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Growth of strained GaAsSb layers on GaAs (0 0 1) by MOVPE

M. Pristovsek*, M. Zorn, U. Zeimer, M. Weyers

Ferdinand-Braun-Institut für Höchstfrequenztechnik (FBH), Gustav-Kirchhoff-Straße 4, D-12489 Berlin, Germany

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Abstract

We investigated the growth of GaAsSb layers and quantum wells (QW) on GaAs (0 0 1) by MOVPE. Sb concentrations up to 12% were achieved at low arsine partial pressure and low growth temperature. Varying the trimethyl antimony pressure primarily changed the growth rate but not the Sb incorporation. The in situ reflectance anisotropy spectrum during growth resembles that of a GaSb surface. Sb has a strong tendency towards segregation and is only incorporated after reaching a certain critical surface coverage. These findings can be explained by a very mobile and highly Sb enriched surface layer which forms by surface melting due to strain.

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1. Introduction

For the growth of laser structures (especially vertical-cavity surface-emitting lasers) with an emission wavelength of 1.3 μm, GaAs as a substrate is advantageous in comparison to InP, which is normally used in this wavelength range, because of better material properties and the more mature device technology in the GaAs system. Using InGaAsN as the active region, this goal has been recently achieved [1]. However, metal-organic vapour phase epitaxy (MOVPE) of this N-containing material is difficult, since a low growth temperature is needed for high N incorporation [1,2] which directly contradicts good precursor decomposition. Therefore, we investigated GaAsSb as an alternative material for the active region.

Unfortunately, there are very few reports in literature for the MOVPE growth of GaAsSb. The ternary $GaAs_{0.53}Sb_{0.47}$ is lattice matched to InP

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*Corresponding author. Present address: Institut für Festkörperphysik, Technische Universität Berlin PN 6-1, Hardenbergstraße 36, D-10623 Berlin, Germany. Tel.: +49 30 314 22077; fax: +49 30 314 21769.

E-mail address: prissi@physik.tu-berlin.de (M. Pristovsek).

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and mostly used for solar cell or hetero-bipolar transistor applications. For the growth of strained GaAsSb layers on GaAs the need for low V/III ratios to achieve reasonable Sb incorporation was already emphasised in previous works [3–8]. Recently, in situ studies of GaAs and GaAsSb surfaces [9] were reported using reflectance anisotropy spectroscopy (RAS). The growth of GaAsSb multiple quantum well structures was monitored too. In some cases the Sb containing layers were grown just by supplying tri-methyl Sb before the actual growth [10]. This effect demonstrated the strong segregation of Sb during growth even at relatively low temperatures. Strong segregation and growth delay effects were also reported previously in molecular beam epitaxy (MBE) [11,12].

2. Experimental procedure

The GaAsSb layers were grown on GaAs (0 0 1) 2° [1 0 0] epi-ready substrates in a horizontal double-wall rotating disk quartz reactor (Aixtron 200/4). Sources used were tri-methyl gallium (TMGa), tri-methyl antimony (TMSb), and arsine, the carrier gas was hydrogen at 15 kPa. If not stated otherwise the growth temperature was 510 °C.

The growth was monitored in situ by reflectance anisotropy spectroscopy (RAS or sometimes called RDS). Ex situ characterisation was done using X-ray diffraction (XRD), and photoluminescence (PL) at room temperature.

3. Results

The few studies available on MOVPE growth of GaAsSb on GaAs indicate that a rather low arsine partial pressure is needed to achieve at least a small Sb incorporation [3–8]. Bedair et al. [5] especially noted that the arsine partial pressure was the crucial parameter, rather than the TMSb partial pressure. Our findings agree with this. Even increasing the TMSb partial pressure to unreasonably high values like 50 Pa did not lead to an incorporation above 2% Sb. Doubling the V/III ratio led to a small decrease in Sb incorporation, which somehow disagrees with Ref. [7]. However, this might be due to different Ga and As precursors (tri-ethyl gallium (TEGa) and tertiary-butyl arsine (tBAs)) in that study. Since a very low AsH_3 partial pressure is needed to achieve reasonable Sb incorporation the overall V/III ratio must be very low. Therefore, the surface is saturated with methyl groups from TMGa and TMSb decomposition. Since the desorption of methyl groups is limiting the growth rate, the supply of additional methyl groups by raising TMSb partial pressure further reduces the growth rate. Hence, in our studies increasing the TMSb partial pressure beyond the TMGa partial pressure decreased the growth rate (see Table 1) and sometimes slightly decreased the Sb incorporation. Thus, after the initial studies most layers were grown with a TMSb/TMGa ratio close to unity.

