

## Micro-Raman Characterization of Starting Material for Traveling Liquidus Zone Growth Method

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Bulk  $\text{In}_x\text{Ga}_{1-x}\text{As}$  is an excellent lattice-matched substrate material for InGaAs-based laser diodes. However, it is very difficult to grow compositionally homogeneous  $\text{In}_x\text{Ga}_{1-x}\text{As}$  single crystal. The growth of single crystal with homogeneous composition using the newly developed traveling liquidus zone (TLZ) growth method is expected. In the TLZ method, cylindrically shaped polycrystalline starting material with a graded compositional profile is the basic requirement. This paper presents some results of micro-Raman scattering studies of the compositional fraction in these starting materials. The compositions evaluated by Raman scattering in various  $\text{In}_x\text{Ga}_{1-x}\text{As}$  wafer-type samples show good agreement with those examined by the standard method of chemical analysis. Compositional profiles obtained from as-ground and polished surfaces have been compared to understand the necessity of surface polishing in our experiments. The results presented here demonstrate that micro-Raman scattering is one of the best non-destructive methods for analyzing the entire compositional range of InGaAs compound materials. [DOI: 10.1143/JJAP.41.991]

KEYWORDS: InGaAs, single crystal, polycrystal, micro-Raman, TLZ method

### 1. Introduction

Ternary compound  $\text{In}_x\text{Ga}_{1-x}\text{As}$  bulk crystal is an attractive and promising lattice-matched substrate for fabricating InGaAs-based optoelectronic devices. It can provide superior lattice matching between the substrate and the epilayer, compared to the InP substrate commonly used, because the lattice parameter of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  can be changed<sup>1)</sup> by changing the composition  $x$ . In order to design a wide variety of devices on  $\text{In}_x\text{Ga}_{1-x}\text{As}$  substrate, spatial homogeneity in its composition is an important requirement. However, the growth of single crystals with homogeneous composition is very difficult,<sup>2–4)</sup> because convection in a melt combined with segregation at the time of solidification causes compositional variation in the grown crystal, particularly at high values of  $x$ , where the separation between the solidus and liquidus lines is large in the phase diagram of pseudo-binary system InGaAs. With increasing the InAs component, the variation in the composition of the solidifying material becomes more sensitive to temperature fluctuation, leading to large compositional inhomogeneity in the resultant material. Under micro-gravity conditions,<sup>5)</sup> it is expected that the growth of single crystal with homogeneous composition will be easier as the convective flow will be suppressed in such conditions. Our initial studies indicate<sup>6)</sup> that the effect of weak melt convection due to residual acceleration can be overcome by using a InGaAs polycrystalline starting material with a certain graded compositional profile.

Various crystal growth methods, such as the double crucible method<sup>7)</sup> and the zone melting method,<sup>8)</sup> have been applied to grow  $\text{In}_x\text{Ga}_{1-x}\text{As}$  single crystal with homogeneous composition, but these methods resulted in the insufficient control of homogeneity. The stable transportation of solute is fundamental to homogeneous crystal growth. On the basis of this, one of the present authors has developed a new crystal growth method, named the traveling liquidus zone (TLZ) method,<sup>9)</sup> which is a modified form of the vertical Bridgman method. This method has shown some success in growing

small diameter single crystals with homogeneous composition in experiments performed on the ground. The growth of large diameter single crystals under micro-gravity conditions using this method is planned. In the TLZ method, it is the basic requirement that the starting material be cylindrically shaped polycrystalline  $\text{In}_x\text{Ga}_{1-x}\text{As}$  with a certain gradient in its compositional profile.

There are several factors that govern the growth of homogeneous single crystal. Selection of a proper starting material is one of the most important factors, particularly for a system such as  $\text{In}_x\text{Ga}_{1-x}\text{As}$ , where the growth of single crystal with a high  $x$  value has presented a significant challenge. In our attempt to grow homogeneous  $\text{In}_x\text{Ga}_{1-x}\text{As}$  single crystal, we used cylindrically shaped  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystal with a certain gradient in the compositional profile as the starting material in the TLZ method. First,  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystalline materials with graded compositional profiles were grown. Some samples were prepared in the form of wafers with various compositions, and some were ground to the required cylindrical shape. It is important first to characterize the composition of these materials using a non-destructive method. In this paper, we present some results of micro-Raman studies carried out in order to analyze the compositional profile of these starting materials as well as to clarify the effect of surface polishing on the results obtained by the Raman scattering technique. Raman shift in optical phonons induced by the change in composition provides a convenient non-destructive method for estimating the composition with good results and high accuracy, compared to other conventional methods such as electron probe micro-analyzer (EPMA) and energy dispersive X-ray (EDX). Chemical analysis (CA), on the other hand, can provide good results, but being a destructive method, it is not useful for routine characterization. Particularly, if the sample is large, micro-Raman scattering is the best method for investigating the entire sample at about 1  $\mu\text{m}$  spatial resolution. We have estimated compositions in wafer-type  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystalline samples using Raman scattering. Independently, the compositional fractions were also determined in these samples using the standard method of CA. The accuracy of

