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Evolution of Surface Structure and Phase Separation in GaInAsSb*

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Abstract

Atomic force microscopy was used to study changes in the surface step structure of GaInAsSb layers with varying degrees of phase separation. The layers were grown by organometallic vapor phase epitaxy on (001) GaSb substrates with 2° miscut angles toward (-1-11)A, (1-11)B, and (101). Alloy decomposition was observed by contrast modulations in plan-view transmission electron microscopy, and broadening in x-ray diffraction and photoluminescence peaks. GaInAsSb layers with a minimal degree of phase separation exhibit a step-bunched step structure. A gradual degradation in the periodicity of the step structure is observed as the alloy decomposes into GaAs- and InSb-rich regions. The surface eventually develops trenches to accommodate the local strain associated with composition variations, which are on the order of a few percent. The surface decomposition is affected by substrate miscut angle, and although phase separation cannot be eliminated, its extent can be reduced by growing on substrates miscut toward (1-11)B.

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1. Introduction

$\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}$ is an important III-V semiconductor for detectors, lasers, and thermophotovoltaics that operate in the mid-infrared range between 2 to 4 μm [1-3]. The growth of these alloys, however, is fundamentally difficult because of the existence of a large miscibility gap [4,5]. Metastable alloys have a tendency to decompose into regions with non-uniform alloy composition, which is undesirable since structural [6-7], optical [3,6-8], and electrical properties [9-10] are degraded. Nevertheless, non-equilibrium growth techniques such as organometallic vapor phase epitaxy (OMVPE) and molecular beam epitaxy (MBE) have been used to grow metastable GaInAsSb alloys [3,4,7,11]. The data on material characteristics, however, suggest that phase separation cannot be completely eliminated, but rather the extent or degree to which it degrades the material quality can be reduced when the layers are grown under certain conditions [3,12].

It was previously reported that improvements in the photoluminescence (PL) properties of GaInAsSb grown by OMVPE were achieved by decreasing the growth temperature from 575 °C to 525 °C, and increasing the growth rate from 1 to 5 $\mu\text{m/h}$ [12]. These results imply that phase separation was limited for these growth conditions. However, thermodynamic considerations indicate that decomposition should be enhanced for growth at increasingly lower temperatures [4]. Thus, kinetic effects also play an important role in the degree of decomposition.

Recent studies have shown that the surface step structure, which is affected by growth kinetics, can be related to the GaInAsSb material quality [12]. It was reported that the surface is vicinal when the layers were grown at the lower temperature of 525 °C,

while it is step-bunched at the higher temperature of 575 °C. Vicinal surfaces also exhibited the best PL properties. On the other hand, the PL peaks were extremely broadened for epitaxial layers with an irregular step structure. In this study, the evolution of the surface step structure of GaInAsSb grown nominally lattice-matched to GaSb substrates by OMVPE is reported. The alloy composition was varied to obtain layers with compositions that were predicted to be at different regions in the miscibility gap, and thus have varying degrees of phase separation. These results were correlated with bulk structural and optical properties of the layer. The effect of substrate miscut direction was also investigated.

2. Epitaxial growth and characterization

$\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}$ epitaxial layers were grown in a vertical rotating-disk OMVPE reactor with H_2 carrier gas at a flow rate of 10 slpm, reactor pressure of 150 Torr, and typical rotation rate of 50 to 100 rpm. Solution trimethylindium, triethylgallium, tertiarybutylarsine, and trimethylantimony were used as precursors [7]. Although previous results have shown that the degree of phase separation is minimal when GaInAsSb is grown at a low temperature of 525 °C [3,12], a higher growth temperature of 575 °C was used to enhance the extent of phase separation and study its evolution. Layers with nominal alloy composition (x, y) of (0.1, 0.09), (0.16, 0.14), and (0.17, 0.16) were grown, with the larger x- and y-values representing alloys deeper in the miscibility gap. The growth rate was $\sim 5 \mu\text{m/h}$.

GaInAsSb layers were grown on vicinal (001) Te-doped GaSb substrates with miscut angles of $2^\circ \rightarrow (101)$, $(-1-11)\text{A}$, or $(1-11)\text{B}$. Atomic force microscopy (AFM)

operated in tapping mode was used to study the surface step structure. Etched Si cantilevers with a nominal tip radius of 5 to 10 nm and a sidewall angle of 10° were used. In addition, transmission electron microscopy (TEM) and high-resolution x-ray diffraction (HRXRD) were used to characterize the structural properties, and PL measurements at 4 and 300 K were used to characterize the optical properties.

