Analysis of Compositional Fraction in Polycrystalline $\text{In}_x\text{Ga}_{1-x}\text{As}$ Using Raman Scattering


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In$_x$Ga$_{1-x}$As substrate material provides a tunable lattice matching between the substrate and the epilayer for InGaAs-based optoelectronic devices. However, it is very difficult to grow InGaAs substrate crystal with a spatial homogeneity in compositional fraction. One of the most important parameters to control the homogeneity of compositional fraction is to choose a proper starting material in the growth process. It has been observed that if the starting material is polycrystalline InGaAs with a certain spatial distribution in compositional fraction, then there is a possibility that we can grow homogeneous InGaAs substrate crystal. It is important to analyze these starting materials, especially, the compositional fraction with a non-destructive method. Here, we present some results of micro-Raman scattering studies on the compositional fraction in these polycrystalline starting materials. Compositional fractions evaluated by Raman scattering studies in various InGaAs polycrystals show good agreements with those examined by conventional chemical analysis. Micro-Raman scattering presented here is confirmed to be one of the best non-destructive methods to analyze the compositional fraction and its spatial distribution in InGaAs bulk crystals.

1. Introduction

In$_x$Ga$_{1-x}$As bulk crystals are attractive and promising lattice-matched substrate materials for various InGaAs-based laser diodes and optoelectronic devices. By changing the compositional fraction, $x$, in In$_x$Ga$_{1-x}$As substrates, lattice parameter can be changed. Therefore, by choosing a suitable value of the compositional fraction, InGaAs substrates can provide superior lattice-matching between an epilayer and a substrate, compared to the conventional InP substrates. However, it is very difficult to grow InGaAs single crystals with homogeneous distribution in compositional fraction, especially for higher values of $x$, because InGaAs has a large gap between the liquidus and the solidus lines in pseudo-binary system. Under micro-gravity conditions, it is expected that the growth of single crystal with homogeneous composition would be easier, as the convective flow is suppressed in such conditions. However, the growth qualities are still limited by melt convection due to residual acceleration. This drawback can be overcome by using polycrystalline In$_x$Ga$_{1-x}$As starting material, which has a certain gradient of compositional fraction in its spatial distribution.

In our attempt to grow homogeneous InGaAs single crystals, we are going to use In$_x$Ga$_{1-x}$As polycrystals with certain gradient in compositional fraction as the starting material. In the sequence of performing various characterization experiments on these polycrystalline In$_x$Ga$_{1-x}$As starting materials, we present some results of micro-Raman scattering studies, which are performed on these samples to analyze the compositional fraction. Raman scattering provides a non-destructive technique to estimate compositional fraction in a ternary compound semiconductor material with much better results and high accuracy, compared to the other conventional methods such as EPMA and XDS. Chemical analysis, on the other hand, can also provide good results, but due to destructive method, it is not useful for routine characterization. Especially, if the sample is large, micro-Raman
scattering is the best method to investigate the entire sample at a spatial resolution of a few microns. We have estimated the compositional fraction in various In$_x$Ga$_{1-x}$As polycrystalline samples using Raman scattering. Independently, the compositional fraction was also determined in these samples using conventional chemical analysis. Our Raman results show good agreement with the results obtained from the chemical analysis. Micro-Raman analysis is confirmed to be one of the best non-destructive techniques to have an accurate estimation of compositional fraction and its spatial variation in ternary compound materials.

2. Experiment

The samples investigated in the present work are In$_x$Ga$_{1-x}$As polycrystals with various values of the compositional fraction, $x$, ranging over the whole range of zero to one. The crystal growth was carried out using a vertical heating furnace. A large temperature gradient of 40~60 °C/cm, which was necessary to prevent constitutional supercooling, was achieved using a cooling plate. Compositional profiles were preliminarily investigated using fluorescence X-ray and EPMA techniques.