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Raman results was confirmed through comparison with that obtained from CA. For the cylindrical sample, the results obtained from the as-ground surface are compared with those obtained from the polished surface. The estimated compositional profiles before and after polishing the surface of the sample are close to each other. We further confirmed that by means of Raman scattering it is possible to characterize the entire compositional range of the actual starting material, which is required in the TLZ method to grow  $\text{In}_x\text{Ga}_{1-x}\text{As}$  single crystal.

## 2. Experiment

The samples investigated in the present work are square-shaped  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystal wafers with various compositions ranging from  $x = 0$  to  $x = 1$ , and two cylindrical polycrystal samples with graded compositional profiles. The first cylindrical sample has a low InAs content whereas the second cylindrical sample contains low to high values of InAs content. These samples were prepared in a vertical heating furnace. The details are provided elsewhere.<sup>10)</sup> The cylindrical shapes were obtained by grinding the as-grown samples to the required diameters. One portion of the surface was polished along the length of the sample after grinding the first sample to a cylindrical shape. Raman spectra were measured from the as-ground surface as well as from the polished surface along the length of the sample. Hence, the effect of surface polishing on the estimation of the composition was also studied for each of the cylindrical samples.

Raman scattering measurement was performed at room temperature with backscattering geometry by employing the 514.5 nm line of an argon-ion laser. Low laser power was used to prevent local heating of the sample. The incident laser was focused by a 50X objective lens to a spot of about  $2\ \mu\text{m}$  diameter on the sample surface. The scattered light was collected via the same objective lens. The slit width was reduced to about  $200\ \mu\text{m}$  in order to reduce the background noise and a suitable notch-filter was used in order to increase the accuracy of the measurement. 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 a suitable number of Lorentzian functions and a proper background. The peak positions and widths were obtained from the fitting.

## 3. Results and Discussions

The first order Raman spectrum from a semiconductor typically contains LO and TO phonons.<sup>11)</sup> However, depending upon the crystal orientation and experimental geometry, one of them may be optically forbidden. The ternary compound semiconductor  $\text{In}_x\text{Ga}_{1-x}\text{As}$  shows two-mode behavior<sup>11–13)</sup> in the first-order Raman scattering, in which LO and TO phonons corresponding to both InAs and GaAs binary parent materials are found. The frequency positions of all of these four optical phonons depend on the compositional fraction,  $x$ .<sup>12–14)</sup> Therefore, it is possible to estimate the compositional fraction from the frequencies of these phonons.  $\text{In}_x\text{Ga}_{1-x}\text{As}$  epilayers have been investigated in the past using Raman scattering.<sup>12,13)</sup> In these Raman investigations, the

existence of two-mode behavior was observed and the compositional fraction was determined from the shifts in optical phonons. However, the residual strain in such epilayers due to the lattice mismatch between the epilayer and the substrate was found to be unavoidable, which gives an additional shift to the phonon positions in Raman spectra. Estimation of the composition can therefore be misleading, unless proper correction has been made for the shifts due to residual strain. On the other hand, in the case of polycrystalline samples, the residual strain, even if present, is randomly distributed over the samples and is relaxed at the grain boundaries. Therefore, the strain in polycrystal averages out to zero at any particular point in the sample. The shifts of phonon frequencies in Raman spectra for such samples originate only from the change in the compositional fraction, and hence Raman scattering gives more accurate results. Most of the previous researchers<sup>13–15)</sup> have also neglected the lineshape analysis on Raman spectra containing convoluted bands. Lineshape analysis is very important for deconvoluting complicated spectral responses and obtaining precise and accurate phonon frequencies. For better accuracy, we have used proper lineshape analysis to estimate the phonon frequency positions.

The optical phonons in Raman spectra of compound semiconductors show a composition-dependent shift which was first observed in infrared reflection experiments.<sup>16)</sup> Figure 1 shows Raman spectra obtained from some of the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  wafer-type samples listed in Table I. The spectrum from sample S1 shows two structures, namely, LO and TO phonons at 291 and 268  $\text{cm}^{-1}$ , respectively, which correspond to binary GaAs. Similarly, the LO and TO phonons appear at 238 and 220  $\text{cm}^{-1}$ , respectively, which correspond to binary InAs from the spectrum obtained from sample S8. Due to their polycrystalline nature, the crystal face at the measurement point changes from sample to sample and therefore the intensity ratio of LO and TO phonons changes in different samples.

