Effects of Ga- and Sb-precursor chemistry on the alloy composition in pseudomorphically strained GaAs_{1-y}Sb_{y} films grown via metalorganic vapor phase epitaxy

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Abstract

GaAs-based multiple quantum well (MQW) heterostructures comprised of metastable alloys such as GaAs\textsubscript{1-y}Sb\textsubscript{y}-GaAs\textsubscript{1-y}N\textsubscript{y} have potential for realizing high-performance and low temperature-sensitivity lasers in the 1.55 $\mu$m wavelength region. However, strain-induced ‘lattice-latching’ and Sb-surface segregation effects limit the Sb-mole fractions in the pseudomorphically strained GaAs\textsubscript{1-y}Sb\textsubscript{y} layers to $y \leq 0.2$. The effect of Ga- and Sb-precursor chemistry and the growth temperature on the Sb-incorporation efficiency in strain-relaxed and strained, pseudomorphic GaAs\textsubscript{1-y}Sb\textsubscript{y} films was studied using metalorganic vapor phase epitaxy. Both trimethyl- and triethyl-gallium (TMGa and TEGa) and trimethyl- and triethyl-antimony (TMSb and TESb) were used as Ga- and Sb-precursors, in four different source combinations, with arsine. The Sb-mole fraction in the strained GaAs\textsubscript{1-y}Sb\textsubscript{y} films was found to be lower than that in the relaxed films for all of the precursor chemistries. The highest Sb-incorporation rates were found with the TEGa-based growth with strained-layer compositions up to $y/24 \leq y \leq 0.48$ being obtained for the growth conditions employed. The results were discussed in terms of the strain-related thermodynamic effects and the chemical kinetics of precursor surface decomposition for the different precursor chemistries.

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1. Introduction

The active regions of conventional diode lasers that achieve 1.55 $\mu$m wavelength operation based on In\textsubscript{x}Ga\textsubscript{1-x}As- or In\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{1-y}P\textsubscript{y}-multiple quantum wells (MQWs) on InP-substrates suffer from high temperature sensitivity [1,2]. In an alternative materials system, laser structures based on GaAs\textsubscript{1-y}Sb\textsubscript{y} and related antimonide-based ternary and quaternary alloys such as In\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{1-y}Sb\textsubscript{y}, In\textsubscript{x}As\textsubscript{1-y}Sb\textsubscript{y} and Al\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{1-y}Sb\textsubscript{y} have been demonstrated to emit over the mid-infrared (IR) wavelength range of 2–6 $\mu$m [3–8]. Developed from this materials system, quantum well (QW) structures with type-II ‘W’ configuration, comprised GaAs\textsubscript{1-y}Sb\textsubscript{y} layers alternating with dilute nitride In\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{1-z}N\textsubscript{z} or GaAs\textsubscript{1-y}N\textsubscript{z} layers, on GaAs substrates have been proposed to emit at 1.55 $\mu$m wavelength [9,10]. This approach has the potential for realizing high-performance monolithic GaAs-based vertical cavity surface emitting lasers (VCSELS), as well as reduced-temperature-sensitivity edge-emitting lasers in the 1.55 $\mu$m wavelength region. GaAs\textsubscript{1-y}Sb\textsubscript{y}-based type-II QW structures with $y = 0.2–0.3$ and $z \geq 0.02$ in the In\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{1-z}N\textsubscript{z} layers have resulted in photoluminescence (PL) emission wavelengths between 1.4 and 1.6 $\mu$m [11–14]. The PL emission wavelengths and efficiency of these
type-II structures can be extended by increasing the Sb-mole fraction in the GaAs$_{1-y}$Sb$_y$ layers. The higher Sb-mole fraction would result into a larger valence band offset between the alternating In$_x$Ga$_{1-x}$As$_{1-y}$Sb$_y$ and GaAs$_{1-y}$Sb$_y$ layers and would enhance the carrier confinement and extend the PL wavelength to longer ranges [15].

The incorporation of Sb in epitaxial GaAs$_{1-y}$Sb$_y$ films, however, is rendered difficult due to a large thermodynamic miscibility gap manifested for the GaAs–GaSb binary alloy system [16,17]. Non-equilibrium deposition conditions comprised low growth temperatures (≈500 °C), low V/III ratios (~2) and very high gas-phase Sb-precursor fractions (Sb/V ratio, ~0.8) are employed in MOVPE to achieve a substantial (y = ~0.5) Sb incorporation in the GaAs$_{1-y}$Sb$_y$ films [18,19]. The growth of thin layer superlattices (SL) containing GaAs$_{1-y}$Sb$_y$ layers is further complicated by the surface segregation of Sb-atoms [20,21] and the As-for-Sb exchange reactions [22–24] at the interfaces between the alternating layers. An optimized gas-switching sequence has to be employed to achieve abrupt interfaces without any Sb-compositional grading between the alternating layers [25]. The Sb-mole fraction in thin pseudomorphically strained GaAs$_{1-y}$Sb$_y$ films on GaAs substrates is reported to be lower than in strain-relaxed films, grown under identical deposition conditions [25]. For the strained GaAs$_{1-y}$Sb$_y$ layers grown at 530 °C using trimethylgallium ((CH$_3$)$_3$Ga, TEGa), trimethylantimony ((CH$_3$)$_3$Sb, TMSb) and arsine (AsH$_3$), the Sb-mole fraction was limited to y = 0.2, whereas relaxed films with Sb-mole fraction up to y ≈0.4 could be obtained under identical growth conditions [25]. The strain-induced lattice-latching-coupled with the precursor site-blocking effects during the MOVPE are thought to limit the Sb-incorporation rate in the strained GaAs$_{1-y}$Sb$_y$ layers. The incomplete decomposition, at the low growth temperatures, of arsine and methyl-based Ga- and Sb-precursors used in that report resulted in kinetic limitations on the GaAs$_{1-y}$Sb$_y$ growth, giving rise to the observed difference in the Sb-mole fractions between the strained and relaxed films [25].

