bi is alloyed with As on the group-V sublattice; growth conditions (flux ratios and temperatures) are identified at which the growth of high-quality droplet-free InAsBi occurs, and a mechanism is proposed for Bi incorporation based on the amount of As present on the surface.

The radial profile of the As/In flux ratio shown in Fig. 2 is measured/calibrated during the growth of InAs at 300 °C on a 50 mm InAs wafer under rotation. The As/In flux ratio at the center of the wafer is calibrated using reflection high-energy electron diffraction (RHEED). Starting with an As-overpressure, the As-flux is progressively reduced until the surface reconstruction transforms from an As-rich (2×4), to a (1×1), to an In-rich (4×2); the transitional (1×1) surface reconstruction indicates that the As/In flux is unity. The radial profile is determined under growth, starting with unity As/In flux at the wafer center and incrementally reducing the As-flux in 1% steps. As the As-flux is reduced, distinct concentric rings of haze develop due to the formation of In-droplets on the In-rich growth surfaces. The As/In flux ratio in the center region of the wafer is relatively constant, but increases by approximately 4% from a radius of 10 mm to the edge of a 50 mm wafer. The nonuniformity of the As/In flux ratio is mainly due to a ~3% decrease in the In-flux moving radially from the center to the edge of the wafer.

This small nonuniformity is not that important for the growth of many materials that are grown with As/III ratios greater than unity, but 4% is very significant when the fluxes are near-stoichiometric, as is the case for the growth of III-V-Bi materials. In the following experiments, InAsBi is grown with a target As/In flux ratio at the center of each wafer keeping in mind the change of the As/In flux ratio across the wafer. By keeping track of the As/In flux ratio and characterizing the InAsBi radially across the wafer, multiple designs (different As/In fluxes) are studied on a single 50 mm wafer.

The samples are grown on 1/4 50 mm or whole 50 mm Zn-doped GaSb substrates in a VG-V80H solid source molecular beam epitaxy system at temperatures from 260 to 300 °C, calibrated using an Ircon Modline 3 (model 3G-10C05) infrared pyrometer. For the particular As/In flux profile shown in Fig. 2, samples grown on 1/4 wafers have a relatively uniform As/In flux ratio (within 1%), whereas samples grown on full 50 mm wafers have a 4% greater As/In flux ratio at the edge of the wafer than in the center.

The InAsBi bulk and quantum well sample cross-sections are shown in Fig. 3. The bulk samples consist of a 500 nm thick GaSb buffer, a 15 nm thick InAs spacer, and a 1 μm thick InAsBi layer; the entire structure is capped with a 10 nm thick InAs layer (samples A-E), a 10 nm thick GaSb layer (sample H), or left uncapped (samples F and G). The quantum well samples consist of a 500 nm thick GaSb buffer, a 10 nm thick AlSb barrier, a 50 nm thick InAs confinement layer, a 10 nm thick InAsBi quantum well, a 50 nm thick

FIG. 2. Radial profile of the As/In flux ratio (under rotation) measured during the growth of InAs on InAs at 300 °C on a 50 mm wafer. The unity flux ratio is given at the wafer center by the (1×1) surface reconstruction (measured by reflection high-energy electron diffraction) and the radial profile is determined by further reducing the As-flux in 1% increments, which results in the formation of concentric haze rings across the wafer as In-droplets form in regions deficient in As.

InAs confinement layer, a 10 nm thick AlSb barrier, and a 10 nm thick GaSb cap. The AlSb/InAs/InAsBi/InAs/AlSb structure provides confinement for photogenerated carriers. The growth conditions and Bi mole fractions are summarized in Table I for the bulk material and in Table II for the quantum wells.

All growths are done at a constant In-flux of 2.73×10^{14} atoms $\text{cm}^{-2} \text{s}^{-1}$ that corresponds to an InAs on InAs growth rate of about one half monolayer per second. This flux corresponds to growth rates of 9.10 nm per minute for InAs on InAs, 9.15 nm per minute for InAs on GaSb, and 9.27 nm per minute for InAsBi lattice-matched to GaSb. The 9.15 nm per minute growth rate and the inferred In-flux is accurately calibrated by x-ray diffraction (XRD) measurements of the period thickness of strain-balanced InAs/InAsSb superlattices grown on GaSb. The InAsBi layers grown between 280 and 260 °C with V/In flux ratios greater than unity and Bi/In flux ratios ~ 0.065 exhibited group-V terminated surface reconstructions: (2×3) for droplet-free growth and (2×1) for

FIG. 3. Cross-section schematics of InAsBi bulk samples (a), quantum well samples (b), and tensilely strained InAs reference sample (c).

growth with Bi-droplet formation that evolves to a spotty $2 \times$ with chevrons as droplets begin to cover the surface. The InAsBi quantum well layers grown at 300 °C with near unity V/In flux ratios exhibited an In-terminated (4×2) surface reconstruction.