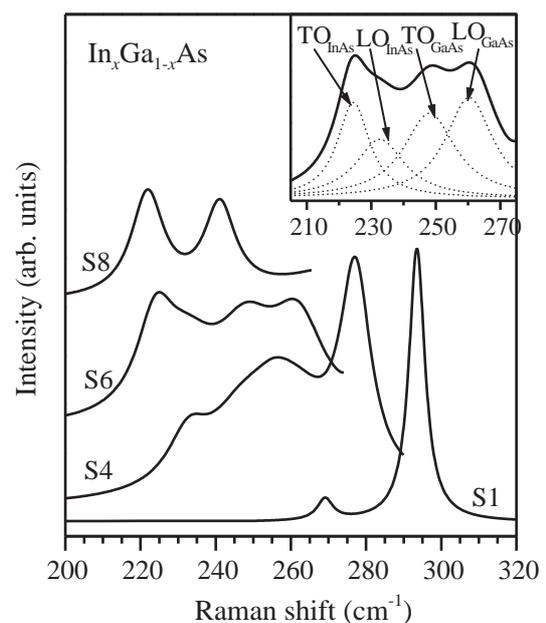


Fig. 1. Raman spectra obtained from some of the wafer-type  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystalline samples. Inset shows lineshape fitting to the spectrum obtained from sample S6, as an example. Solid line shows experimental spectrum and broken lines present various Lorentzian components.

Table I. Peak positions of GaAs-like and InAs-like LO and TO phonon frequencies for various samples evaluated after proper lineshape fitting.

| Sample   | LO <sub>GaAs</sub><br>(cm <sup>-1</sup> ) | TO <sub>GaAs</sub><br>(cm <sup>-1</sup> ) | LO <sub>InAs</sub><br>(cm <sup>-1</sup> ) | TO <sub>InAs</sub><br>(cm <sup>-1</sup> ) |
|----------|---|---|---|---|
| S1(GaAs) | 291.0                                     | 268.0                                     | —   | —   |
| S2       | 284.8                                     | 264.4                                     | —   | —   |
| S3       | 281.5                                     | 263.9                                     | 231                                       | —   |
| S4       | 274.5                                     | 259.9                                     | —   | 227.2                                     |
| S5       | 263.5                                     | 252.9                                     | 233                                       | 226.2                                     |
| S6       | 258.7                                     | 249.4                                     | 233                                       | 223.7                                     |
| S7       | 251.1                                     | 246.9                                     | 234                                       | 222.7                                     |
| S8(InAs) | —   | —   | 238                                       | 220.0                                     |

Table II. Ga and In contents obtained by CA for various In<sub>x</sub>Ga<sub>1-x</sub>As polycrystalline samples. The composition, *x*, was obtained by CA using the equation  $x = \text{In}/(\text{In} + \text{Ga})$ . Compositional fractions obtained from Raman studies are also listed.

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

Raman spectra from other ternary samples show four peaks, which are GaAs-like and InAs-like LO and TO phonons. Since the energy gaps between these phonons are not large, they are convoluted together in the form of broad structures. In order to determine the actual phonon frequencies, these broad structures are deconvoluted using lineshape fittings. An example of such a lineshape fitting for the spectrum obtained from S6 is shown in the inset in Fig. 1. The positions of GaAs-like and InAs-like LO and TO phonons for various samples are listed in Table I. The GaAs-like phonons and the InAs-like TO phonon shift towards low frequencies whereas the InAs-like LO phonon moves in the high frequency direction with increasing In content. The simple compositional dependence of the frequency positions of GaAs-like and InAs-like LO and TO phonons can be represented by the following equation

$$\begin{aligned} \omega(\text{LO}_{\text{GaAs}}) &= 291 - 53x, & \omega(\text{TO}_{\text{GaAs}}) &= 268 - 30x, \\ \omega(\text{LO}_{\text{InAs}}) &= 230 + 8x, & \omega(\text{TO}_{\text{InAs}}) &= 230 - 10x. \end{aligned} \quad (1)$$

Figure 2 shows the experimental values of phonon frequencies along with the theoretical lines calculated using eq. (1). By comparing the experimental values with theoretical lines, the compositional fraction is estimated for each sample listed in Table II. Compositions were also obtained for these samples independently using the conventional method of CA. A comparison of the two results is presented in the inset in Fig. 2, which shows good agreement between the results obtained from the Raman scattering technique and those obtained from CA.