Room temperature Raman scattering experiments were performed in the backscattering geometry by employing the 514.5 nm line of an argon-ion laser. Local heating of the sample was avoided by using low laser power on the sample. The incident laser was focused and the scattered signal was collected by a 50X objective, where the incident laser was focused to a spot of about 2 µm on the sample surface. In order to reduce the background signal and to increase the accuracy of measurements, the near-laser signal was chopped-off by a suitable notch-filter and the slit width was reduced to about 20 µm. The scattered light was dispersed by a Ranishaw spectrometer and the spectra were recorded using a CCD detector.

In order to obtain the true line shapes in the experimental results, the raw data were fitted with suitable number of Lorentzian functions and a proper background. The peak positions, widths, etc. were obtained from the fitting.

3. Results and discussions

The first-order Raman spectrum from a semiconductor typically contains LO and TO phonons. However, depending upon the experimental geometry, one of them may be optically forbidden. The ternary In$_x$Ga$_{1-x}$As alloy exhibits a two-mode behavior in the first-order Raman scattering, which contains LO and TO phonons corresponding to both InAs and GaAs as parent materials. The positions of all four optical phonons depend on the compositional fraction. Therefore, it is possible to determine the compositional fraction from the frequencies of these phonons. Using Raman scattering, In$_x$Ga$_{1-x}$As epilayers were investigated in the past. In these Raman investigations, the existence of a two-mode behaviour was observed and the compositional fraction was determined from the shifts in optical phonons. However, the residual stress in such epilayers has been unavoidable, which gives an additional shift to the phonon positions in Raman spectra. The estimation of compositional fraction from the phonon shifts can therefore be misleading, unless proper correction has been made for the shifts due to residual stress. On the other hand, in the case of polycrystalline samples, the residual stress is randomly distributed over the samples, and hence it is averaged out to zero at any particular point in the sample. The phonon-shifts in Raman spectra for such samples come only from the change in compositional fraction, and hence Raman investigation gives much accurate results.

Moreover, most of the previous workers have neglected the use of line-shape analysis on Raman spectra containing convoluted bands. Line shape analysis is imperative in deconvolving complicated spectral responses and obtaining precise and accurate phonon frequencies.

Figure 1 shows Raman spectra obtained from some of the In$_x$Ga$_{1-x}$As polycrystalline samples listed in Table 1. Samples S1 and S8 are binary GaAs and InAs, respectively. Raman spectrum from sample S1 shows two structures, namely LO and TO phonons at 293.5 and 269.1 cm$^{-1}$, respectively. Similarly, the LO and the TO phonons for S8 appear at 241 and 221.8 cm$^{-1}$, respectively. Due to the polycrystalline nature, the intensity ratio of LO and TO phonons differs in
various samples. For all other ternary samples, Raman spectra show four peaks, which are GaAs-like and InAs-like LO and TO phonons. Since the energy gaps between these phonons are not large, so they are convoluted together in the form of broad structures. In order to estimate the accurate phonon frequencies, all phonon structures were deconvoluted using line-shape fitting. Figure 2 shows an example of line-shape fitting for sample S6. Table 2 displays the frequency positions of the GaAs-like and the InAs-like LO and TO phonons for all samples. With decreasing Ga content, the GaAs-like phonons move towards low frequencies. InAs-like LO phonon moves in the high frequency direction, whereas the InAs-like TO phonon moves in the low frequency direction with decreasing Ga content. The linear composition dependence of the optical phonons can be given by the following equations:

\[
\begin{align*}
\text{LO}_{\text{GaAs}} &= 293 - 52.4 \cdot x \\
\text{TO}_{\text{GaAs}} &= 269 - 28.4 \cdot x \\
\text{LO}_{\text{InAs}} &= 232 + 9 \cdot x \\
\text{TO}_{\text{InAs}} &= 232 - 10 \cdot x
\end{align*}
\]