Alternative Ga- and Sb-precursors, such as triethyl gallium ((C$_2$H$_5$)$_3$Ga, TEGA) and triethyl antimony ((C$_2$H$_5$)$_3$Sb, TESb), are completely decomposed at much lower temperatures compared to their methyl-counterparts [26]. These ethyl-based precursors are known to yield elemental Ga- and Sb-species at the growth surface reducing the kinetic limitations on the growth behavior [27–30]. The present study determines the effect of the Ga- and Sb-precursor chemistry on Sb-incorporation efficiencies during the GaAs$_{1-y}$Sb$_y$ MOVPE. Both ethyl- and methyl-precursors for Ga and Sb were utilized in four different combinations to deposit relaxed and strained GaAs$_{1-y}$Sb$_y$ films at various gas-phase precursor ratios and growth temperatures. The results in Sb-incorporation obtained in this study are discussed in terms of the different surface stoichiometries corresponding to various growth conditions employed.

2. Experimental methods

Relaxed and pseudomorphic GaAs$_{1-y}$Sb$_y$ films were deposited on the (100) GaAs substrates in a horizontal conventional MOVPE reactor, operated at 78 Torr [31,32]. The substrates were annealed under arsine at 650 °C prior to the growth, to desorb any oxides from the GaAs surface. Two gallium precursors, TMGa and TEGa, along with two antimony precursors, TMSb and TESb, were used in four different combinations along with arsine as the As-precursor, for the deposition of GaAs$_{1-y}$Sb$_y$ films. The effect of three growth parameters on the Sb-mole fraction in GaAs$_{1-y}$Sb$_y$ films was determined: AsH$_3$/III-precursor ratio, Sb/III-precursor ratio and the growth temperature. The variation in the precursor ratios was carried out at a constant growth temperature of 530 °C. The mole fraction of TMGa or TEGa in the gas phase was fixed at 4.3 × 10$^{-5}$ for the growth of all these samples. The relaxed GaAs$_{1-y}$Sb$_y$ growth was studied by depositing 1 μm thick GaAs$_{1-y}$Sb$_y$ layers on GaAs. Four-period GaAs–GaAs$_{1-y}$Sb$_y$ SL were deposited on GaAs to obtain pseudomorphically strained GaAs$_{1-y}$Sb$_y$ films. An additional sample was grown using the TMGa–TESb growth chemistry at 530 °C. This sample was grown at a higher growth rate through the adjustment of the TMGa mole fraction. The growth rate of this sample was increased at constant As/III and Sb/III ratios to study the influence of changing growth rate at a constant temperature.

For the TMGa chemistries (TMGa–TMSb and TMGa–TESb), the AsH$_3$/TMGa ratio was varied between 0.76 and 3.93 at a fixed Sb/TMGa-precursor ratio of 1.55. The Sb/TMGa ratio was also varied from 0.76 to 3.1 at a constant AsH$_3$/TMGa ratio of 0.76 for both the TMGa chemistries. A narrow range of Sb/TMGa-precursor ratio has to be employed for the TMGa chemistries, as the formation of Sb hillocks was reported during GaSb MOVPE, when a TMSe/TMGa ratio > 2 was used [33]. For the SL samples, the GaAs layer was grown for 36 s and the GaAs$_{1-y}$Sb$_y$ layer growth time was 9 s, in the case of TMGa chemistries. For the TEGa chemistries (TEGa–TMSb and TEGa–TESb), the AsH$_3$/TEGa ratio was varied from 1 to 6, at a fixed Sb/TEGa-precursor ratio of 4 [34]. To determine the effect of Sb/TEGa-precursor ratio on the Sb-mole fraction in the pseudomorphic films, additional SL samples were grown with a Sb/TEGa-precursor ratio of 2, at a fixed AsH$_3$/TEGa ratio of 4. The SL samples were grown with a GaAs deposition time of 24 s and GaAs$_{1-y}$Sb$_y$ deposition time of 12 s, using the TEGa chemistries.

The effect of growth temperature on the Sb incorporation in the pseudomorphic films was also determined. For the TMGa chemistries, the growth temperature was varied between 500 and 560 °C, whereas for the TEGa chemistries the SL samples were grown in the temperature range of 485–545 °C.

The alloy composition was determined using a combination of X-ray diffraction, TEM analysis on selected samples and electron microprobe analysis (EMPA).
Double crystal X-ray diffraction (DC XRD) θ–2θ scans were obtained from the relaxed as well as pseudomorphically strained GaAs–GaAs$_{1-y}$Sb$_y$ SL structures. In the case of the thick (1 μm) strain-relaxed samples, the angular difference between the substrate GaAs and GaAs$_{1-y}$Sb$_y$ peaks in the θ–2θ scan was used to calculate the Sb-mole fraction in the relaxed films, using the Vegard’s law. The layers were assumed to be completely relaxed. The composition during the pseudomorphic phase of growth would be different from that of the strain-relaxed material. The films used in these measurements were 1 μm thick and the critical thickness at 10% Sb would be about 20 nm. The X-ray peak position would be dominated by the strain-relaxed materials as a result. The thickness of the film was determined independently through the use of profilometry. The thickness of the film was the critical thickness at 10% Sb would be about 20 nm. The EMPA measurements agreed with the X-ray diffraction determination of the composition within $\Delta y = \pm 0.015$ in GaAs$_{1-y}$Sb$_y$.

