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Journal of Crystal Growth 251 (2003) 360–366

JOURNAL OF
**CRYSTAL
GROWTH**

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The role of Sb in the MBE growth of (GaIn)(NAsSb)

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Abstract

(GaIn)(NAs) can be grown pseudomorphically strained on GaAs with a very small band gap, opening up the possibility of achieving 1.3 or even 1.55 μm emission; however, wavelengths are actually limited by the N solubility limit and the high In strain limit. By adding Sb to the quaternary (GaIn)(NAs) we have observed a remarkable shift towards longer luminescent wavelengths, while maintaining good crystal quality. The growth of this now five-component system poses several challenges in regards to the epitaxial growth and the compositional characterization. The present paper elucidates the role of Sb as an alloy constituent as well as a surfactant in the growth of this pentanary alloy. The compositional changes of the material resulting from the addition of Sb will be shown.

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PACS: 81.15.Hi; 68.65.Fg; 81.05.Ea; 61.10.-i; 81.70.Jb

Keywords: A1. High resolution X-ray diffraction; A3. Molecular beam epitaxy; B1. Nitrides; B2. Semiconducting III–V materials; B3. Long wavelength laser diodes

1. Introduction

Mixed III–V nitride semiconductor alloys have a theoretically predicted [1,2] and experimentally observed large band gap bowing, which would allow 1.3–1.55 μm wavelength emission based on GaAs substrates. Wavelengths between 1.3 and 1.6 μm are of importance for applications in optical local area networks (LANs), metro area networks (MANs) and long haul communications due to the minimum losses in optical fibers in these wavelength regions. Several studies have shown the feasibility of 1.3 μm emitting lasers [3–6],

however longer wavelength emission devices are still limited by the poor material quality of the active regions.

Because of the large miscibility gap of (GaIn)(NAs), the growth of high-quality structures such as multiple quantum well (MQW) devices requires a detailed understanding of the composition of the alloy as well as of phase separation effects. It has been shown that N concentrations above 3–4% [7] or In concentrations above 35% cannot be achieved in the quaternary material system without significantly deteriorating the crystal structure. This seems to be an intrinsic material property and is found in both MBE and MOVPE grown material. On the one hand, the N solubility limit is approached and on the other hand, strain limits the maximum accessible In content in the quantum

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wells (QWs), limiting the achievable wavelength to approximately 1.4 μm .

Sb has first been proven to have beneficial effects when it was applied to improve PL characteristics of AlGaAs/GaAs structures [8]. It also has been shown that Sb has a surfactant effect in (GaIn)(NAs) and increases the PL intensity considerably [9]. We have also shown that adding small amounts of Sb to the quaternary material can circumvent this structural degradation, which offers the possibility of longer wavelength emission [10].

In this study, the novel quaternary (GaIn)(NAs) and pentenary (GaIn)(NAsSb) material systems were grown compressively strained on GaAs substrates at low substrate temperatures by MBE. The determination of the composition of a pentenary material is difficult but crucial for a reliable process. Therefore, we have investigated in detail the composition of several layer systems with up to 39% In, up to 4% N and up to 14% Sb using high-resolution X-ray diffraction (HRXRD), including dynamical simulation of the diffraction patterns. Determining the composition of quaternary and pentenary materials by HRXRD is—in contrast to ternary materials—not straightforward. It has been shown that the structure factors of (GaIn)As and In(NAs) are identical—within the accuracy of the technique used—for material of the same strain grown on GaAs substrates. Small amounts of Sb do not influence the scattering factors significantly either. Hence, the integral strain of the quaternary and pentenary materials can be determined by HRXRD exactly but not the composition of these materials.

Therefore, supporting secondary ion mass spectrometry (SIMS) analysis has been undertaken.

Special attention has been given to the role of Sb in changing the composition of the grown alloy compared to the quaternary material system.

2. Experimental

Ga(AsSb) and Ga(NAsSb) bulk as well as (GaIn)(NAsSb)/Ga(NAsSb) MQW samples were grown by solid source molecular beam epitaxy

(MBE) with thermally cracked arsenic and antimony. An As overpressure of $20 \times$ group III flux has been chosen for the growth of the QWs. The As flux was maintained during the growth of the barriers, resulting in a higher As overpressure. This has the advantage of not changing V/V ratios when growing a mixed group V system. Nitrogen was added using an RF plasma source. For all growths, the nitrogen flow rate was fixed at 0.5 sccm and RF power was 300 W. The Sb beam flux was recorded during growth. Indium and nitrogen growth rates were calibrated using HRXRD of GaInAs and GaNAs MQWs and thin films. Due to the metastability of the material system, substrate temperatures were kept low, around 420 °C, to enhance solid solubility.