The effects of surface polishing on the Raman spectrum were investigated for the first cylindrical sample. Some rough

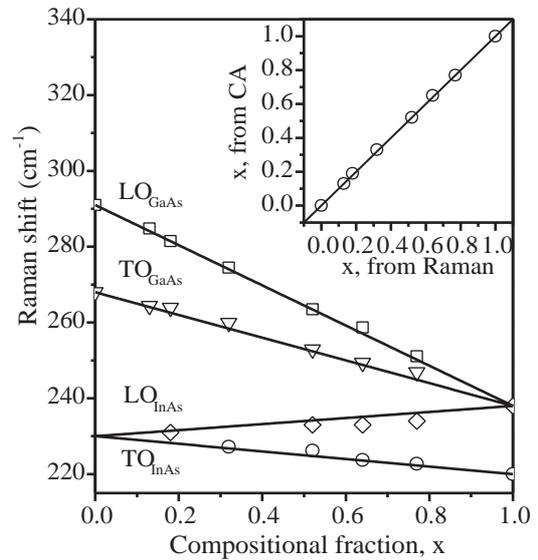


Fig. 2. Variation of frequency positions for various optical phonons with respect to the compositional fraction. Symbols represent experimental data points and solid lines indicate theoretical estimations. Inset shows a comparison of the results obtained from the CA and Raman scattering experiments for various samples. A close linear dependence shows good agreement between the two results.

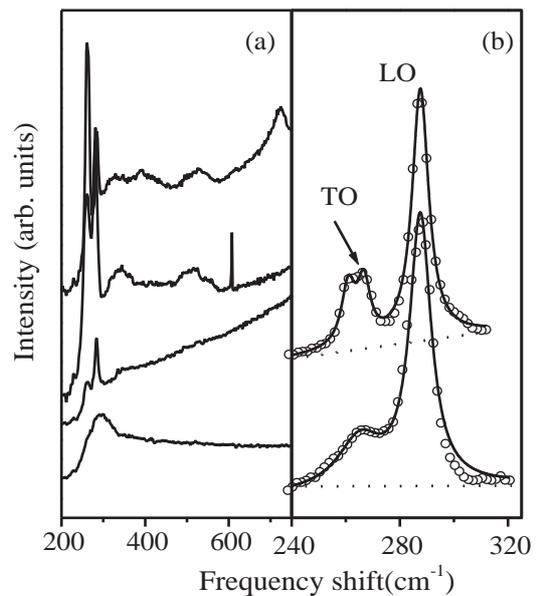


Fig. 3. (a) Some of the “bad” spectra from the as-ground surface of the cylindrically shaped sample and (b) a comparison of a “good” spectrum from the as-ground surface (upper spectrum) with a spectrum from the polished surface (lower spectrum).

spots were found from the as-ground surface of the sample, where crystal faces were changed randomly. Raman spectra from these spots show arbitrary structures. We call these spectra “bad” spectra. Figure 3(a) shows some examples of such “bad” spectra. Therefore, it is important to avoid the points where Raman spectra are “bad” and to select the points where Raman spectra are “good”, while measuring Raman spectra from the as-ground surface. In addition to this, a “good” spectrum from the as-ground surface shows some additional structures. Figure 3(b) compares a “good” Raman spectrum from the as-ground surface with a spectrum from a corre-

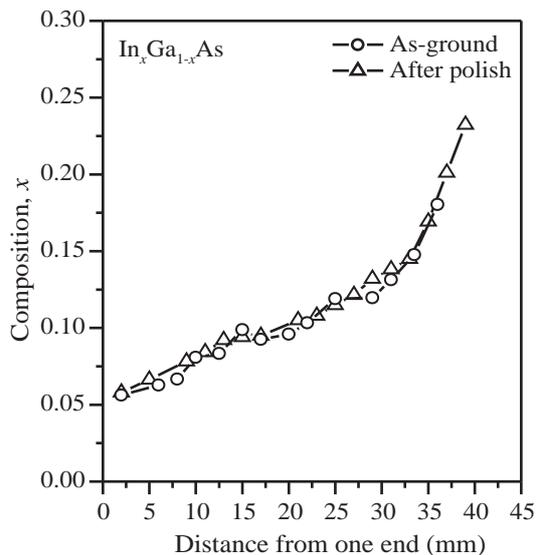


Fig. 4. Estimated compositional profile for the low In content cylindrical sample. The results before and after surface polishing are comparable.

sponding point on the polished surface. For comparison, the spectrum from the as-ground surface is enhanced five times. There are three major differences between the two spectra. The spectrum from the polished surface is about five times more intense. The spectrum from the as-ground surface has an increasing background and it shows some additional structure. However, the frequency position of the GaAs-like LO phonon, which is used to estimate the compositional profile in the present study, remains the same in both spectra. Therefore, in the case of the “good” spectrum, the compositional fraction is independent of the surface condition.