The composition of the pseudomorphic layers is more difficult to determine and a combination of X-ray diffraction, EPMA, and TEM was again used. X-ray diffraction scans from the SL structures were used to determine the period of the SL and the zero-order SL peak was used to determine the average composition of the SL structure [35]. EMPA was also performed on selected samples to independently determine the Sb-mole fractions in the relaxed and strained layers. The EMPA-generated composition values were compared to those deduced using the XRD scans. A commercial analysis program was used to assess the composition within a layer thinner than the depth of the EPMA sampling volume. The total thickness of one period of the SL, known from the spacing of the X-ray SL satellite peaks, and the number of periods are required for this analysis. Therefore, the average composition of Sb within the SL can be determined through analysis and modeling of the EPMA data. These average compositions from the X-ray and EPMA measurements agreed within $\Delta y = \pm 0.015$ in GaAs$_{1-y}$Sb$_y$. Determination of the specific Sb content within the GaAs$_{1-y}$Sb$_y$ SL layer requires additional data. The X-ray scan from the SL can be fit using a dynamical simulation model [35]. The individual layer thicknesses were assumed to be determined solely by the Ga-precursor mole fraction in the gas phase and the growth rate was determined to be independent of the alloy composition at a given temperature. High-resolution transmission electron microscopy (HRTEM) was performed in cross-section on two SL samples; one grown using TMGa–TMSb and the other grown using TEGa–TESb chemistry. The TEM micrographs were used to verify that the constant growth rate assumption was valid. The individual layer thicknesses, and hence the growth rate, derived from the TEM images were then used in the dynamical simulation model to fit the secondary diffraction peaks in the XRD θ–2θ scans to determine the specific Sb-mole fractions in individual alloy films [35].

3. Results

All the SL samples discussed in this paper were pseudomorphic and hence strained. Fig. 1 presents the cross-sectional HR-TEM image obtained from a GaAs$_{1-y}$Sb$_y$–GaAs SL sample, grown using TEGa–TESb chemistry at 485 °C. The thicknesses of GaAs and GaAs$_{1-y}$Sb$_y$ layers, as calculated by counting the atomic planes in the TEM image, were 5.088 and 2.82 nm, respectively. Since the TEM thickness measurement relies on counting the atomic planes between the interfaces, the error in this measurement is of the order of one monolayer (ML) of the crystal. One ML corresponds to ~0.3 nm for the GaAs$_{1-y}$Sb$_y$ lattice constant. The ratio of these growth thicknesses agrees with the ratio of the growth times within this stated experimental error. The Sb-mole fraction in the individual GaAs$_{1-y}$Sb$_y$ layers for this sample was found to be $y = 0.43$ using the simulation fit to the XRD spectrum and EPMA data. The presence of defect-free interfaces between the alternating layers in the TEM image and the narrow X-ray line width indicated that the GaAs$_{1-y}$Sb$_y$ layers were pseudomorphically strained to the GaAs lattice constant. The Sb-mole fractions in this study determined using the TEM-derived layer thicknesses would therefore possess an error in their values based on the one ML error in the determination of the individual layer thickness from TEM. The error of 0.3 nm in the measurement of GaAs$_{1-y}$Sb$_y$ layer thickness translates into a 1.02% error in the Sb-mole fraction, calculated using the XRD simulation fits. Hence, all the $y$-values determined for various GaAs$_{1-y}$Sb$_y$ layers described in this paper should be assumed to have a $\Delta y/y = \pm 0.0102$ error in their
The error bars for the reported compositions in the graph-figures are smaller than the data points shown. The surface morphology of the relaxed, 1-μm thick, GaAs$_{1-y}$Sb$_y$ samples was rough and somewhat limited the accuracy of the thickness measurements. The SL structures possessed specular surfaces.

### 3.1. Effect of precursor ratios

Table 1 summarizes the dependence of the Sb-mole fraction in strained and relaxed GaAs$_{1-y}$Sb$_y$ films with the gas-phase AsH$_3$/Ga-precursor ratio, for various precursor chemistries. Fig. 2 presents the variation in Sb-mole fraction with AsH$_3$/TMGa ratio, in relaxed (closed symbols) and pseudomorphically strained (open symbols) GaAs$_{1-y}$Sb$_y$ layers, for the TMGa–TMSb and TMGa–TESb chemistries. The solid lines in the figure are shown as a guide for the trends in the data points and do not represent any functional fit to the data. The samples in this study were grown at 530 °C and at a constant Sb/TMGa-precursor ratio of 1.55. The highest Sb-mole fraction of $y = 0.49$ obtained in this study was in the relaxed GaAs$_{1-y}$Sb$_y$ films deposited at an AsH$_3$/III ratio of 0.76 using the TMGa–TESb chemistry. The Sb-mole fraction in both the relaxed and strained GaAs$_{1-y}$Sb$_y$ films decreased with an increasing AsH$_3$/TMGa ratio. The Sb concentration in the pseudomorphically strained GaAs$_{1-y}$Sb$_y$ layers was always lower than that in the relaxed GaAs$_{1-y}$Sb$_y$ films, deposited under the identical growth conditions. At the lowest AsH$_3$/TMGa ratio of 0.76, Sb-mole fractions of $y = 0.2$ and 0.16 were achieved in the strained layers using TMSb and TESb as the Sb-precursors, respectively. The Sb-mole fraction in the strained GaAs$_{1-y}$Sb$_y$ films decreased rapidly to $y \geq 0.05$ as the AsH$_3$/TMGa ratio was increased above unity. The Sb-mole fraction in the strained layers grown at higher AsH$_3$/TMGa ratios was independent of the choice of Sb-precursor. The difference in the Sb-mole fraction between the relaxed and strained GaAs$_{1-y}$Sb$_y$ layers also decreased with the increasing AsH$_3$/TMGa ratio.