The surface and structural quality of 1 μm thick bulk InAsBi samples is found to be strongly dependent on the group-V fluxes. Each sample developed concentric rings of rough and smooth growth. Photos of samples A, B, and E are shown in Fig. 4, where the rough regions are identified as droplets using Nomarski interference contrast and scanning electron microscope images. Energy-dispersive x-ray spectroscopy verifies that the droplets are composed of Bi, a result that is consistent with ω -2 θ XRD measurements of the Bi mole fraction which show that the droplet-free regions have significantly larger Bi-content than the droplet-covered regions. The plot in Fig. 4 shows the 004-plane XRD from the smooth surface regions of the six bulk samples A, B, D, E, F, and G. The Bi-composition is calculated using Vegard's law and the 6.686 Å theoretical lattice constant of InBi.¹ Bi mole fractions up to the nearly lattice-matched composition of 5.8% Bi are attained.

Transmission electron micrographs from the smooth areas of sample A (with 5.8% Bi) are shown in Fig. 5 where the regions imaged are shown on the cross-section schematic. The upper micrograph (a) is a high-resolution image that confirms excellent crystallinity at the top of the InAsBi layer

TABLE I. Growth conditions and Bi composition measured by x-ray diffraction for 1 μm thick InAsBi samples grown on $1/4$ or full 50 mm GaSb substrates.

Sample	Run No.	Substrate ($1/4$ or full 50 mm)	Growth temperature (°C)	Bi/In flux ratio	As/In flux ratio (center)	Maximum Bi mole fraction	As/In flux ratio (at point of x-ray diffraction measurement)
A	B1975	Full	280	0.065	0.96	0.058	0.98–0.99
B	B1976	Full	270	0.065	0.96	0.055	0.99–1.00
C	B1982	Full	260	0.065	1.00	0.054	1.03–1.04
D	B1979	Full	270	0.065	1.00	0.052	1.00–1.02
E	B1974	full	280	0.060	1.00	0.049	1.00–1.03
F	B1973	$1/4$	280	0.060	1.00	0.047	1.00
G	B1972	$1/4$	280	0.060	1.05	0.045	1.05
H	B1967	$1/4$	300	0.100	1.50	0.0022	1.50

TABLE II. Growth conditions and Bi composition for 10 nm InAsBi quantum wells (samples 1 and 2) and tensilely strained InAs (sample 3) grown at 300 °C on 50 mm GaSb substrates.

Sample	Run No.	Substrate (1/4 or full 50 mm)	Growth temperature (°C)	Bi/In flux ratio	As/In flux ratio (center)	Bi mole fraction (peak)	As/In flux ratio (at point of peak incorporation)
1	B1990	Full	300	0.021	1.00	0.0029	1.01
2	B1987	Full	300	0.021	0.97	0.0029	1.01
3	B1991	Full	300	—	1.30	—	—

and InAs cap. The lower micrograph (b) is a bright-field image which shows that this sample has no visible defects over large lateral distances. These results indicate excellent crystal quality with few defects over many hundreds of nanometers.

The growth space for high-quality InAsBi is mapped in Fig. 6 by plotting growth temperature versus the V/In flux ratio for the five bulk samples A, B, C, D, and E grown on full 50 mm wafers (see Table I). The radial location of InAsBi growth with and without droplet formation is determined across each of the 50 mm wafers, and the corresponding As/In flux ratios are established at each location using the As/In flux ratio profile given in Fig. 2 scaled by the As/In flux ratio setting at the center of each wafer. The growth space sampled by each wafer is shown by the thick horizontal line of each rectangular area labeled by sample name. The ovals drawn along each sample region indicate the location and the percentage Bi mole fraction measured by XRD. Three distinct regions of growth are identified in the plot, droplet-free high-quality crystalline growth (not shaded), <1 μm diameter Bi-droplets with 1 × 10⁷ cm⁻² density

(shaded with vertical lines), and 3 μm diameter Bi-droplets with 5 × 10⁶ cm⁻² density (shaded with diagonal lines).