In this paper, only as-grown samples are compared with HRXRD and SIMS. Only when photoluminescence (PL) wavelengths are given for comparison did samples undergo post-growth rapid thermal annealing (RTA) to improve optical output. RTA was done under nitrogen ambient using GaAs as a proximity cap.

HRXRD profiles were recorded in the ω - 2θ geometry around the (004) reflection of the GaAs substrate. Reciprocal space maps of asymmetric reflections have been measured for selected samples—especially for the ones under the highest compressive strain—and prove that the (GaIn)(NAsSb) QWs are fully strained for all samples chosen for the present study.

3. Results and discussion

At present, there is a good understanding of the nitrogen incorporation in (GaIn)(NAs) grown by MBE at low substrate temperatures around 420 °C. Nitrogen has been shown to have a constant sticking coefficient resulting in a linear increase of the N content with inverse growth rate [4]. The N content is—at these growth temperatures—not influenced by the In content in the quaternary alloy.

As simulations of HRXRD patterns of quaternary and pentenary alloys are only capable of deriving the strain of the structures, SIMS calibration samples have been grown in order to

study the possible influence of the Sb on the N and In composition. This kind of calibration study could open up the possibility of deriving the composition, even for this five-component system, solely by simulation of HRXRD patterns.

The SIMS calibration structure presented here consisted of 10 nm thick triple (GaIn)(NAsSb) QWs separated by 50 nm thick Ga(NAsSb) barriers. The only parameter changed was the Sb flux in three steps from 0 to 1.2×10^{-7} Torr. This gives the possibility of comparing the influence of Sb containing to Sb-free structures and of studying the effect of In as well. The sample was grown under conditions that would yield a $1.3 \mu\text{m}$ PL emission for Sb-free samples, which usually consist of $(30 \pm 2)\%$ In and $(1.6 \pm 0.5)\%$ N in the quaternary QW and $(2.3 \pm 0.2)\%$ N in the ternary barrier. SIMS analysis shows that adding Sb to the quaternary (GaIn)(NAs) does not change the In content of the QWs. It stays unchanged at $(30 \pm 2)\%$. However, Sb has an influence on the N content in the pentanary (GaIn)(NAsSb) as well as in the quaternary Ga(NAsSb). Fig. 1 depicts the N content in the QWs, as well as in the barriers, as a function of the Sb flux. The N content in the QWs and in the barriers increase with increasing

Sb flux with approximately 0.06–0.07% for 1×10^{-8} Torr Sb. The increase is slightly higher in the In-free barriers than in the In-containing QWs. This may be due to the lower growth rate of the barriers ($0.35 \mu\text{m/h}$) compared to that of the QWs ($0.5 \mu\text{m/h}$). This clearly shows that adding Sb to (GaIn)(NAs) increases the sticking coefficient of N in these material systems.

In the following, it is shown that—knowing that there is no influence of the Sb on the In content in the material and that there is an increased N sticking in the presence of Sb—HRXRD can be used to determine the composition of the five component alloys. Analyzing Ga(AsSb) and Ga(NAs) films with both techniques, it has been shown that there is no significant contribution of either N or Sb interstitials to the SIMS signal. HRXRD samples used in this study always consisted of 8 nm thick triple (GaIn)(NAs(Sb)) QWs, separated by 20 nm thick Ga(NAs(Sb)) barriers.

In Fig. 2, $\omega-2\theta$ scans around the (004) reflection of the GaAs substrate for different structures are compared. Fig. 2a shows the influence of adding Sb to a structure designed for PL emission at $1.3 \mu\text{m}$, whereas Fig. 2b depicts the diffraction