The right side of Fig. 1 shows the RAS spectra during TMSb exposure and growth at the most extreme conditions in our series of experiments. The spectra during growth of GaAsSb with TMSb

Table 1
Comparison of different GaAsSb QWs grown using 2.0 Pa AsH_3 at 510 °C embedded in 20 nm $GaAs_{0.84}P_{0.16}$

No.	Growth time (s)	TMGa (Pa)	TMSb (Pa)	GaAs (nm)	$GaAs_{1-y}Sb_y$ (nm)	y(Sb)	Growth rate (nm/s)
A829	4400[a]	0.95	1.0	??	122	0.092	0.029
A869	48	0.75	0.7	3.2	1.5	0.02	0.098
A870	309	0.5	0.5	4.7	5.3	0.04	0.032
A900	309	0.5	1.0	3.0	4.8	0.043	0.025
A898	618	0.5	0.67	7.3	10.5	0.05	0.029
A899	1236	0.5	0.67	7.3	28	0.035	0.029

[a] Thick layer without GaAsP barriers.

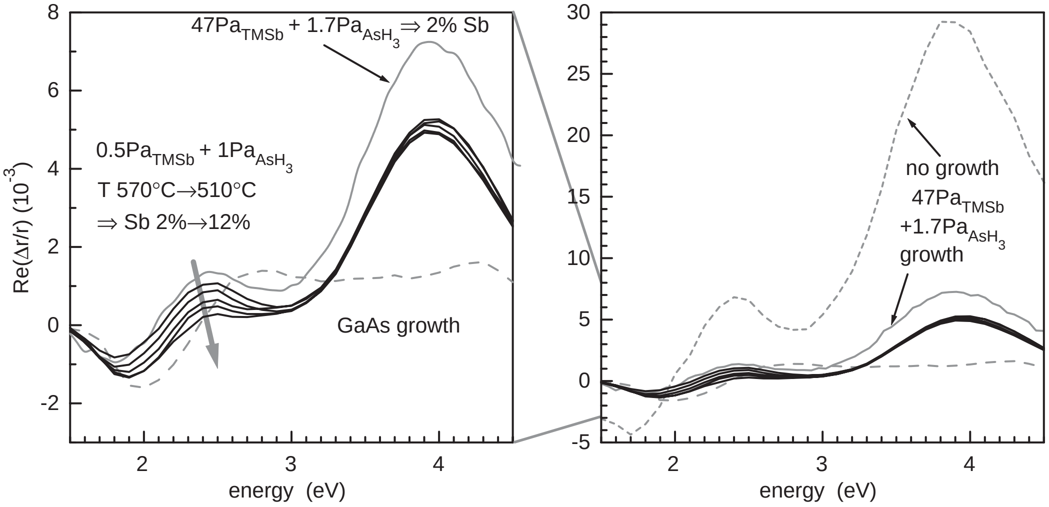

Fig. 1. Typical RAS spectra measured during growth of GaAsSb, partial pressures were 0.5 Pa TMGa, 0.5 Pa TMSb and 1 Pa AsH_3 unless marked otherwise.

are obviously very different from the spectrum during GaAs growth at the same low AsH_3 partial pressure. The general shape of the RAS spectra with TMSb is similar to spectra recorded on GaSb [9,13] and $GaAs_{0.5}Sb_{0.5}$ on InP [9], although the total amplitude differs. This similarity indicates that the upper layer of the surface is GaSb-like arranged and therefore the Sb concentration on the surface is much higher than the 12% incorporated into the bulk. This GaSb-like RAS spectrum disappears quickly when the surface is exposed to 100 Pa arsine (even at 510 °C) indicating that the highly Sb-rich layer on the surface is only loosely bound.