Samples A and E are grown at 280 °C with different group-V fluxes. Sample A is grown with a Bi/In flux ratio of 0.065 and an As/In flux ratio of 0.96 at the wafer center increasing to 1.00 at the edge. This sample is very rough at the center of the wafer, having formed a dense array of 1–3 μm diameter droplets (see left-hand photo in Fig. 4), and abruptly becomes smooth near the point at which the As/In flux ratio is 0.97. The Bi composition in the smooth region of the sample is 5.8%, measured by XRD. Sample E is grown with a Bi/In flux ratio of 0.060 and an As/In flux ratio of 1.00 at the wafer center increasing to 1.04 at the edge. This sample is smooth in the wafer center, with the formation of submicron sized Bi-droplets at the wafer edge. Samples B and D are grown at 270 °C with a Bi/In flux ratio of 0.065 and an As/In flux ratio of 0.96–1.00 (center to edge) for sample B and 1.00–1.04 (center to edge) for sample D, resulting in a continuous range of growth conditions at 270 °C. Sample C is grown at 260 °C with a Bi/In flux ratio of 0.065 and an As/In flux ratio of 1.00–1.04 (center to edge). Under these growth conditions, Bi-droplets are formed across the entire growth surface, though the droplets

Fig. 4. Plot shows x-ray diffraction from the 004-planes of 1 μm thick InAsBi layers grown on GaSb. For three of the samples, the position of the measurement is shown by the solid lines to the photos below.

Fig. 5. Cross-section electron micrographs showing nearly lattice-matched bulk InAs_{0.942}Bi_{0.058}; high-resolution (a) and bright-field (b); sample regions imaged are shown on the cross-section schematic. The high-resolution image shows excellent crystallinity at the top of the InAsBi layer and InAs cap, and the bright-field image shows that the material has no visible defects over large lateral distances.

FIG. 6. Growth temperature vs the V/In (As/In + Bi/In) flux ratio (lower horizontal axis) during the growth of InAsBi. The As/In flux ratio is shown on the upper horizontal axis for sample E (top scale) with a Bi/In flux ratio of 0.060 and for the other samples (bottom scale) with a Bi/In flux ratio of 0.065. Three distinct growth regions are shown: droplet-free (not shaded), submicron diameter Bi droplets with density of $\sim 1 \times 10^7 \text{ cm}^{-2}$ (vertical lines), and $\sim 3 \mu\text{m}$ diameter Bi droplets with density of $\sim 5 \times 10^6 \text{ cm}^{-2}$ (diagonal lines). The growth space sampled by each growth is shown by the thick horizontal line of each rectangular area labeled by sample name. The ovals drawn along each sample region indicate the location and Bi mole fraction measured by x-ray diffraction.

within 4 mm of the edge are much smaller than those in the center.

The growths on $\frac{1}{4}$ 50 mm GaSb wafers (samples F, G, and H) are not shown in Fig. 6, and due to their smaller size the As/In flux is uniform to within 1% across the samples. Sample F is grown under the same conditions as the center of the larger sample, sample E (280 °C, 1.00 As/In flux ratio, and 0.060 Bi/In flux ratio) and it has a slightly smaller Bi mole fraction (4.7% compared to 4.9%). Sample G has a slightly lower Bi mole fraction (4.5%) compared to samples E (4.9–4.8%) and F (4.7%) grown at the same temperature and Bi-flux, which is consistent with the presence of a larger As/In flux ratio. However, the observed Bi deficiency did not result in as many Bi droplets as would be expected from the results presented in Fig. 6. Sample H is grown at 300 °C with a 1.50 As/In flux ratio and a 0.10 Bi/In flux ratio. Under these nonstoichiometric As/In growth conditions, only a small percentage of the Bi incorporates with most of the Bi remaining on the surface to form a dense $\sim 4 \times 10^7 \text{ cm}^{-2}$ coverage of $1 \mu\text{m}$ diameter droplets. This is approximately four times more surface Bi than observed in the droplet covered regions of samples A through E presented in Fig. 6, which were grown with near-stoichiometric As/In flux ratios and lower Bi fluxes. This growth (sample H) resulted in a thick, 90% relaxed, InAsBi layer containing 0.22% Bi; the relaxation and composition are determined self consistently from the perpendicular strain of the InAsBi lattice measured

by 004-plane XRD and the shift in the photoluminescence peak predicted by strain and the band anticrossing model.