**Table 1** Ga and In contents obtained from the chemical analysis (CA) for various In\(_x\)Ga\(_{1-x}\)As polycrystalline samples. The compositional fraction, \(x\), was obtained from CA by using the equation \(x = \frac{\text{In}}{\text{In} + \text{Ga}}\). Compositional fractions obtained from Raman studies are also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ga(%)</th>
<th>In(%)</th>
<th>(x)(CA)</th>
<th>(x)(Raman)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>53.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>S2</td>
<td>47.4</td>
<td>7.0</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>S3</td>
<td>46.5</td>
<td>10.9</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td>S4</td>
<td>35.7</td>
<td>17.7</td>
<td>0.33</td>
<td>0.32</td>
</tr>
<tr>
<td>S5</td>
<td>25.7</td>
<td>27.3</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>S6</td>
<td>17.7</td>
<td>33.3</td>
<td>0.65</td>
<td>0.64</td>
</tr>
<tr>
<td>S7</td>
<td>12.4</td>
<td>40.7</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>S8</td>
<td>0.0</td>
<td>52.4</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Fig. 1** Raman spectra obtained from some of the In\(_x\)Ga\(_{1-x}\)As polycrystalline samples.

**Fig. 2** Line-shape fitting to Raman spectrum obtained from sample S6. The solid line shows experimental spectrum and the broken lines present various Lorentzian components.
Table 2  The frequency positions of the GaAs-like and the InAs-like LO and TO phonons for various samples calculated after proper line-shape fitting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LO_{GaAs} (cm^{-1})</th>
<th>TO_{GaAs} (cm^{-1})</th>
<th>LO_{InAs} (cm^{-1})</th>
<th>TO_{InAs} (cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1(GaAs)</td>
<td>293.5</td>
<td>269.1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>S2</td>
<td>287.3</td>
<td>265.5</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>S3</td>
<td>284</td>
<td>265</td>
<td>234</td>
<td>---</td>
</tr>
<tr>
<td>S4</td>
<td>277</td>
<td>261</td>
<td>---</td>
<td>229</td>
</tr>
<tr>
<td>S5</td>
<td>266.4</td>
<td>254</td>
<td>236</td>
<td>228</td>
</tr>
<tr>
<td>S6</td>
<td>261.2</td>
<td>250.5</td>
<td>236</td>
<td>225.5</td>
</tr>
<tr>
<td>S7</td>
<td>253.6</td>
<td>248</td>
<td>237</td>
<td>224.5</td>
</tr>
<tr>
<td>S8(InAs)</td>
<td>---</td>
<td>---</td>
<td>241</td>
<td>221.8</td>
</tr>
</tbody>
</table>

By substituting the experimental values of the phonon frequencies in the above equations, one can estimate the compositional fraction, \(x\). Figure 3 shows the experimental values of the phonon frequencies (full circles) and the theoretical lines. By comparing the experimental values with theoretical lines, the compositional fraction is estimated for each sample, which are listed in Table 1.

In addition, we obtained the value of compositional fraction for all the samples independently using the conventional chemical analysis method. Table 1 and Fig. 4 show a good agreement between the results obtained from Raman scattering technique and the chemical analysis. Our results indicate that Raman scattering technique gives very accurate estimation of the compositional fraction for In_{x}Ga_{1-x}As samples, making it a better characterization method compared to the conventional methods such as EPMA and XDS. Furthermore, since Raman scattering is a non-destructive technique, it can be a much preferred routine characterization method, compared to chemical analysis or other destructive methods.

The spatial resolution in Raman scattering can be as low as a few micron, which makes it possible to investigate the sample at high spatial resolution. Raman scattering technique can therefore be the best method to investigate the spatial homogeneity of compositional fraction in large samples.

Fig. 3  Variation of frequency positions for various optical phonons with respect to compositional fraction. The full circles present experimental data points and the solid lines represent theoretical estimations.

Fig. 4  A comparison of the compositional fraction obtained from the chemical analysis and Raman scattering experiments for various samples. A close linear dependence shows good agreement between the results of two experimental techniques.

4. Conclusions
We have estimated the compositional fraction in various In_{x}Ga_{1-x}As polycrystalline samples by measuring shifts in optical phonons in Raman
spectra. Independently, the molar fraction was also determined in these samples using conventional chemical analysis. Raman scattering results show good agreement with the results obtained from the chemical analysis. Micro-Raman analysis presented here is one of the best non-destructive techniques to have an accurate estimation of molar fraction and its spatial variation in ternary compound materials.

References