3. Results

Figure 1 shows AFM images of GaInAsSb layers with the three nominally different alloy compositions grown on the three different substrate misorientations. The layers are identified by their peak emission in 300-K PL spectra: an increase in emission wavelength corresponds to an increase in alloy composition. AFM images of layers with the lowest (x,y) values, which corresponds to $\sim 2.1\text{-}\mu\text{m}$ GaInAsSb, are shown in Figs. 1a, 1b, and 1c. The surface is step-bunched [13,14] for layers grown on each of the various misorientations, with multilayer steps that typically range from three to six monolayers in height and flat terraces that are about 25 to 50 nm in width. The step edges are aligned with the miscut direction, and the substrate miscut angle of 2° is maintained. The length of the terrace is variable, and is generally in the range of hundreds of nanometers long. Larger scale height undulations with a periodicity of about 150 nm are observed for layers grown on the 2° miscut $\rightarrow$ (1-11)B and (101) substrates. These undulations are not always present [12], and the origin is unclear at this point.

AFM images of layers with the intermediate alloy composition are shown in Figs. 1d, 1e, and 1f, while those with a slightly higher alloy composition are shown in Figs. 1g, 1h, and 1i. The 300-K PL emission is somewhat less than $2.3\text{ }\mu\text{m}$ for the samples in Figs.

1d, 1e, and 1f, and just slightly longer than 2.3 μm for those in Figs. 1g, 1h, and 1i. The periodicity of the step-bunched step structure deteriorates for all these layers. The sharply defined step edges become irregular, and the long terrace surfaces break up. The feature size is typically in the range 10 to 20 nm (Figs. 1d, 1e, and 1f). The orientation of surface features, however, still shows the directionality of the miscut direction. When the alloy composition is increased further (Figs. 1g, 1h, and 1i), the surfaces become increasingly irregular, and the layers appear to be at various stages in breakdown of the surface structure. Figure 1i shows that eventually the surface bears no resemblance to the original substrate miscut direction. The surface consists of relatively large (100 to 300 nm) flatter regions separated by narrow trenches, which are aligned nearly parallel with $[-110]$ and on the order of several nanometers deep.

Plan-view TEM micrographs corresponding to GaInAsSb layers grown on (001) $2^\circ \rightarrow (101)$ GaSb substrates are shown in Fig 2 (AFM images in Fig. 1c, 1f, and 1i). Fine-scale contrast modulation is observed in Fig. 2a for 2.088- μm GaInAsSb and is indicative of a relatively uniform alloy composition. On the other hand, Figs. 2b and 2c show that the length scale for contrast modulation increases from about 10 to 20 nm for 2.295- μm GaInAsSb (Fig. 2b) to 100 to 300 nm for 2.315- μm GaInAsSb (Fig. 2c). Compositional variations could not be measured by energy dispersive x-ray analysis (EDX) for the layer shown in Fig. 2b, which indicates that the variation is less than 1% (absolute concentration). The distinct coarse contrast modulations shown in Fig. 2c are associated with composition variations detected by EDX. It was determined that the darker regions (smaller areas) are GaAs-rich by only 2 to 3% compared to the average

composition, while the larger regions of lighter contrast appear to be InSb-rich [3]. The spacing of this contrast modulation is on the same order as the trenches observed in the AFM image shown in Fig. 1i.

Figure 3 shows HRXRD ω - 2Θ scans of GaInAsSb layers grown on $(001) 2^\circ \rightarrow (101)$ GaSb substrates (AFM images in Fig. 1c, 1f, and 1i). All layers are nominally lattice-matched to the GaSb substrate. There is, however, significant broadening of the diffraction peak associated with the GaInAsSb layer as the wavelength of the material increases. Reciprocal space maps indicated that the broadening is associated with an increase in tilt as well as variations in lattice constant. Similar trends in broadening in ω - 2Θ scans with increasing alloy composition were observed for GaInAsSb layers grown on (001) GaSb substrates with the $2^\circ \rightarrow (-1-11)A$ and $2^\circ \rightarrow (1-11)B$ misorientations.

Previously, it was reported that values of full width at half maximum (FWHM) of 4-K PL spectra increased as the PL peak energy decreased, which corresponds to GaInAsSb layers with higher alloy composition [7,12]. Furthermore, the difference between the 4- and 300-K PL peak energy E_{4-300K} was ~ 70 meV for layers with FWHM values in the 5 to 10 meV range. This value is in line with the expected difference based on the energy gap dependence on temperature. As the PL peak energy decreased, the energy difference decreased, and eventually was negative. Those layers were grown on $(001) 2^\circ \rightarrow (101)$ GaSb substrates. Similar trends were observed for layers grown on the miscut substrates used in this study with 2° miscut angles toward $(-1-11)A$ and $(1-11)B$, as well as (101) . However, a distinct improvement in the PL properties was measured for GaInAsSb grown on substrates miscut toward $(1-11)B$. Figure 4 shows 4- and 300-K PL

spectra for GaInAsSb with the highest alloy composition, grown on the three different substrate misorientations. The FWHM values are 36 and 42 meV for layers grown on the substrates miscut toward (-1-11)A and (101), respectively, and E_{4-300K} is only 18 meV. These values are significantly better for the layer grown on the substrate miscut toward (1-11)B, with FWHM of 12 meV and E_{4-300K} of 68 meV.

