

Raman characterization of cylindrical polycrystalline $\text{In}_x\text{Ga}_{1-x}\text{As}$ starting material

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Crystal growth of spatially homogeneous $\text{In}_x\text{Ga}_{1-x}\text{As}$ substrates, which has a tunable lattice matching between the substrate and the epilayer for InGaAs-based optoelectronic devices, is very difficult due to the considerable amount of convective flow on ground. This problem can be overcome, if the crystal growth is carried out in micro-gravity conditions and the starting material is chosen with particular specifications. The initial studies have indicated that the starting material is required to be cylindrically shaped polycrystalline InGaAs with a particular gradient in its compositional profile. We have grown this starting material and grinded it to the required shape. In a view to analyze the compositional profile of this cylindrical polycrystalline starting material using a non-destructive method, we report some results of micro-Raman scattering studies. Further, we also discuss the effect of the surface condition on Raman results, by comparing the results obtained from as-grinded and polished surfaces.

1. Introduction

$\text{In}_x\text{Ga}_{1-x}\text{As}$ 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 $\text{In}_x\text{Ga}_{1-x}\text{As}$ substrates, lattice parameter can be changed[1]. 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. A wide variety of devices can be designed on a multi-component InGaAs single crystal, for which an important requirement becomes the homogeneity of the molar fraction across the whole crystal. The InGaAs bulk crystal growth has received great attention in the recent past [2–4], however, growth of homogeneous single crystal with high x value still remains unsuccessful. Growing multi-component crystals with homogeneous molar fraction is very difficult [2–7] from both fluid dynamical and thermodynamical points of view. The liquidus and the solidus lines in the phase diagram of the pseudo-binary system, InGaAs, are far apart. Therefore, the high segregation coefficient and convective flow prevent constant liquid concentration and cause constitutional supercooling. This leads to inhomogeneity in the compositional profile as well as local polycrystallization. With increasing 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 [8], it is expected that the growth of single crystal with homogeneous composition would be easier, as the convective flow and the supercooling are suppressed under such conditions. However, the growth qualities are limited by still existing melt convection and residual acceleration. This drawback can be overcome by using polycrystalline InGaAs starting material with a certain graded composition, which compensates the effect of weak melt convection.

There are several factors that control the growth of homogeneous crystals. Selection of a proper starting material is one of the most important factors, particularly for a system like InGaAs, where the growth with high x value has been a matter of big challenge. Our preliminary studies have indicated that if the starting material is a cylindrically shaped polycrystalline InGaAs with a certain gradient in its compositional profile, then it is possible to overcome the effect of melt convection under micro-gravity conditions and hence achieve homogeneous InGaAs single crystal. Therefore, in our attempt to grow homogeneous InGaAs single crystals, we are going to use cylindrically shaped InGaAs polycrystal, with certain gradient in its compositional profile, as the starting material. To

start with, we have grown $\text{In}_x\text{Ga}_{1-x}\text{As}$ polycrystalline material with a graded compositional profile, and have grinded it to the required cylindrical shape. It is important first to analyze this starting material, particularly, the molar fraction, using a non-destructive method. In this report, we present some results of micro-Raman studies to analyze the compositional profile of this starting material, as well as to understand the effect of surface treatment to the results obtained by Raman scattering technique. Raman shift in optical phonons induced by change in molar fraction provides a convenient non-destructive method to estimate molar fraction 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 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 to investigate the entire sample at a spatial resolution of a few microns, and hence determine the accurate compositional profile. We have already shown [9] that the results obtained by Raman analysis have very good agreement with standard method of chemical analysis.

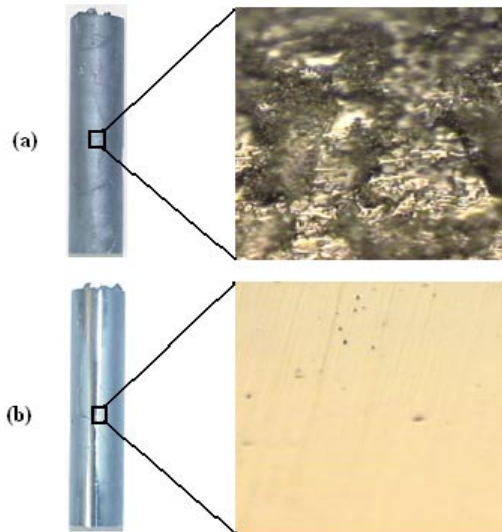


Fig.1 Magnified picture of the sample surface (a) as-grinded, and (b) polished.