The above results indicate that Bi incorporation is very sensitive to the As/In flux ratio, and that droplet-free growth occurs near As/In stoichiometry. Furthermore, the incorporation of Bi in the droplet-free growth window peaks when the As-flux is slightly lean (As/In < 1.00); is reduced by 0.1–0.3% for As/In flux ratios between 1.00 and 1.02; and is further reduced for As/In flux ratios greater than 1.02, indicating that As is a significantly stronger competitor than Bi for group-V lattice sites. Moreover, the formation of Bi-droplets on the surface indicates that at least some of the Bi that is not incorporated stays on the surface and coalesces into droplets. Nevertheless, there is a region with reduced Bi incorporation (1.00–1.02 As/In flux ratio) where the surface remains droplet-free. In this As rich (As/In > 1.00) growth region not all of the Bi or As incorporates, resulting in an excess of approximately 1% Bi/In and 6% As/In that evaporates, indicating there is an interaction between the two elements when dilute amounts are present on the surface. When the As/In flux ratio is increased beyond 1.02, there is an additional accumulation of Bi on the surface that initiates the formation of droplets.

The incident and excess flux ratios and mole fractions of As and Bi at the droplet-free and small droplet boundaries of the As-lean and As-rich growth regimes are summarized in Table III. From the point of view of the competition of Bi with As for group-V sites, it is expected that reducing the As/In flux ratio would enable further incorporation of Bi. However, as the As/In flux ratio is reduced, there is an unexpected reduction in Bi incorporation and the onset of Bi-droplet formation as the excess Bi coalesces on the surface during As-lean growth, indicating that the interaction between Bi and As also plays a significant role in the incorporation of Bi. For example, the droplet-free boundary for As-lean growth occurs where the As mole fraction is 0.942 ($\text{InAs}_{0.942}\text{Bi}_{0.058}$) grown at 280 °C with As/In = 0.97 and Bi/In = 0.065, and 0.945 ($\text{InAs}_{0.945}\text{Bi}_{0.055}$) grown at 270 °C with As/In = 0.99 and Bi/In = 0.065. These growth conditions result in excess fluxes of As/In of 0.028 and Bi/In of 0.007 at 280 °C, and As/In of 0.045 and Bi/In of 0.010 at 270 °C (see Table III and Fig. 6). In terms of the excess group-V fluxes impinging on the growth surface, the excess As/Bi flux ratio for the formation of small Bi-droplets is ≤ 4.0 at 280 °C and ≤ 4.5 at 270 °C. Likewise, the excess As/Bi flux ratio in the As-rich growth regime is ≥ 7.2 at 280 °C and ≥ 5.6 at 270 °C; similar values are observed at the small droplet boundary (see Table III).

These results indicate that the incorporation of Bi is strongly affected by its interaction with As on the growth surface, where an optimal amount of As results in the maximum amount of Bi incorporation without the formation of Bi droplets. The presence of too little or too much As reduces the incorporation of Bi. It seems that under the appropriate concentration, As on the growth surface behaves like a reactive surfactant enhancing the incorporation of Bi during the growth of InAsBi, much like Te does for In during the growth of InGaAs (Refs. 11 and 13) or the growth of

TABLE III. Incident and excess flux ratios and mole fractions of As and Bi at the boundaries of droplet-free InAsBi growth and small Bi-droplet formation shown in Fig. 6.

		Growth temperature (°C)	As/In flux ratio	Bi/In flux ratio	As mole fraction	Bi mole fraction	Excess As/In	Excess Bi/In	Excess As/Bi
Droplet-free boundary	As-lean growth (As/In<1)	280	0.970	0.065	0.942	0.058	0.028	0.007	4.0
		270	0.990	0.065	0.945	0.055	0.045	0.010	4.5
	As-rich growth (As/In>1)	280	1.030	0.060	0.951	0.049	0.079	0.011	7.2
		270	1.021	0.065	0.948	0.052	0.073	0.013	5.6
Small droplet boundary	As-lean growth (As/In<1)	280	0.968	0.065	0.943	0.057	0.025	0.008	3.1
		270	0.983	0.065	0.948	0.052	0.035	0.013	2.7
	As-rich growth (As/In>1)	280	1.035	0.060	0.952	0.048	0.083	0.012	6.9
		270	1.038	0.065	0.950	0.050	0.087	0.015	5.9