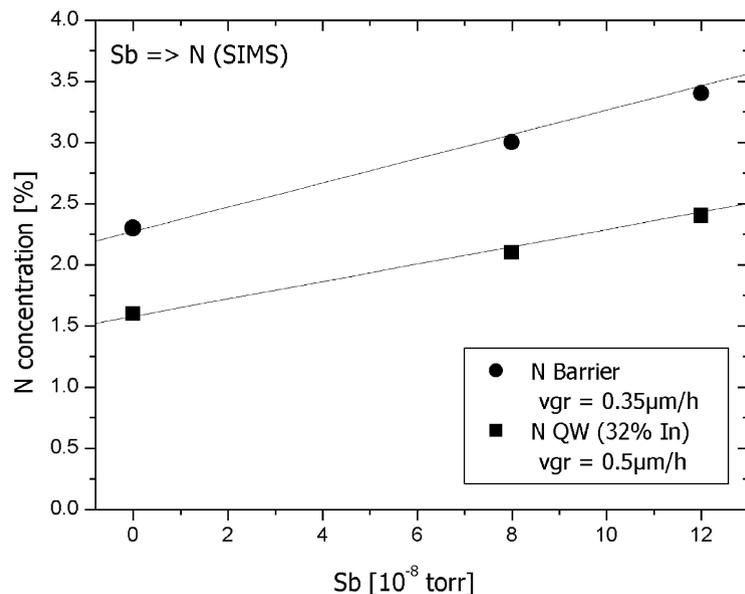
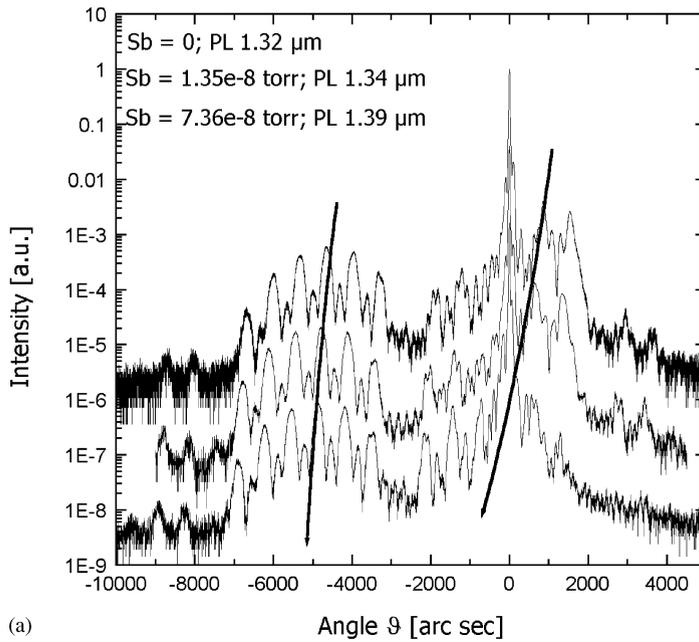
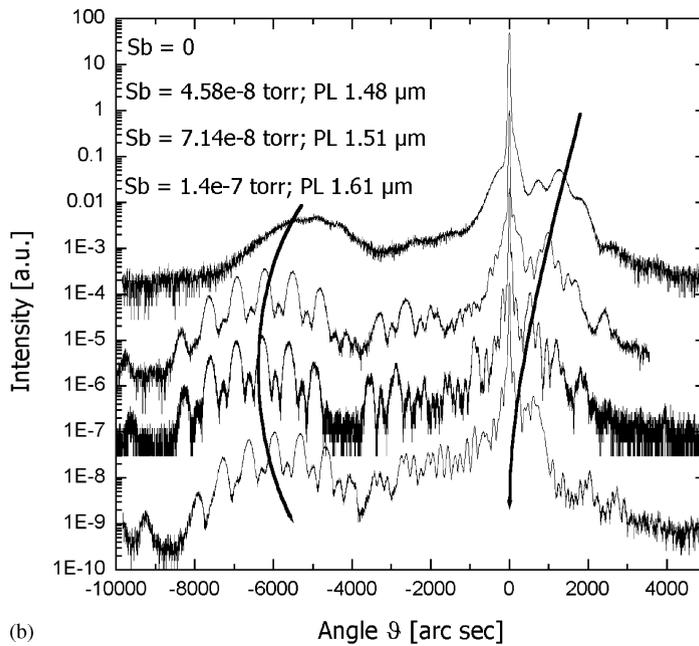


Fig. 1. Nitrogen content in (GaIn)(NAsSb) QW and Ga(NAsSb) barriers as a function of Sb flux from SIMS analysis.