2. Experiment

The samples investigated in the present work are $\text{In}_x\text{Ga}_{1-x}\text{As}$ polycrystals with graded compositional profiles. The first sample has low InAs-content whereas the second sample contains low to high value of InAs-content. These samples were grown in a vertical heating furnace. The details are provided elsewhere [10]. The

cylindrical shape was obtained by grinding the as-grown sample to required diameter. One side of the surface of the first sample was polished along the length. Raman spectra were measured from both, the as-grinded surface, as well as from the polished surface. Hence, the effect of surface treatment on estimation of composition was also studied. The second sample was first grinded to the cylindrical shape, and then was cut along its length. Raman spectra were measured along the length from the cut surface without polish after a normal etching process.

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 $2\ \mu\text{m}$ 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 $20\ \mu\text{m}$. 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 lineshape functions. The peak positions, widths, etc. were obtained from the fitting.

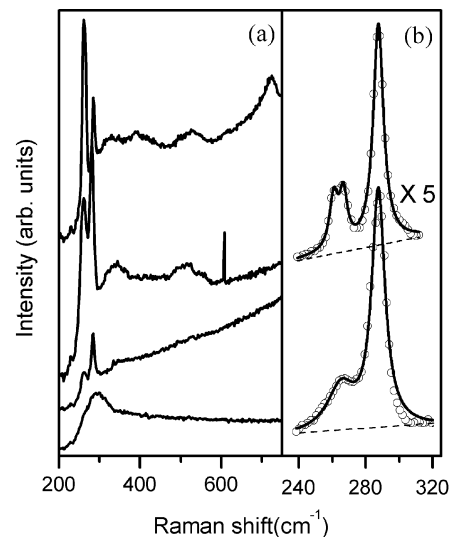


Fig. 2 (a) Some of the “bad” spectra from the as-grinded surface. (b) Comparison of a “good” spectrum from the as-grinded surface (upper spectrum) with a spectrum from the polished surface (lower spectrum).

3. Results And Discussions

The first-order Raman spectrum from a semiconductor typically contains LO and TO phonons [11]. However, depending upon the crystal face and the experimental geometry, one of them may be optically forbidden. The ternary $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloy exhibits a two-mode behavior [12-14] in the first-order Raman scattering, which contains LO and TO phonons corresponding to both InAs and GaAs. The frequency positions of all these four optical phonons depend on the compositional fraction [12-15]. Therefore, it is possible to determine the compositional fraction from the frequencies of these phonons. $\text{In}_x\text{Ga}_{1-x}\text{As}$ epilayers were investigated by Raman scattering in the past [12-14]. In these Raman investigations, the existence of a two-mode behavior 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. Similarly, a single crystal with non-uniform compositional profile normally has internal residual stress, because of the non-uniformity in the lattice constant. On the other hand, in the case of polycrystalline samples, the residual stress is randomly distributed over the samples and is relaxed at the grain boundaries. Therefore, the stress in a polycrystal is averaged out to zero at any particular point in the sample. The shifts in the phonon frequencies in Raman spectra of such samples originate only from the change in compositional fraction, and hence Raman investigation gives much accurate results. Moreover, most of the previous workers [14-15] have neglected the use of line-shape analysis on Raman spectra containing convoluted bands. Line shape analysis is essential in deconvolving complicated spectral responses and obtaining precise and accurate phonon frequencies. In our case, we have used proper lineshape analysis to estimate the phonon frequency positions for better accuracy. A simple compositional dependence of the frequency positions of the GaAs-like and the InAs-like LO and TO phonons can be given by

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

Therefore, from the experimental values of the phonon frequencies, ω , the composition x can be estimated. In our case, the GaAs-like LO phonon remains the most prominent phonon, therefore we will use only the first equation to estimate the composition. However, in principle, all of the above equations should give similar results, as long as the corresponding phonon can be measured with certain degree of accuracy.