binaries such as GaAs.^{11,18} When the As flux is decreased below a critical level, excess Bi on the surface coalesces forming droplets as less Bi is incorporated into the growing InAsBi film via the As-Bi interaction. Likewise, when the As-flux is increased above a critical level, excess Bi on the surface coalesces forming droplets as less Bi is incorporated into the growing InAsBi film via the As-Bi interaction. In the former case, there is not sufficient As on the surface to react with all of the Bi and in the latter case the interaction of As with itself overwhelms its interaction with Bi.

III. OPTICAL PROPERTIES OF InAsBi

The optical properties of several InAsBi bulk and quantum well samples are investigated using PL. The InAsBi quantum wells (listed in Table II) contain carrier confinement barriers that greatly reduce the loss of photogenerated carriers outside of the active region, and exhibit luminescence from low to room temperature. In contrast, the bulk

InAsBi structures do not contain carrier confinement barriers and do not exhibit luminescence for the most part due to weak confinement of photogenerated carriers. Nevertheless, low temperature luminescence is observed from sample H with 0.22% Bi. The PL spectra from sample H, a 300 μm thick InAs substrate, and a 1 μm thick lattice-matched $\text{InAs}_{0.91}\text{Sb}_{0.09}$ layer confined by 10 nm AlSb layers on GaSb are compared in Fig. 7. These results indicate that a small amount of Bi provides a large reduction in the bandgap of InAs and that the rate of reduction is much greater than for Sb.

The temperature-dependent PL from InAsBi quantum well samples 1 and 2 grown at 300 °C with a 0.021 Bi/In flux ratio is compared to a reference structure (sample 3) grown under identical conditions without Bi (see Fig. 8). In all samples, the tensile InAs layers and compressive AlSb layers are coherently strained. As a result of Bi incorporation, the PL peak energy of the two quantum well samples is ~ 9 meV below the PL peak energy of the tensilely strained InAs reference (sample 3). Band anticrossing model calculations indicate that the Bi mole fraction is roughly 0.15% at the center of these wafers. The variation in the temperature dependence of the bandgap of these two samples grown under nearly identical conditions is likely due to the unique bandgap reduction mechanisms of Bi. In addition to moving the valence band up toward the conduction band, Bi clusters may form which introduce distributions of states near the valence band edge which also give photoluminescence.^{6,7} The temperature dependence of the PL peak energy of each sample is fit to an Einstein single oscillator model for temperatures up to 120 K; the respective Einstein temperatures for the reference structure and quantum wells 1 and 2 are 74, 162, and 151 K.

The two quantum well samples are grown with slightly different As/In fluxes such that the two samples have overlapping growth conditions at different parts of the wafer. Quantum well sample 1 is grown with a 1.00–1.04 (center to edge) As/In flux ratio. Quantum well sample 2 is grown with a 0.97–1.01 (center to edge) As/In flux ratio. The peak energy and integrated intensity of the 12 K PL is measured radially across each 50 mm substrate and is shown along with the As/In flux ratio in Fig. 9. The small variation in the As/In flux ratio is found to significantly affect the incorporation of Bi in

Fig. 7. Low temperature (12 K) photoluminescence intensity as a function of photon energy for a 300 μm thick InAs substrate, a 90% relaxed 1 μm thick $\text{InAs}_{0.9978}\text{Bi}_{0.0022}$ layer on GaSb (sample H), and a 1 μm thick lattice-matched $\text{InAs}_{0.91}\text{Sb}_{0.09}$ layer on GaSb. Low Bi incorporation in the InAsBi layer resulted in its relaxation and the formation of Bi surface droplets, both of which act to reduce the photoluminescence intensity.

Fig. 8. Photoluminescence peak position (energy) as a function of temperature measured at the center of the wafer for two 10 nm thick $\text{InAs}_{0.998}\text{Bi}_{0.002}$ quantum wells (samples 1 and 2) and a 110 nm thick tensilely strained InAs layer (sample 3), which for comparison is the equivalent structure without Bi. For each sample, the temperature dependence of the photoluminescence peak energy is fit to an Einstein single oscillator model shown in the upper right corner of the plot. The best fit values for each is shown in the lower left corner.

the InAsBi quantum wells. In both samples, the photoluminescence peak energy is roughly 356 meV at the center and decreases to a minimum of 348 meV at the radial locations grown with a 1.01 As/In flux ratio. Comparing these two points with sample 3, the equivalent structure grown without Bi that emits at 364 meV (see Fig. 8), the Bi mole fraction nearly doubles to a peak value of 0.29% at its maximum.