The effect of changing the Sb-precursor flux on the pseudomorphic GaAs$_{1-y}$Sb$_y$ composition, at a constant AsH$_3$/TMGa ratio of 0.76, is presented in Fig. 3 for both TMGa chemistries. For the TMGa–TMSb chemistry, the Sb-mole fraction in the strained layers remained constant at $y = 0.2$ with perhaps a slight increase, when TMSb/ TMGa ratio was varied between 0.77 and 3.1. For the TESb case, the Sb-mole fraction was initially $y = 0.2$ at a TESb/TMGa ratio of 0.77 and remained constant at $y = 0.16$ for TESb/TMGa ratios of 1.55 and 3.1. This trend of decreasing Sb-mole fraction with the increasing TESb flux was further explored by measuring the Sb-mole fraction in relaxed GaAs$_{1-y}$Sb$_y$ films with varying TESb/ TMGa ratio. The Sb-mole fraction in relaxed films, again using a As/TMGa = 0.76, was also found to decrease from $y = 0.52$, for the TESb/TMGa ratio of 0.77 to $y = 0.45$ for the TESb/TMGa ratio of 3.1. This trend of a decrease in the Sb-incorporation efficiency with an increasing Sb-flux for the TESb chemistry existed for both strained and relaxed GaAs$_{1-y}$Sb$_y$ layers. On the other hand, the Sb-mole fraction in the relaxed films grown using the TMGa–TMSb chemistry increased from $y = 0.31$ to 0.4, when TMSb/TMGa ratio was increased from 1.55 to 3.1. These results demonstrate that the mechanism determining the Sb incorporation in the strained and relaxed films is different for the TMSb and TESb chemistries.

![Graph showing variation in Sb-mole fraction with AsH3/TMGa ratio](Image)

#### Table 1

The dependence of Sb-mole fraction in the relaxed and strained GaAs$_{1-y}$Sb$_y$ layer for various precursor chemistries

<table>
<thead>
<tr>
<th>Precursor chemistry III–V</th>
<th>Sb/III ratio</th>
<th>AsH$_3$/III ratio</th>
<th>Sb-mole fraction (y in GaAs$_{1-y}$Sb$_y$) (relaxed films)</th>
<th>Sb-mole fraction (y in GaAs$_{1-y}$Sb$_y$) (strained films)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMGa–TMSb</td>
<td>1.55</td>
<td>0.76</td>
<td>0.31</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
<td>1.9</td>
<td>0.13</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
<td>3.93</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
<td>0.76</td>
<td>0.49</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
<td>1.9</td>
<td>0.17</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
<td>3.93</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>TEGa–TMSb</td>
<td>4</td>
<td>1</td>
<td>—</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>0.57</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3</td>
<td>—</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>0.40</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5</td>
<td>—</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6</td>
<td>0.30</td>
<td>0.19</td>
</tr>
<tr>
<td>TEGa–TMSb</td>
<td>4</td>
<td>1</td>
<td>—</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>0.54</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3</td>
<td>0.46</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>0.36</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5</td>
<td>—</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6</td>
<td>0.17</td>
<td>0.12</td>
</tr>
</tbody>
</table>

All samples were grown at 530 °C.
The variation of Sb-mole fraction in the relaxed and strained GaAs$_{1-y}$Sb$_y$ films with AsH$_3$/TEGa ratio is plotted in Fig. 4 for the TEGa–TMSb and TEGa–TESb chemistries. Closed symbols represent the Sb-mole fraction in relaxed films, whereas open symbols are used for the strained GaAs$_{1-y}$Sb$_y$ layers. For both the chemistries, the Sb-mole fraction in the relaxed layers decreased monotonically as the AsH$_3$/TEGa ratio was varied from 1 to 6, at a constant Sb/TEGa-precursor ratio of 4. The samples for this study were also grown at 530 °C, when compared to the TMGa-based growth, strained layer Sb-mole fractions were always lower when compared to those in the relaxed films, for both the TEGa-chemistries. For the TMSb-grown samples, the Sb-mole fraction in the strained layers showed a maximum of $y = 0.38$ when at AsH$_3$/TEGa ratio of 2. For the lowest AsH$_3$/TEGa ratio of 1, identical Sb-composition of $y = 0.26$ was obtained for both the TMSb and TESb chemistries. The Sb-mole fraction in the strained layers decreased for the samples grown using TMSb when the AsH$_3$/TEGa ratio was increased above 2, and an Sb-mole fraction of $y = 0.19$ was obtained at the AsH$_3$/TEGa ratio of 6. The strained layer Sb-incorporation possesses a peculiar trend for the TEGa–TESb chemistry. The Sb-mole fraction remained constant at $y \approx 0.29$ for the AsH$_3$/TEGa ratios between 2 and 4, and dropped to $y = 0.12$ for the AsH$_3$/TEGa ratios of 5 and 6. This rapid decrease in the Sb-mole fraction for the strained layers grown using TESb, coupled with the large difference in Sb-mole fraction in relaxed films between TMSb and TESb chemistries at higher AsH$_3$/TEGa ratios indicated the presence of different Sb-incorporation mechanisms for the two cases. For both of the TEGa chemistries, the difference in Sb-mole fraction between the strained and relaxed layers was more pronounced at lower AsH$_3$/TEGa ratios.