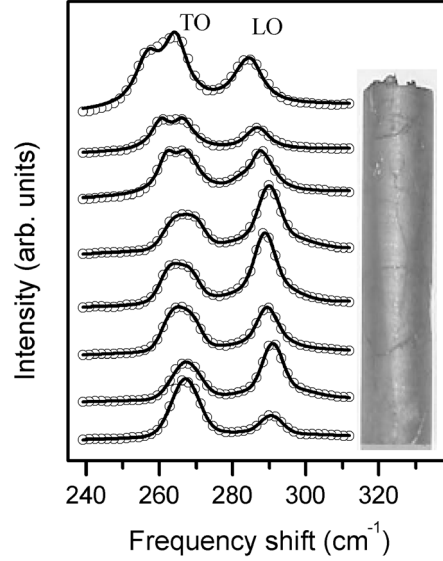


Fig.3 “Good” Raman spectra from some of the points on the as-grinded surface. The position of each spectrum in the figure shows the corresponding measuring point on the sample surface.

First, we would compare the effect of surface treatment on the Raman spectrum by investigating the first sample. Figure 1 shows magnified pictures of the sample surface in as-grinded and polished states. In addition to the rough surfaces with randomly changing crystal face for the as-grinded surface, the figure shows some dark spots, which were oxidized during the grinding process. Raman spectra from these spots show arbitrary structures. We call these spectra as “bad” spectra. Figure 2(a) shows some examples of such “bad” spectra. Therefore, it is important to select a good point, while measuring Raman spectra from the as-grinded surface. In addition to this, a “good” spectrum from the as-grinded surface shows some additional structures. Figure 2(b) compares a “good” Raman spectrum from the as-grinded surface with a spectrum from a corresponding point on the polished surface. For comparison, the spectrum from the as-grinded surface is enhanced by five times. There are three major differences in the two spectra. The spectrum from the polished

surface is about five times more intense, the spectrum from the as-grinded 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, we will show later that if “good” spectra are selected, the estimated value of composition is independent of the surface condition.

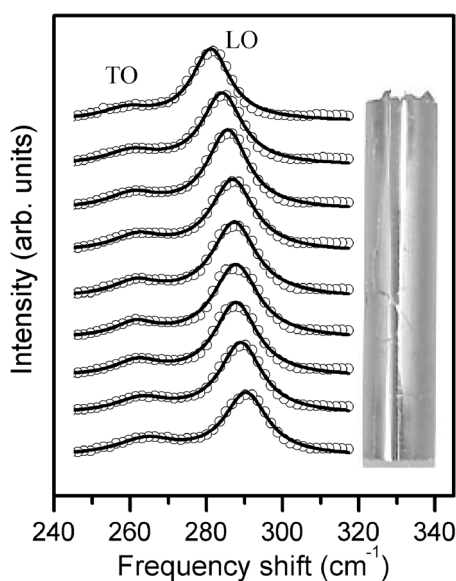


Fig.4 Raman spectra from some of the points on the polished surface. The position of each spectrum in the figure shows the corresponding measuring point on the sample surface.

Figures 3 and 4 show some of the Raman spectra taken along the length of the sample, respectively, from the as-grinded and the polished surfaces. The sample surfaces are also shown in the figures. A typical Raman spectrum from pure GaAs shows LO and TO phonons at 291 and 268 cm^{-1} , respectively, and that from a pure InAs shows the LO and TO phonons at 238 and 220 cm^{-1} , respectively. For the mixed compound, $\text{In}_x\text{Ga}_{1-x}\text{As}$, these phonons shift according to Eqn. (1). Figures 3 and 4 show that the most prominent phonon, GaAs-like LO phonon, shifts from about 288 cm^{-1} to about 278 cm^{-1} . In addition to this, the GaAs-like TO phonon can be observed in most of the spectra. The spectra from the as-grinded surface in Fig. 3 show some additional structures below the TO phonon, which should be ignored. The InAs-like phonons are too weak to be observed, because the InAs content is quite low in this sample. Raman spectra was measured at an

interval of about 2 mm from the 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 profile thus estimated from the as-grinded and the polished surfaces are shown in Fig. 5. The calculated value of the composition, x , varies 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 fast towards the other end. As shown in Fig. 5, the estimated composition from as-grinded and the polished surfaces are close to each other. However, due to the stronger intensity of Raman spectra from the polished surface, the reliability of the results from the polished surface would be better.