Raman spectra were measured at intervals of about 2 mm from one end to the other end of the sample along its length, and the corresponding composition was calculated from the shift in the GaAs-like LO phonon. The compositional profiles thus estimated from the as-ground and the polished surfaces are shown in Fig. 4. The calculated values of the composition,  $x$ , vary from about 0.05 to about 0.23 from one end to the other end of the sample. The composition increases slowly from one end of the sample and then increases more rapidly towards the other end. As shown in Fig. 4, the estimated compositional fractions from the as-ground and the polished surfaces are close to each other. However, due to the stronger intensities of Raman spectra from the polished surface, the reliability of the results from the polished surface could be better.

For the growth of homogeneous InGaAs single crystal, the required compositional profile of the starting polycrystalline material should have the InAs content varying up to about 0.8. We therefore grew another  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystal, which contains the InAs content ranging up to about 0.8. This sample was cut along its length so that the compositional profiles from the inner and outer parts of the cylinder could be compared. This sample was etched to eliminate the “bad” points and Raman spectra were measured without polishing. Our results show that the compositions estimated from two comparable points at the inner and outer parts of the sample were the same. We measured Raman spectra along the length of this sample and then estimated the compositional profile, as

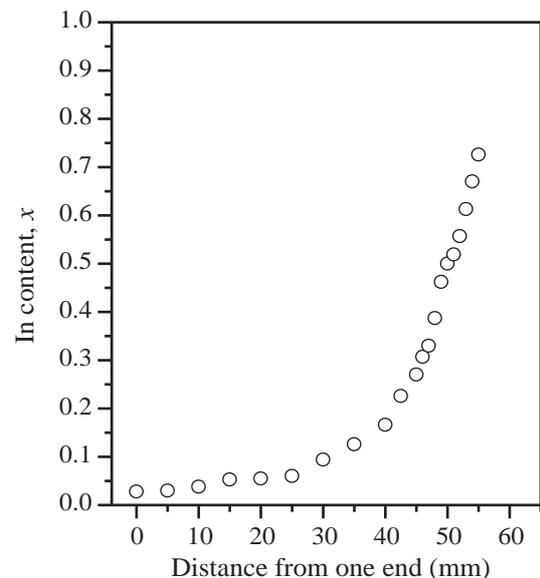


Fig. 5. Estimated compositional profile for the high In content cylindrical polycrystalline sample.

discussed for the first sample. Figure 5 represents the compositional profile estimated for the second cylindrical sample. The composition of this sample changes from about 0.02 to 0.73. This compositional profile is close to that required for the starting material in the TLZ growth method in order to grow homogeneous InGaAs single crystal.

#### 4. Conclusions

We have estimated the compositional fraction for various wafer-type  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystalline samples with various compositions over the entire range of  $x = 0$  to  $x = 1$ , as well as cylindrically shaped  $\text{In}_x\text{Ga}_{1-x}\text{As}$  polycrystalline samples with graded compositional profiles, by measuring the shifts in optical phonons in the Raman spectra. Independently, the compositions were also determined for the wafer-type samples by CA. The accuracy of the Raman results is confirmed by the results obtained from CA. Furthermore, we confirmed that by means of Raman scattering it is possible to characterize the entire range of compositional fraction ( $0 \leq x \leq 1$ ) with high accuracy. In addition, we have studied the effect of surface polishing on the results obtained from Raman analysis, by comparing Raman spectra from the as-ground surface as well as from the polished surface of the sample. Our study shows that the estimated compositional profiles from the as-ground and the polished surfaces are close to each other. However, some points on the unpolished surface randomly show “bad” Raman spectra. The “good” Raman spectra from the as-ground surface are weak and have some additional structures, but the phonon position remains the same as that for the polished surface. We also studied another cylindrical polycrystalline sample, which was cut along its length and etched to eliminate “bad” points. The InAs content of this sample varies from a low to a high value. The estimated compositional profile of this sample is close to that required for the starting material in the TLZ growth method to grow single crystal with homogeneous composition. It is confirmed from our study that micro-Raman scattering is capable of es-

timating the compositional fraction and its spatial variation in ternary compound  $\text{In}_x\text{Ga}_{1-x}\text{As}$  materials with high accuracy, even for the as-ground surface condition of the sample.

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