On the left side of Fig. 1 spectra taken during growth of thicker layers are plotted. The general shape is very similar for all concentrations. Only the height of the smaller peak at 2.5 eV slightly anti-correlates with the Sb concentration in that layer: the smaller the amplitude the more Sb is incorporated. However, the spectra are dominated by the GaSb-like surface contribution at 3.8 eV.

GaAsSb quantum wells (QW) were grown by switching on TMSb and TMGa at the same time. The resulting QWs were only half as thick and with an Sb content lower than expected. When measuring X-ray rocking curves of GaAsSb-QWs with GaAsP barriers we could not simulate the results successfully with a single GaAsSb QW. But the simulation improved much, by assuming a splitting of the QW into a GaAs layer and a GaAsSb layer (Fig. 2). The growth of two layers instead of the intended single layer could be also seen in the in situ reflectance signal. The reflectance transient in Fig. 3 during growth of the GaAsSb QW possesses two slopes. The ratio of

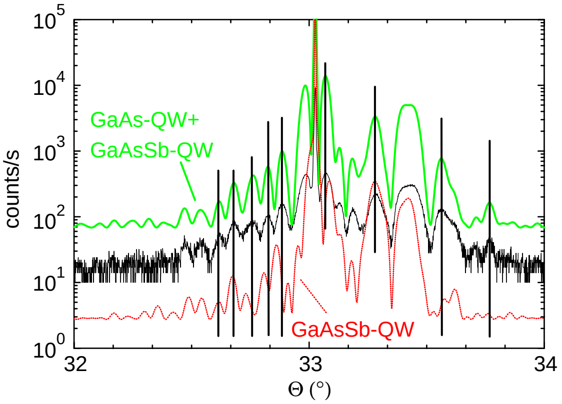

Fig. 2. X-ray rocking curve and simulation for sample A870 consisting of a GaAsP barrier enclosed GaAsSb-QW. Simulations are made for single thick GaAsSb-QW (as intended) and for a split QW of a GaAs and a GaAsSb layer (free parameters were thickness and GaAsSb composition). The fits are shifted for clarity.

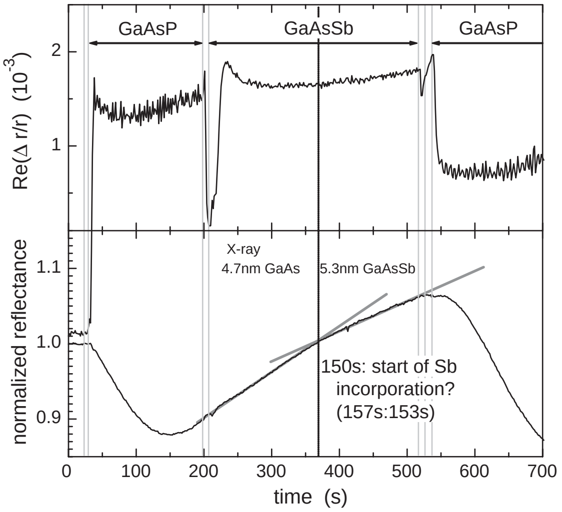

Fig. 3. RAS and reflectance transient of sample A870 at 2.6 eV during a GaAsP/GaAsSb/GaAsP QW growth sequence at 510 °C. The two different slopes in the reflectance signal during GaAsSb-QW growth can be clearly distinguished.

growth times with different slopes (157–153 s) agrees nicely to the ratio of 4.7 nm GaAs to 5.3 nm GaAsSb from the X-ray simulation. The slopes themselves are evolving due to Fabry–Perot interference, so a change of the slope can indicate a change of growth rate or of material composition.