Fig. 9. Low temperature (12 K) photoluminescence from two InAsBi quantum well samples grown at 300°C with a Bi/In flux ratio of 0.021, measured along the substrate radius; the peak-position energy is shown in subplot (a) and the integrated intensity in subplot (b). The radial variation in the As/In flux ratio during growth is shown in subplot (c). Both samples luminesce at $\sim 356 \text{ meV}$ (0.15% Bi mole fraction) at the wafer center and the minimum photoluminescence peak-position energy of $\sim 348 \text{ meV}$ (0.29% Bi mole fraction) occurs at a radial location with a 1.01 As/In flux ratio.

IV. Bi MEDIATED GROWTH OF InAs/InAsSb SUPERLATTICES

The performance of Bi as a surfactant is examined during the growth of strain-balanced InAs/InAsSb superlattices at 430°C on GaSb substrates. The sample structures consist of a $1 \mu\text{m}$ thick 56 period superlattice with 9 nm of InAs and 8 nm of $\text{InAs}_{0.81}\text{Sb}_{0.19}$ between *p*- and *n*-type GaSb layers, as shown in the inset of Fig. 11. In total, five superlattice samples are grown (listed in Table IV), four with Bi as a surfactant and one reference sample without; the Bi/In flux ratios are 0.0% (sample a), 0.3% (sample b), 1.0% (sample c), and 3.0% (samples d and e). The samples are characterized using RHEED, XRD, atomic force microscopy, and PL. The presence of Bi on the surface during growth changes the surface reconstruction of InAs from a faint (2×1) to a strong (1×3) while InAsSb remains unchanged with a (2×3) reconstruction as shown in Fig. 10. Although the presence of Bi modifies the surface reconstruction, there is no observed change in the surface morphology of the completed samples. Tapping-mode atomic force microscope measurements show that the surfaces are very smooth with a RMS roughness of $\sim 0.05 \text{ nm}$ over $1 \times 1 \mu\text{m}^2$ areas for all samples grown with and without Bi as surfactant.

Reciprocal space mapping shows that the superlattices are pseudomorphic; as a result, the layer thicknesses and Sb

Fig. 10. Reflection high-energy electron diffraction patterns from InAs and InAsSb grown without (a) and with (b) a Bi/In flux ratio of 3.0% as a surfactant. Bi causes the surface reconstruction of InAs to change from a weak (2×1) to a strong (1×3), while InAsSb remains a (2×3).

FIG. 11. Sticking coefficient of Sb during the Bi mediated growth of InAs/InAsSb superlattices (structure shown as inset) as a function of the Bi/In flux ratio. The results from samples a–d grown with a 0.48 Sb/In flux ratio are shown by the solid circles and indicate that the presence of Bi on the surface reduces the Sb sticking coefficient. Sample e is grown with a 0.51 Sb/In flux ratio and a 3% Bi/In flux ratio (solid square), and results in similar Sb mole fraction (18.9%) to sample a (19.0%) achieved with 0.48 Sb/In and no Bi.

mole fraction are accurately acquired from 004-plane XRD measurements of each superlattice. For all samples, the layer thicknesses are identical to the target thicknesses shown in the inset of Fig. 11. Furthermore, a trend of decreasing Sb mole fraction in the InAsSb layers grown with a constant Sb/In flux ratio and an increasing Bi/In flux ratio is observed; these measurements indicate that the presence of Bi on the surface reduces the sticking coefficient of Sb. The results from superlattices grown with an As/In flux ratio of 1.20, an Sb/In flux ratio of 0.48, and Bi/In flux ratios of 0.0, 0.3, 1.0, and 3.0% are shown as solid circles in Fig. 11. Sample a is grown without Bi and is perfectly strain-balanced with an Sb sticking coefficient of 39.6% and an Sb mole fraction of 19.0%, while sample d is grown with a Bi/In flux ratio 3.0% and is 0.03% tensilely strained with an Sb sticking coefficient of 37.7% and an Sb mole fraction of 18.1%. The growth of sample d with a Bi/In flux ratio of 3.0% is repeated using a larger Sb/In flux ratio of 0.51 to compensate for the reduced sticking coefficient, while keeping the As/In flux ratio the same at 1.20; this sample (sample e) is near perfectly strain-balanced (0.005% tensile strain) with an Sb