3.2. Effect of growth temperature

The variation in the Sb-mole fraction in the strained GaAs$_{1-y}$Sb$_y$ layers with the growth temperature is presented in Figs. 5 and 6 for all the precursor chemistries studied. The Arrhenius plot in Fig. 5 shows the effect of growth temperature on the Sb-mole fraction in the strained GaAs$_{1-y}$Sb$_y$ layers for the TMGa–TMSb and TMGa–TESb chemistries. The growth temperature was varied between 500 and 545 °C at constant AsH$_3$/TMGa and TMSb/TMGa ratios of 0.76 and 1.55, respectively. The Sb-mole fraction increased from $y = 0.13$ to 0.21 with
increasing growth temperature, with an apparent activation energy of 14 kcal/mol. For the same temperature range, the GaAs$_{1-y}$Sb$_y$ growth rate was also found to increase from 0.08 to 0.14 μm/min, with an activation energy of 15 kcal/mol. For the TMGa–TESb chemistry, the Sb-mole fraction in the strained layers increased from $y = 0.08$ to 0.3 with the increasing growth temperature, with an activation energy of 30 kcal/mol. Over the same temperature range, GaAs$_{1-y}$Sb$_y$ growth rate also showed an increase from 0.075 to 0.15 μm/min, with an activation energy of 15.7 kcal/mol. This enhancement in growth rate for the TMGa–TESb chemistry was similar to that for the TMSb case, but the increase in the Sb-incorporation with deposition temperature was faster with the TESb than the TMSb chemistry. Thick GaAs$_{1-y}$Sb$_y$ layers were also grown at 500 and 545 °C using the TMGa–TESb chemistry. The relaxed film GaAs$_{1-y}$Sb$_y$ compositions did not show a substantial dependence on the growth temperature. To determine the correlation between the increment in the growth rate and the Sb-mole fraction, an additional sample was grown at 530 °C using the TMGa–TESb chemistry, with a growth rate equivalent to that observed at 545 °C. The Sb-mole fraction in the strained GaAs$_{1-y}$Sb$_y$ films grown at 530 °C increased from $y = 0.16$ at a growth rate of 0.075 μm/min to $y = 0.21$ at the higher growth rate to 0.015 μm/min.

The effect of growth temperature on Sb-mole fraction in strained layers for the TEGa–TMSb chemistry is shown in Fig. 6. The growth temperature was varied over the range of 485–545 °C at a constant TMSb/TEGa ratio of 4 and AsH$_3$/TEGa ratio of 4. The Sb-mole fraction remained constant at a value of $y \approx 0.28$ from 485 to $\sim 515$ °C and decreased to $y = 0.20$ at 545 °C. A different trend in Sb incorporation with growth temperature was observed for the TEGa–TESb case. Fig. 6 also presents the Arrhenius plot for the TEGa–TESb case, with the solid line representing an exponential fit to the experimental data. For the TEGa–TESb chemistry, the Sb-mole fraction decreased monotonically from $y = 0.48$ at 485 °C to $y = 0.23$ at 545 °C, with apparent activation energy of 15 kcal/mol. For both the TEGa chemistries, GaAs$_{1-y}$Sb$_y$ growth rate did not show any significant variation with the growth temperature.

4. Discussion

The Sb-incorporation efficiencies during the MOVPE growth of GaAs$_{1-y}$Sb$_y$ are determined by the concerted interaction between the thermodynamic and chemical kinetic phenomena at the growth surface. In this study, the Sb-mole fractions in the strained GaAs$_{1-y}$Sb$_y$ films were found to be lower compared to those obtained in the relaxed films deposited under identical growth conditions. The Sb-incorporation efficiencies for both strained and relaxed GaAs$_{1-y}$Sb$_y$ films were also found to be dependent on the choice of precursor chemistry, with higher Sb-mole fractions obtained for the TEGa chemistries. This influence of precursor chemistry indicates that thermodynamics alone cannot describe the observed compositional dependencies on growth conditions. Chemical surface kinetics must play a critical role therefore in determining the Sb composition. The following sections discuss the experimental results in terms of the thermodynamic and kinetic aspects of the GaAs$_{1-y}$Sb$_y$ MOVPE growth.

4.1. Thermodynamic aspects of GaAs$_{1-y}$Sb$_y$ epitaxy

The epitaxial growth of strain-relaxed GaAs$_{1-y}$Sb$_y$ layers on InP and GaAs substrates using MOVPE has been extensively studied [16,18,36–39]. The alloy system possesses a miscibility gap [40] and the thermodynamically stable state is that of a phase separated material for a broad range of alloy compositions at typical growth temperatures below the critical temperature of $\sim 745$ °C at $y \approx 0.52$ regardless of the growth conditions. If homogenous materials with compositions within the miscibility gap are produced by non-equilibrium growth techniques, thermal annealing of such metastable alloys of GaAs$_{Sb1-y}$ leads to the formation of phase separated materials [36]. This miscibility gap and the subsequently low Sb-incorporation efficiencies during the MOVPE growth are most easily characterized by the lower equilibrium constant for the formation of GaSb relative to GaAs [41–43].