The growth rate of the respective layers could be calculated directly taking the time from the in situ reflectance signals and the thickness from X-ray data. They were $(0.030\pm0.004)\,\mathrm{nm/s}_{\mathrm{GaAs}}$ and $(0.034 \pm 0.004)\,\mathrm{nm/s}_{\mathrm{GaAsSb}}$ for sample A870 and $(0.026 \pm 0.005)\,\mathrm{nm/s}_{\mathrm{GaAs}}$ and $(0.025 \pm 0.005)\,\mathrm{nm/s}_{\mathrm{GaAsSb}}$ for sample A900. Since these growth rates are not changing within the error level, the change of slope indicates a change of the composition of the just-growing layer, i.e. the onset of Sb incorporation. Hence, a critical Sb coverage must be built up before Sb is incorporated into the layer. Beyond this critical Sb surface coverage the Sb content in thicker QWs did not increase (Table 1). The amount of Sb necessary to start Sb incorporation can be calculated from the Sb content and the thickness of the initial GaAs layer. The mean value was (0.7±0.4) ML Sb. Since excess Sb desorbs easily, this value is rather the lower limit of the floating Sb amount.

The formation of such a segregating and quickly desorbing Sb layer was also found by MBE experiments [11,12]. For 515 °C the amount of Sb floating on the surface was estimated to be 1.2 ML, which agrees well with our findings. Also the thickness of the initial GaAs layer before GaAsSb growth is similar in MBE and MOVPE. At 450 °C in MBE it took about 3 nm to achieve a steady Sb incorporation [11,12], similar to the thicknesses of 3–7 nm at 510 °C for the initial GaAs layers in our experiments. The thickness of these initial GaAs layers decreased when increasing the TMSb partial pressure, because the critical Sb concentration builds up faster.

4. Discussion

The main findings of our experiments are:

- Sb is segregating strongly.
- The surface coverage with Sb is much higher than the incorporation.
- Sb incorporation increases with decreasing temperature.

The first explanation for the difficulties in growing GaAsSb with higher Sb content on GaAs was spinodal decomposition. However if spinodal decomposition is the cause, then at high temperatures a higher Sb incorporation would be expected, contrary to the experimental findings. Moreover, it should not be possible to grow lattice matched $GaAs_{0.5}Sb_{0.5}$ alloys on InP [6] which is stable during annealing. The explanation of a *substrate stabilised phase* is rather a statement of the experimental results. Thus spinodal decomposition cannot explain all the findings.

Another explanation might be spinodal decomposition together with decreasing precursor decomposition. But there are strong indications against this assumption. Similar to our results, Iwamura et al. [7] observed an increasing incorporation with decreasing temperature too, however they used TMSb together with TEGa and tBAs. These precursors decompose at much lower temperatures but the results in Fig. 4 agree nicely with our findings. Furthermore, the trend of

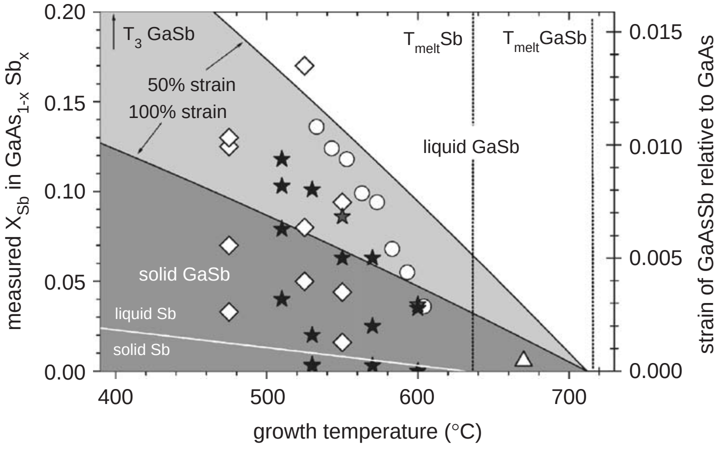

Fig. 4. Calculated melting for a strain due to lattice mismatch as function of the temperature (lines). Fifty percent strain means that half of the strain is relieved in the bottom, 100% strain means all strain contributes to melting an upper layer either of GaSb or Sb. The points correspond to measured Sb compositions of strained GaAsSb (★: our data, △: [17], ◇: [7], ○: [11] (MBE)).

increasing Sb incorporation at lower temperatures was also observed in MBE [11]. So the effect of decreasing AsH_3 decomposition must be excluded as the cause for increasing Sb incorporation.