FIG. 12. Low temperature photoluminescence from InAs/InAs_{1-x}Sb_x strain-balanced superlattices grown with and without Bi as a surfactant, with integrated photoluminescence intensity shown as an inset. The Bi/In flux ratio and the Sb mole fraction are shown for each curve. The period of each superlattice is unchanged, but the photoluminescence peak positions differ due to changes in the incorporation of Sb, which decreases when Bi is present on the surface and increased when the Sb flux was increased to compensate.

sticking coefficient of 37.1% (slight decrease) and an Sb mole fraction of 18.9% (net increase).

The five samples grown with and without Bi as a surfactant exhibit low temperature PL with comparable line widths (see Fig. 12). Since the individual superlattice layers have the same thicknesses, the PL peak shifts are due to variations of the Sb mole fraction in the InAsSb layer. The integrated PL intensity is plotted as a function of Bi/In flux ratio in the inset of Fig. 12, and shows an increase in PL with increasing Bi-flux up to a Bi/In flux ratio of 1.0%, indicating that there is a slight improvement in the optical quality with the use of small amounts of Bi surfactant. The two samples grown with a Bi/In flux ratio of 3.0% exhibit a reduced intensity compared to the sample grown without Bi. Under these growth conditions the optimal Bi/In flux ratio is around 1.0%. Although Bi-mediated growth did not significantly impact the surface morphology and only slightly improved the optical properties of the InAs/InAsSb superlattices in this study, it is possible that samples grown at lower temperatures with a higher Sb content (larger strain) may benefit further from the use of Bi as a surfactant.

TABLE IV. Growth conditions, Sb sticking coefficient, and Sb composition measured by x-ray diffraction for 1 μ m thick InAs/InAsSb superlattices grown on $\frac{1}{4}$ 50 mm GaSb substrates with and without Bi as a surfactant.

Sample	Run No.	Substrate ($\frac{1}{4}$ or full 50 mm)	Growth temperature ($^{\circ}$ C)	Bi/In flux ratio (%)	As/In flux ratio	Sb/In flux ratio	InAs _{1-x} Sb _x mole fraction x (%)	Sb sticking coefficient (%)
A	B2023	$\frac{1}{4}$	430	0.0	1.20	0.48	19.0	39.6
B	B2035	$\frac{1}{4}$	430	0.3	1.20	0.48	18.8	39.2
C	B2024	$\frac{1}{4}$	430	1.0	1.20	0.48	18.2	37.9
D	B2026	$\frac{1}{4}$	430	3.0	1.20	0.48	18.1	37.7
E	B2028	$\frac{1}{4}$	430	3.0	1.20	0.51	18.9	37.1

V. CONCLUSIONS

The substrate temperatures and group-V fluxes for the growth of smooth, high structural-quality, nearly lattice-matched InAsBi on GaSb substrates without the formation of Bi-droplets are identified as $\approx 270^\circ\text{C}$ and $0.98 \leq \text{As/In} \leq 1.02$ with $\text{Bi/In} \approx 0.065$. The maximum incorporation of Bi occurs in this growth window, where Bi compositions up to 5.8% are realized. Outside this growth window, less Bi incorporates and the excess Bi coalesces into surface-droplets. Droplet formation occurs when the excess As/Bi flux ratios are either ≤ 4 or ≥ 6 , indicating that the presence of an optimal amount of As on the growth surface functions as an efficient reactive surfactant assisting the incorporation of Bi. Likewise, the incorporation of Bi in InAsBi/InAs quantum wells grown at 300°C is found to be sensitive to the As/In flux ratio; the maximum 0.29% Bi mole fraction observed occurs at a 1.01 As/In flux ratio and a 0.021 Bi/In flux ratio. During the growth of InAs/InAsSb superlattices at 430°C , Bi as a surfactant modifies the surface reconstruction of InAs, reduces the Sb sticking coefficient, does not significantly impact the surface morphology, and enhances the optical properties of the completed structures for Bi/In flux ratios around 1.0%.

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