(a)



(b)

Fig. 2. HRXRD $\omega-2\theta$ scans around the GaAs(004) reflection for (GaIn)(NAsSb)/Ga(NAsSb) MQW structures plotted for increasing Sb flux. (a) In content 31%, and (b) In content 38%.

patterns of structures with a PL redshifted to the 1.5 μm range. The patterns are displayed so that the Sb flux increases for the samples from top to

bottom. It can be clearly seen in Fig. 2a that increasing the Sb flux from 0 to 7×10^{-8} Torr shifts both envelopes, the compressively strained

QWs and the tensilely strained barriers to the more compressive side, indicating Sb incorporation in both the QWs and the barriers. The shift of the barrier signal is stronger than the QW, pointing at an In or growth rate-dependent Sb incorporation. The peak PL emissions of the samples, all after identical annealing, are also indicated in the figure. It can be seen that—as the composition changes—the PL emission also slightly redshifts, which is of course due to both increased Sb and N content in these samples.

As redshifting the emission wavelength by increasing the N content in the structures is mainly limited by the transition from two- to three-dimensional growth, the In content in the structures has to be increased if the band gap is to be further reduced. Fig. 2b shows the diffraction patterns of structures with In contents in the range of $(35\text{--}38)\pm 3\%$, again for different Sb fluxes during growth. From these diffraction patterns, several conclusions can be drawn: firstly, Sb acts also as a surfactant in the growth of the pentanary material system. This is obvious from comparing the Sb-free sample to the ones containing Sb. While for the first one the pendellösung fringes are not resolved any more, indicating poor interface morphology and the onset of relaxation, Sb affects the diffusivity of the species at the surface allowing more highly strained material to be grown pseudomorphically strained with high crystal quality. Secondly, Sb acts as an alloy constituent as already seen for the lower In samples. The compressive strain in the samples is increased as the Sb flux is increased to 7×10^{-8} Torr. However, as the Sb flux is further increased, the strain in the QWs is reduced, indicating an increased incorporation of N. These findings are qualitatively confirmed by checking the PL emission. The PL redshifts with increasing Sb, indicating a decrease in the band gap due to Sb and increased N incorporation. This occurs despite an increase in the compressive strain in the QWs, which actually should blueshift the emission. This effect is overcompensated by the bowing of the band gap due to compositional changes. For the sample grown with the highest Sb flux, a PL signal at $1.6 \mu\text{m}$ is measured, indicating that it is possible to redshift the PL to the second window important

for telecommunications applications while circumventing the deterioration of the crystal quality, what is usually observed.

Fig. 3 summarizes the Sb content as determined from the strain evaluation from dynamical simulation of the HRXRD diffraction patterns presented in Fig. 2a and b. The dependence of the Sb content on the Sb flux is depicted for different sample sets. The triangles correspond to ternary Ga(AsSb) bulk films and MQW samples, where a composition determination is possible simply by evaluating the strain in the HRXRD profiles. It can be seen that for the ternary alloy we are still in a regime where the Sb incorporation increases linearly with increasing Sb flux. These samples have been grown at a rate of $0.5 \mu\text{m/h}$ and an As overpressure of $20 \times$ so that their Sb content can be directly compared to that in the previously discussed pentanary QW of the other samples (circles). HRXRD analysis has also shown that the Sb content shows a strong dependence on the growth rate as well as on the As overpressure [11] so that the Sb content in the quaternary barriers (squares) should only be compared with caution to these results as the barriers are grown with a different growth rate from the QWs. Nevertheless, if one corrects the composition for the increased N sticking, derived from SIMS analysis, one also finds an increasing Sb incorporation in the quaternary Ga(NAsSb) barriers with increasing Sb flux (closed squares). However, at a certain Sb flux (open square), there is either a saturation of the Sb content in the barriers or even further increased N incorporation. The same is observed for the In containing QWs (open circle) but the effect is even more severe. From the strain of the QWs alone, an Sb content of zero would be calculated. This is highly improbable, suggesting an increased N incorporation for an Sb flux above 1.4×10^{-7} Torr. This might be related to a certain fraction of surface coverage of the wafer with Sb. Apart from that, the Sb incorporation also increases linearly with Sb flux for the In containing material (filled circles). Further investigation is under progress to clarify the N incorporation in this regime of Sb flux.