The growth of GaAs$_{Sb1-y}$ by MOVPE and its dependence on the growth parameters, such as gas-phase stoichiometry and temperature, has been modeled extensively by Stringfellow [43]. Thermodynamically based models make specific assumptions about the extent of decomposition of the metal-organic precursors. The most typical assumption is complete source decomposition at the growth temperature. Additionally, thermodynamic equilibrium must be assumed to be established between the gas-phase constituents adjacent to the growth front and their corresponding surface concentrations. The thermodynamic equilibrium is determined by the temperature and the
activities or partial pressures of the constituent elements comprising the alloy, i.e. \( p_{\text{Ga}} \), \( p_{\text{Sb}} \), and \( p_{\text{As}} \) (assuming the tetrameric form of As and Sb are the dominant gas-phase species). Specification of the activities at the growth front is further complicated by the fluid flow environment within the system. The metal-organic compounds decompose at or near the surface to generate Ga, As or Sb which can be adsorbed on the surface and incorporated into the growing film or desorbed into the gas phase. The specific activity of the species, Ga, Sb\(_4\) and As\(_4\), at the growth front is therefore the result of the combined influence of the decomposition kinetics at or near the growth front and the gas-phase transport of Ga, Sb\(_4\) and As\(_4\) away from the growth front into the gas stream. It is also assumed that if the partial pressures of Ga, Sb\(_4\) and As\(_4\) are below that of the species, Ga, Sb\(_4\) and As\(_4\), at the growth front is the specific activity of the gas-phase constituents. This phenomenon has also been referred to as a coherency strain [45,46] or a form of ‘lattice latching’ [44,47,48]. Another finding of these studies is the calculated suppression of the critical temperature of the miscibility gap can be as low as 493 °C for GaAs\(_{0.8}\)Sb\(_{0.2}\) pseudomorphically strained to a GaAs substrate [44].

The rejection of Sb from the growing films due to such strain coherency or lattice-latching effects would lead to the formation of a Sb-rich surface layer. The strained-layer Sb-incorporation efficiency would be affected by the Sb-surface segregation [20]. The surface science studies during the MBE growth of GaAs\(_{0.8}\)Sb\(_{0.2}\) layers indicated the presence of a steady state Sb-coverage of \( \sim 0.8 \text{ ML} \), after a deposition of 10 ML of GaAs\(_{0.8}\)Sb\(_{0.2}\) at 450 °C [20]. The GaAs\(_{1-y}\)Sb\(_{y}\) surface during MOVPE growth is reported to have an Sb-rich \( (1 \times 3) \) reconstruction [49]. The lower equilibrium Sb-incorporation rate for the strained GaAs\(_{1-y}\)Sb\(_y\) films leads to even higher Sb-surface coverage, compared to the relaxed films. The excess Sb on the surface could prohibit the further adsorption of Sb-precursors via a site blocking mechanism or other chemical kinetic effects. The lattice of strained GaAs\(_{1-y}\)Sb\(_y\) films is confined to the smaller GaAs lattice constant and possesses a smaller area for absorption per lattice site when compared to the relaxed films at its bulk lattice constant. Therefore, the Sb-surface segregation and site blocking effects can play an important role for the growth of strained GaAs\(_{1-y}\)Sb\(_y\) layers.

The comparatively lower Sb-incorporation efficiencies observed for the growth of strained GaAs\(_{1-y}\)Sb\(_y\) layers can be only partially attributed to thermodynamic considerations. The differences in the strained-layer Sb-incorporation rates between the ethyl- and methyl-Ga chemistries and the temperature dependence of Sb incorporation cannot be explained by the purely thermodynamic considerations and warrant a discussion based on surface kinetics coupled with Sb-segregation and desorption effects.

In the present study, the Sb-mole fractions in the relaxed GaAs\(_{1-y}\)Sb\(_y\) films decreased monotonically overall with an increasing AsH\(_3\)/Ga-precursor ratio for both TMGa and TEGa chemistries. The increasing AsH\(_3\)/Ga-precursor ratio at a constant Sb/Ga-precursor ratio employed in this study corresponds to an increasing V/III- and decreasing Sb/V-ratio used in the earlier reports. Hence, the dependence of the Sb-mole fraction in the relaxed GaAs\(_{1-y}\)Sb\(_y\) films on the gas-phase AsH\(_3\)/Ga ratio, particularly at ratio value > 1, in the present study can be generally rationalized by the thermodynamic growth model [43]. The small differences in the relaxed-layer Sb-mole fractions for various precursor-chemistries observed in Figs. 2 and 4 are attributed to the kinetic effects specific to surface decomposition and adsorption reactions for different precursors. It can be noted that the relaxed films are quite rough altering the number and nature of the surface sites from the purely planar, strained surfaces.
4.2. Kinetic effects in GaAs$_{1-x}$Sb$_x$ MOVPE

4.2.1. Methyl and ethyl-based source: chemical kinetic studies

In situ reflectance difference spectroscopy (RDS) studies have been utilized to determine the TMGa decomposition pathways and the surface reconstructions during the GaAs MOVPE [50,51]. The RDS generated phase diagram of GaAs surface during MOVPE indicates the presence of a kinetically limited growth regime under As-deficient surface conditions arising at lower growth temperatures (<550 °C) and low V/III ratios (<10) [51]. This kinetic regime in the RDS-phase diagram for GaAs MOVPE was attributed to the (1 × 2)-CH$_2$ reconstruction, in which the Ga-atom with an attached methyl group is bonded to two surface As-atoms and one As-adatom [50]. TMGa dissociatively adsorbs at As or Sb surface sites on the GaAs surface, via the loss of two methyl groups, giving rise to monomethyl gallium (MMGa) as the dominant surface Ga-species [52]. The TMGa decomposition in the gas-phase has been reported to be only 50% complete at 450 °C and also yields MMGa-species on the surface [26]. The dissociation of the surface MMGa-species to elemental Ga is achieved by the removal of the methyl groups in the form of CH$_2$, C$_2$H$_6$, or through homolysis. The desorption temperature for these surface methyl groups was found to be 427 °C, using temperature programmed static secondary ion mass spectroscopy (TP-SSIMS) [52]. The surface decomposition of TMSb during MOVPE is also reported to follow a similar mechanism with monomethyl antimony (MMsB) as the dominant surface species [53].