4. Discussion

In earlier studies on epitaxial growth of metastable InGaAsP and GaAsSb, it was suggested that phase separation likely occurs at the surface, since bulk diffusion coefficients are too small to account for the length scales observed in TEM [9,15,16]. Furthermore, models that describe decomposition during step flow growth have been proposed [17-19]. The AFM images and corresponding structural and optical properties of epitaxial GaInAsSb reported in this study show clear evidence that decomposition develops on the surface during growth. Alloys with relatively uniform composition grow via a step-flow mode since these surfaces exhibit a step-bunched surface. The periodic structure degrades with alloy decomposition, and the step bunches break up into smaller features. The feature sizes observed in AFM images are similar to the contrast modulation length scales observed in plan-view TEM micrographs. As GaAs- and InSb-rich regions develop, the surface structure evolves to accommodate the local strain. Trenches observed in AFM images appear to be GaAs-rich by EDX. Thus, surface decomposition, which may have been initially driven by underlying thermodynamics, is also affected by local stress that results from compositional nonuniformities [17,20].

Although evolution of the step structure follows similar trends for layers grown on substrates with the various miscut directions, the onset of the surface deterioration and the optical properties degradation is dependent on miscut direction. GaInAsSb grown on substrates miscut toward (1-11)B is less susceptible to surface decomposition compared to those miscut toward (-1-11)A and (101). A possible explanation may be related to anisotropic adatom surface mobilities, which are affected by the complex

interrelationship between miscut direction, chemical bonding at step edges, strain effects, and surface reconstructions.

5. Summary

In summary, the evolution of surface step structure and structural and optical properties of GaInAsSb epilayers was studied using samples with varying degrees of phase separation. It was found that GaInAsSb with a minimal degree of alloy decomposition exhibits a step-bunched surface. Alloy decomposition is detected by gradual deterioration in the regularity of the step structure, and can be related to contrast modulations in plan-view TEM, and broadening in HRXRD and PL curves. These results are observed for layers grown on substrates miscut toward (-1-11)A, (1-11)B, and (101), although the decomposition is somewhat less for layers grown on (1-11)B miscut substrates.

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Figure Captions

Figure 1. Atomic force microscope images of (a) 2.088- μm GaInAsSb on (001) $2^\circ \rightarrow (-1-11)\text{A}$, (b) 2.080- μm GaInAsSb on (001) $2^\circ \rightarrow (1-11)\text{B}$, (c) 2.088- μm GaInAsSb on (001) $2^\circ \rightarrow (101)$, (d) 2.291- μm GaInAsSb on (001) $2^\circ \rightarrow (-1-11)\text{A}$, (e) 2.263- μm GaInAsSb on (001) $2^\circ \rightarrow (1-11)\text{B}$, (f) 2.295- μm GaInAsSb on (001) $2^\circ \rightarrow (101)$, (g) 2.397- μm GaInAsSb on (001) $2^\circ \rightarrow (-1-11)\text{A}$, (h) 2.313- μm GaInAsSb on (001) $2^\circ \rightarrow (1-11)\text{B}$, and (i) 2.315- μm GaInAsSb on (001) $2^\circ \rightarrow (101)$. Vertical scale is 5 nm/division in all cases.

Figure 2. $\langle 220 \rangle$ two-beam plan-view transmission electron microscope micrographs for (a) 2.088- μm GaInAsSb, (b) 2.295- μm GaInAsSb and (c) 2.315- μm GaInAsSb grown on (001) $2^\circ \rightarrow (101)$ GaSb substrates.

Figure 3. High resolution x-ray diffraction of (a) 2.088- μm GaInAsSb, (b) 2.295- μm GaInAsSb and (c) 2.315- μm GaInAsSb grown on (001) $2^\circ \rightarrow (101)$ GaSb substrates.

Figure 4. Photoluminescence spectra measured at 4 and 300 K of GaInAsSb grown on GaSb substrates: (a) (001) $2^\circ \rightarrow (-1-11)\text{A}$, (b) (001) $2^\circ \rightarrow (1-11)\text{B}$, and (c) (001) $2^\circ \rightarrow (101)$.

Figure 1.

(a)

(b)

(c)

Figure 2

Figure 3

Figure 4