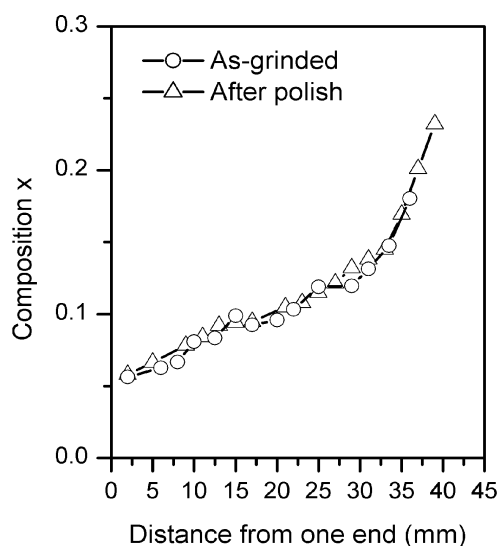


Fig.5 Estimated compositional profile for the first sample. The results before and after surface polishing are comparable.

For the growth of homogeneous InGaAs single crystal, the required compositional profile of the starting polycrystalline material should have the InAs-content varying upto about 0.8. We therefore grew another $\text{In}_x\text{Ga}_{1-x}\text{As}$ polycrystal which contains InAs-content ranging up to about 0.8. This sample was cut along its length so that the compositional profiles from the inner and the outer parts of the cylinder could be compared. This sample was etched to avoid the “bad” points and Raman spectra were measured without polish. Our results show that the compositions estimated from two comparable points at inner and outer of the sample are the same. We measured Raman spectra along the length of this sample and then estimated the compositional profile, as discussed for the first sample. Figure 6 presents the

compositional profile estimated for the second sample. An schematic of the sample is also shown in Fig. 6, which shows the measurement points in the direction indicated by the arrow. The composition of this sample changes from about 0.02 to 0.73. This compositional profile is close to the one required for the growth of homogeneous InGaAs single crystal.

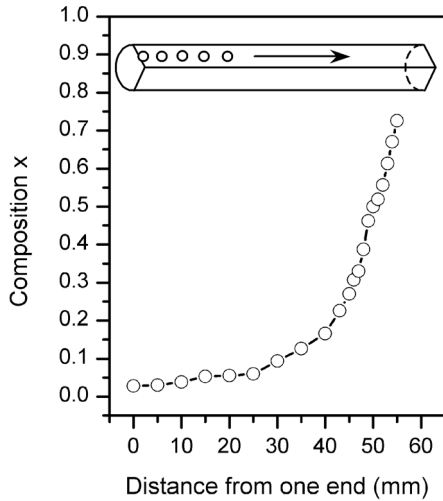


Fig.6 Estimated compositional profile for the second sample. An schematic of the cylindrical sample, which was cut along its length, is also shown. The circles in the schematic indicate the measurement points and the arrow shows the direction of measurement.

4. Conclusions

We have successfully measured Raman spectra from cylindrically shaped polycrystalline $\text{In}_x\text{Ga}_{1-x}\text{As}$ starting materials to analyze the compositional profile. We have further studied the effect of surface treatment on the results obtained from the Raman analysis, by comparing Raman spectra from as-grinded surface and the polished surface of the sample. Our study shows that the compositional profile obtained from the as-grinded surface is in close agreement with the compositional profile obtained from the polished surface. However, some points on the unpolished surface randomly show “bad” Raman spectra. The “good” Raman spectra from as-grinded surface are weak and have some additional structures, but the phonon position is same as that for the polished surface. We also studied another cylindrical polycrystalline sample, which was cut along its length and etched to avoid the “bad” points. The InAs-content of this sample varies from low to high value. The estimated compositional profile of this sample is close to the

one required for the growth of homogeneous InGaAs single crystal.

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