In contrast to the TMGa-case, TEGa is reported to be 50% decomposed in the gas phase at 300 °C due to the efficient removal of at least two ethyl-groups via a β-hydride elimination reaction [26]. The gas-phase decomposition reactions of TEGa result into a combination of surface Ga-species such as elemental gallium, GaC$_2$H$_5$, GaH$_3$, and GaH$_5$. The surface science studies on TEGa adsorption on the GaAs and GaSb surfaces using the TP-SSIMS have shown the presence of surface ethyl–gallium species at low temperatures [28–30]. The deuterium-labeling of TEGa during the desorption studies indicated that the surface ethyl groups are removed exclusively via the β-hydride elimination mechanism giving rise to ethylene (C$_2$H$_4$) as the main desorption product [29]. The desorption of the surface ethyl-species was found to be complete at 327 °C, which is 100 °C lower than the temperature for the complete removal of surface methyl groups for the TMGa-case. The TP-SSIMS adsorption studies of TESb also indicated a surface decomposition mechanism similar to that for TEGa [27,30].

These previous chemical kinetic studies imply that the surface of the growing GaAs$_{1-x}$Sb$_x$ film would be expected to be quite different depending on the growth sources. The use of methyl-based sources should lead to the partial coverage of the surface with methyl radicals, attached to either Ga or Sb, and the ethyl sources should have a higher elemental coverage. In addition, the more rapid TEGa decomposition would lead to a higher Ga surface concentration under similar gas-phase growth conditions and temperatures for the TEGa case. These previous observations must be coupled to the known thermodynamics of the growth system. The growth of films with alloy composition within the miscibility gap will lead to the segregation of Sb onto the surface with the surface concentration of Sb being dependent on the source kinetics, reaction pathways and the growth temperature.

4.2.2. Effect of gas-phase stoichiometry

The large range or matrix of possible growth conditions requires a choice of experimental variables to pursue. The gas-phase stoichiometry was altered in a systematic manner by either a constant Sb/Ga ratio and varying the As/III ratio or a constant As/III ratio and varying the Sb/III ratio, at a fixed Ga source flux into the reactor. This results in a changing total V/III ratio. While not a complete matrix of possible growth conditions, this cross-section of growth gas-phase stoichiometric conditions does provide insight into the growth behavior.

In general from this study, the higher Sb-incorporation rate for the TEGa chemistries compared to that for the TMGa-case can be attributed to the higher decomposition efficiency of TEGa. The efficient gas-phase decomposition of TEGa yields elemental Ga-species on the growth surface independent of the particular surface stoichiometry and adatom coverages. The gas-phase group V sources will then interact with these differing surfaces depending on the use of TMGa or TEGa.

4.2.2.1. TMGa chemistries. The Ga-rich growth conditions should lead to an increased Sb-incorporation rate. At a minimum, the thermodynamic description of GaAs$_{1-x}$Sb$_x$, growth would lead to a higher Sb composition as the Ga surface concentration is increased [43]. In contrast to TEGa, the complete conversion of TMGa to elemental Ga requires the dissociative adsorption reaction of TMGa on the growth surface. The surface composition would therefore have a more pronounced influence during growth utilizing TMGa. The higher decomposition temperature of TMGa and the dissociative adsorption pathway leads to a surface condition quite different from the TEGa case. It is expected that the TMGa-derived surface, at typical growth temperatures, has a higher concentration of adsorbed methyl radicals and lower Ga surface coverage relative to TEGa. The near-constancy of the strained-layer Sb-mole fraction with the variation in the Sb/TMGa-precursor ratio (Fig. 3) for TMGa chemistries would indicate the saturation of the growth surface with Sb-species altering further Sb source decomposition rates.

The chemical picture developed from this present study is that of a Sb-segregated surface, as expected from the
thermodynamic description, which has a high density of adsorbed species, specifically methyl groups. These surface methyl groups would inhibit the adsorption of TMGa and TMSb as well as their derivatives. As surface sites are opened through the removal of these methyl groups, MMGa would preferentially adsorb onto the Sb-terminated surface over MMSb. This newly adsorbed MMGa would then go on to react with the excess Sb reproducing the Sb-terminated surface. The trends in Fig. 3 support this suggestion given the relative independence in the Sb composition with Sb/TMGa ratio. The small difference in Sb incorporation with Sb/TMGa ratio between the TMSb and TESb is not understood at present but both sources follow similar overall trends in Sb composition with gas-phase stoichiometry.

The trends in Sb incorporation with AsH3/Ga ratio in general agree with previous observations. AsH3/Ga ratios greater than unity lead to sharp reductions in the Sb incorporation both in relaxed and strained layers. This behavior can be rationalized on both thermodynamic and kinetic grounds. The higher equilibrium constant for the GaAs formation over that of GaSb strongly favors As incorporation and Sb rejection. The kinetic description presented above would also indicate that AsH3 adsorption, reaction and incorporation on available Ga surface sites would be favored over Sb.