In addition, there is a strong dependence of the Sb incorporation on the In content. In agreement

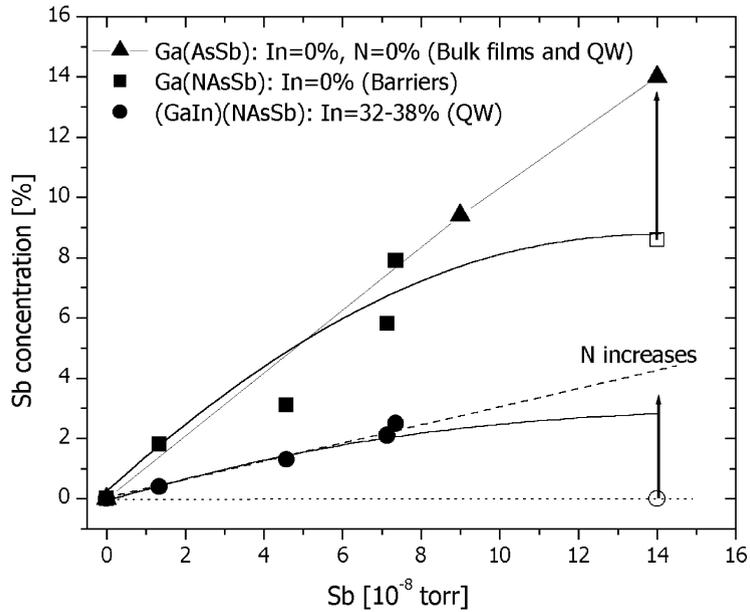


Fig. 3. Sb content in (GaIn)(NAsSb) as a function of Sb flux as determined from the strain evaluation from dynamical simulation of the HRXRD diffraction patterns presented in Fig. 2a and 2b.

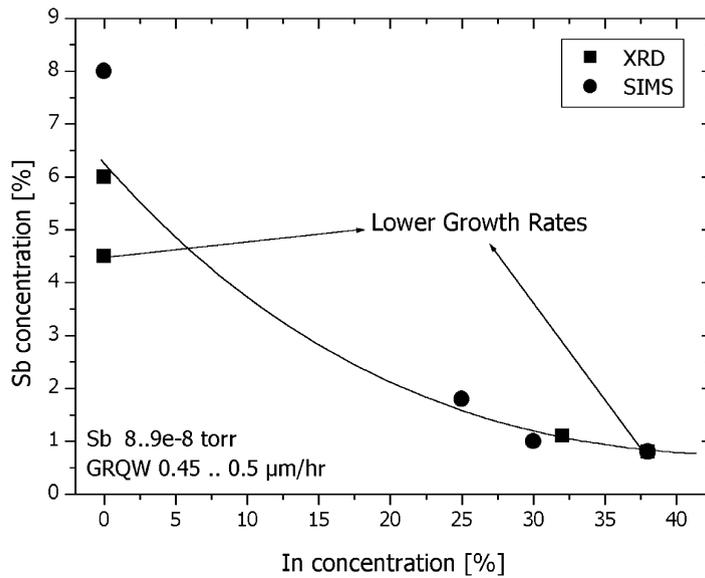


Fig. 4. Sb content as a function of the In content in the pentanry (GaIn)(NAsSb).

with the weaker strength of the InSb bond compared to the GaSb bond, the Sb incorporation decreases with increasing In content. For a

constant Sb flux and growth rate, the Sb content in samples with different In contents are compared in Fig. 4. It is seen that the Sb content decreases

with increasing growth rate, as was also observed by HRXRD from Ga(AsSb) QWs [10]. This suggests an incorporation determined by Sb desorption. On the other hand, a strong decrease of Sb content with increasing In concentration in the samples is observed, suggesting a reduced sticking of Sb in the presence of In. In this plot, data from SIMS measurements as well as from strain evaluation from HRXRD patterns are compared, again indicating that simulation of HRXRD patterns is suitable to determine the composition, if previously calibrated with SIMS analysis.

4. Summary

In summary, we have shown that in growing the pentanary alloy (GaIn)(NAsSb), Sb acts not only as an alloy constituent, further redshifting the emission wavelength, but also as a surfactant improving the crystal quality during growth and allowing growth of more highly strained material.

Moreover, the evaluation of the strain of HRXRD data yields the correct composition if several dependencies are known from SIMS analysis. Sb has been shown to not influence the indium content in the (GaIn)(NAsSb); however, increasing the In content strongly decreases the Sb sticking. In addition, Sb increases the sticking coefficient of the N, resulting in an increased N incorporation and an additional redshift of the emission wavelength. Material of this quality seems to be quite promising for device applications

in the 1.3 μm as well as in the 1.5 μm regions and above.

Acknowledgements

The authors would like to thank Charles Evans and Associates for their SIMS work. KV acknowledges the Alexander von Humboldt foundation for supporting her stay at Stanford.

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