One might also think of a strong Sb desorption to explain the decreasing Sb content with increasing temperature. But an increased desorption should be overcome by raising the Sb partial pressure, which did not work out in our experiments.

In our opinion strain is the key point, as Ito and Kobayashi demonstrated [8]. So we would like to apply the theory of Bottomley on surface melting of thin layers by strain [14,15]. From an atomistic viewpoint strain induced melting is easily understood: the atoms in a strained layer deviate from their bulk equilibrium positions and consequently the binding energy decreases. However, the argument of Bottomley was purely thermodynamically inspired by the fact that nearly all III–V semiconductors lower their melting point when pressure is applied, until a triple point at the temperature T_3 usually 200–400 K below the normal melting point [16]. Strain can supply a strong pressure which would lower the melting point of an overlayer considerably.

It must be emphasised that melting of a layer due to strain cannot lead to droplets. Droplets are weakly coupled to the substrate and therefore unstrained. Thus droplets can only occur above the normal melting point. Melting of a thin overlayer (some ML) means a loss of long-range order like in glasses together with a phase transition of the thermodynamic values. The weaker coupling of the atoms in the molten phase would strongly increase the mobility of the atoms in the molten layer. In our case the more Sb a layer contains the more mobile it will be. Thus surface melting is the cause of segregation.

To calculate the strain required to lower the melting point of a compound, the Gibbs free energy $G(T)$, the enthalpy H_{liquid} (T_{melt}), the entropy $S_{\mathrm{liquid}}(T_{\mathrm{melt}})$, and the elastic constants c_{11} and c_{12} (for fcc compounds) must be known. The elastic constants are needed to convert the lateral strain into an equivalent isotropic pressure. These values are available in tables for binary compounds like GaSb or pure Sb [18,19]. In the case of GaAsSb on GaAs, two possible candidates for a molten surface phase exists: GaSb and Sb. For Sb the elastic constants of the cubic phase are unknown and thus were extrapolated from the rhomboedrical room temperature phase. Furthermore, the calculation assumes that all the strain is relaxed in the molten layer and is not relaxed in any other way. However, in thicker layers much strain is also relaxed in the substrate layer, reducing the strain. Therefore, in Fig. 4 we included for GaSb both cases. For 100% all strain is relieved in the upper layer and in the 50% case the strain is equally distributed between substrate and upper layer.

To decide whether surface melting by strain is really important in our case, one has to compare the strain energy to the energies of competing processes like surface or interface energies, or the mixing enthalpy of ternary compounds. All these energies can be estimated from first principle calculations. For the mixing and ordering of GaAsSb compounds values between 22 and 46 meV per atom were reported [20]. Typical surface energy differences due to reconstructions are on the order of 200 meV per (1×1) unit mesh [21]. That would correspond to values between 10 and 100 meV per atom, depending on how the surface layer is defined (0.5–8 ML). Interface energies should be about the same. On the other hand, the energy required for melting GaSb is 275 meV per atom (13.3 kJ/mol). Since this energy is considerably larger than the other energies, we conclude that these effects do not change the predicted surface melting points much and surface melting is indeed relevant.

According to the theory, surface melting of GaAsSb on the Sb-rich side on GaSb occurs when the strain is higher than the calculated critical strain. In the case of GaAsSb on GaAs we assumed melting takes place, if the energy from the strain exceeded the calculated energy for melting of GaSb, even though GaSb is the minor component in the GaAsSb bulk. In this picture, the strain acts as the energy provider for melting. Once liquid, the lattice mismatch of GaSb to GaAs is large and prevents solidification of GaAsSb beyond the critical value. In this picture, segregation is directly caused by surface melting because the segregating (molten) layer must have an Sb content greater than the layer below to prevent solidification.