4.2.2.2. TEGa chemistries. The high surface coverages of Sb and methyl groups could hinder further adsorption of Sb-precurors, limiting the Sb-incorporation efficiency. Such Sb-surface saturation effects appear minimal for the TEGa chemistries given the higher achieved Sb contents. Limited data were obtained for the incorporation of Sb with Sb/III ratio for the ethyl sources. At 530 °C, for relaxed layers grown using an As/III ratio = 4, the Sb incorporation increased from 0.13 to 0.21 (0.175–0.29) with an increase in TMSb/TEGa (TESb/TEGa) from 2 to 4. This increase is in sharp contrast to the results found in Fig. 3 for the TMGa-based chemistries. The surface ethyl groups are also known to desorb at a lower temperature compared to the surface methyl groups, further reducing any possible site-blocking effects for the TEGa-case. The Ga-rich (or group-V deficient) surface stoichiometries for the TEGa case thus lead to the higher Sb-incorporation efficiencies in both strained and relaxed films, compared to those for the TMGa case by providing more available Ga reaction sites.

The Sb-mole fraction dependence on AsH3/TEGa ratio for the TEGa–TESb case exhibited a peculiar stepwise trend. Such a trend may be attributed to the change in surface stoichiometry of GaAs1-ySby layer with the varying AsH3/TEGa ratio and warrants further investigation. The AsH3 surface decomposition reactions may be slower when an AsH3/TEGa ratio lower than the TESb/TEGa ratio (< 4) is used, leading perhaps to the observed step-wise behavior. The exact origin of the step-change in the Sb-mole fraction remains undetermined at this point.

4.2.3. Effect of growth temperature

4.2.3.1. TMGa chemistries. The temperature dependence of the Sb incorporation using TMGa is complicated by the decomposition kinetics of both the TMGa and the Sb source. The observed increase in the Sb-mole fraction for the strained GaAs1-ySby films with the increasing growth temperature for both the TMGa chemistries can be attributed in part to the enhancement in the growth rate with the temperature and changes in the Sb-surface coverages. The higher growth rate could more effectively trap surface Sb prior to any possible Sb desorption as well as potentially providing more active Ga sites. The combined increase in growth rate and the enhanced thermal desorption of methyl groups can provide an increased availability of Ga-sites which, in the simplest picture would lead to enhanced incorporation of Sb. This growth rate enhancement was substantiated experimentally by increasing the growth rate at 530 °C and noting the increase in Sb incorporation from y = 0.16 to 0.19 under constant As/III and Sb/III ratios using TMGa–TESb chemistry. Hence, the combined effect of an increasing growth rate and faster surface kinetic effects, such as methyl radical desorption, at higher temperatures result in the enhanced Sb-incorporation efficiencies for the TMGa chemistries.

4.2.3.2. TEGa chemistries. For the TEGa chemistries, an opposite trend was observed for the temperature dependence of strained-layer Sb-mole fraction compared to that of TMGa chemistries. The Sb-mole fraction decreased with an increasing growth temperature for both the TEGa chemistries. The GaAs1-ySby growth rate remained constant, however, with the changes in the growth temperature for both the TEGa chemistries. The constancy of the growth rate for the TEGa case eliminates the growth-rate related effects described for the TMGa chemistries. For the TEGa–TMSb chemistry, the Sb-mole fraction remained constant for the lower growth temperatures between 485 and 515 °C and decreased with an increasing growth temperature over the range of 515–545 °C. The observance of two distinct temperature regimes for the TEGa–TMSb chemistry indicated a presence of two differing temperature dependent processes determining the Sb-incorporation efficiency. The lower growth temperatures lead to a reduction in Sb desorption but also reduce the TMSb decomposition efficiencies. The decrease in the Sb-mole fraction with increasing growth temperature can be due to the higher rate of Sb desorption reaction at elevated temperatures. The combined effect of the two opposing processes could result into the observed temperature dependence of the GaAs1-ySby composition for the TEGa–TMSb chemistry, a monotonic decrease in the Sb-mole fraction was observed with increasing growth temperature between 485 and 545 °C. The higher decomposition efficiency of TESb even at lower growth temperatures leads to a constant Sb-flux over the entire temperature range. The decrease in the Sb-mole fraction
with increasing temperature can be more easily attributed to an increasing higher rate of Sb desorption. The activation energy of 15 kcal/mol obtained from the Arrhenius plot for the TEGa–TESb chemistry most likely corresponds to the Sb desorption activation energy.

5. Conclusions

This study extended the understanding of the GaAs$_{1-y}$Sb$_y$ epitaxial growth using MOVPE. The Sb-incorporation efficiencies for the strained GaAs$_{1-y}$Sb$_y$ layers were found to be lower compared to those for the relaxed films, for all the ethyl- and methyl-precursor combinations. The Sb-incorporation rates were described in terms of the thermodynamic and chemical kinetic influences present during growth. The strain-induced ‘lattice-latching’ effects coupled with Sb-segregation effects resulting into a lower Sb-mole fraction in the strained GaAs$_{1-y}$Sb$_y$ epitaxial growth using MOVPE. The Sb-incorporation efficiencies for the strained GaAs$_{1-y}$Sb$_y$ layers were found to be lower compared to those for the relaxed films, for all the ethyl- and methyl-precursor combinations. The strain-induced ‘lattice-latching’ effects coupled with Sb-segregation effects resulted into a lower Sb-mole fraction in the strained GaAs$_{1-y}$Sb$_y$ films. The Sb-mole fraction in the strained GaAs$_{1-y}$Sb$_y$ films was strongly affected by the choice of Ga-precursor. Higher Sb-incorporation efficiencies were observed when TEGa was used as the Ga-precursor.

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Reference