In Fig. 4 experimental data are compared to the calculation. Since most of the experimental data are from thicker layers, we calculate both limits for thin layers (100% strain) and thick layers, assuming that only half of the strain contributes to surfaces melting and the other half is relaxed in the substrate (50% strain). Unfortunately only few measurements of the equilibrium concentration of GaAsSb on GaAs exist, because most of the effort was devoted to grow highly strained (and often) also relaxed layers which gave broad X-ray peaks. Since these materials are no longer homogeneously strained, they should not be compared to the theory. From Iwamura et al. [7] we included all concentrations of about 600 nm thick layers grown at the highest V/III ratio and tBAs partial pressure more than 30% of total group V pressure. The stars indicate our own measurements of Sb concentrations in GaAsSb of QW and thicker layers (20–100 nm) at various conditions. For 670 °C measurements from Yakimova et al. [17] were included. And finally, the maximum Sb concentrations at a constant V/III ratio at different temperatures in MBE were added [11].

All these data show the same trend of an increasing Sb incorporation with decreasing temperature. The line for pure Sb disagrees completely. Therefore, the segregating layer should be not pure Sb but GaSb-like as indicated by the RAS spectra. The observed concentrations are closer to the 50% strain limit, indicating that half of the strain is relaxed in the substrate. Other effects which can account for the remaining disagreement, are non-equilibrium effect like Sb desorption, precursor decomposition and methyl groups, or the effect of high growth rates.

As noted in the previous section the Sb is not incorporated immediately. Instead Sb builds up a surface coverage of at least 0.7 ML before it is incorporated. This Sb is only bound loosely, as it desorbs very fast (within 30 s) when the TMSb supply is stopped. These findings further support the assumption of segregation due to surface melting. Moreover, since the strain in QWs is higher than in thicker layers, surface melting would occur earlier, resulting in lower Sb content in the QWs.

Finally, the origin of the RAS signal has to be discussed. Since a molten layer is optically isotropic, the RAS signals cannot result directly from the molten layer. However, the interface between the bulk and the molten layer can produce an anisotropy as big as from a surface. All the observed RAS spectra in Fig. 1 are very similar to GaSb [9,13]. Therefore, the GaSb-like RAS signal is caused by the great number of Ga–Sb bonds at the solid–liquid layer interface. A higher TMSb supply would only increase the amount of Sb in the liquid layer above but not the Sb incorporation (which is still strain limited). So the number of Ga–Sb bonds at the interface would increase, yielding a more GaSb-like RAS spectrum, as observed in Fig. 1.

A very recent surface study on MOVPE grown and quenched GaAsSb layer on InP at room temperature with low-energy electron diffraction (LEED) showed two surfaces: an As-rich $c(4 \times 4)$ reconstruction with very sharp spots and nearly no background and an Sb-rich surfaces with a higher background scattering and (1×3) symmetry [22]. In the picture of surface melting, the rather diffuse pattern and the high background scattering is directly related to a relatively disordered Sb-rich layer on the surface, resulting from quenching a molten Sb-rich overlayer.

To conclude, in our view it is not the miscibility gap nor the precursor thermodynamics, but surface segregation due to surface melting by strain of GaAsSb on GaAs which is limiting the Sb concentration of bulk layers and strongly influences the growth process.

5. Conclusion

We investigated the growth of GaAsSb layers on GaAs and found an increasing Sb incorporation with decreasing temperature, together with strong segregation and a growth delay of Sb incorporation. These results disagree with the established model of spinodal decomposition. Therefore, we propose a new model, based on the theory of surface melting. In this model, layers which exceed a certain critical strain melt, and only layers below the critical concentration are stable. The molten layer is loosely coupled and causes the observed segregation. Since the critical strain increases with decreasing temperature, surface melting allows for higher bulk Sb concentrations at lower temperatures as observed in the experiments. Finally, the RAS spectra during growth are always GaSb-like due to the Ga–Sb bonds at the solid–melt interface.

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