

Study on polycrystallization and residual strain in bulk $\text{In}_x\text{Ga}_{1-x}\text{As}$ crystal

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Micro-Raman scattering and photoluminescence (PL) studies were performed to understand the polycrystallization mechanism in bulk $\text{In}_x\text{Ga}_{1-x}\text{As}$ crystal grown by the two-step multi-component zone melting (MCZM) method. Raman studies were also performed with the aim to understand the influence of residual strain on the shifts in phonon frequencies in Raman spectra. Unlike the usual observation of polycrystallization at the peripheral region of the ingot, a special polycrystallization was observed in the etching results inside the MCZM crystal. The polycrystalline region was found to have a drastic fluctuation of phonon peak positions as well as PL peak wavelength (composition) in the local region, which could be due to supercooling resulting in formation of polycrystal in the investigated crystal.

Further, it is observed that the LO_{GaAs} phonon frequency is varied for various measurement points, which may be related to the compositional variation in the samples. However, it is found from precise micro-Raman measurements both in a corner region and in a chipped region that there exists a large amount of residual strain in the samples. By comparing the observed LO_{GaAs} phonon frequencies with those estimated from the compositions determined by the energy dispersive x-ray analysis, they are found to be shifted by about 9.5 cm^{-1} due to residual strain, which corresponds to a strain value of the order of 10^{-2} .

1. Introduction

Ternary bulk $\text{In}_x\text{Ga}_{1-x}\text{As}$ single crystal is a promising lattice-matched substrate for InGaAs-based laser diodes used in the future generation of optical communication systems. Homogeneous $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$ single crystals are specially required for laser diodes oscillating at $\lambda=1.3 \mu\text{m}$. Several groups tried to grow bulk $\text{In}_x\text{Ga}_{1-x}\text{As}$ single crystals using cooling liquid encapsulated Czochralski (LEC) [1], Bridgman [2], vertical gradient freeze [3], multi-component zone melting (MCZM) [4-6]. It is very difficult to grow compositionally homogeneous $\text{In}_x\text{Ga}_{1-x}\text{As}$ single crystal at composition $x = 0.3$, because separation between the solidus and liquidus lines are far apart in the InGaAs phase diagram at this

composition. With increasing InAs component, the composition in solidified crystal becomes more sensitive to temperature fluctuation resulting in large variation of composition in the grown crystal. Recently, one of the authors (S.K.) succeeded to grow $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$ single crystals using the two-step MCZM method [7], in which the composition of crystals was gradually increased from $x = 0.05$ to 0.3 on the GaAs seed at the first step and then the crystal was grown at the constant composition $x = 0.3$ in the next step. At the present stage, the last-grown homogeneous region was limited to several millimeters in length, because of polycrystallization. In this growth technique, beginning of

polycrystallization was also found at the end of the first step growth process. The probability of such polycrystallization was found to be about 30% among the grown crystals. The crystals are some times cracked during and after crystal growth. In order to reveal these polycrystallization and cracking issues, we have made the present micro-Raman and photoluminescence (PL) measurements in the $\text{In}_x\text{Ga}_{1-x}\text{As}$ single crystal grown by the two-step MCZM method and found a drastic fluctuation of composition in the polycrystalline region as well as a large amount of residual strain in the crystal.

2. Experimental procedure

Bulk $\text{In}_x\text{Ga}_{1-x}\text{As}$ crystal of 15 mm diameter was grown by the two-step MCZM method [7]. The crystal was cut in two semi-cylindrical pieces along the growth length. The cut surface of one piece was mechanically polished to evaluate the compositional variation at the centerline along the growth direction of the piece using EDX analysis. It was confirmed that the composition gradually increases from $x = 0.05$ to $x \sim 0.3$ from the seed-crystal interface up to a certain distance in the growth direction. The other piece was chemically etched with 90% H_2SO_4 : 5% H_2O_2 : 5% H_2O , so as to check single crystal region by means of etching image. Later, both semi-cylindrical pieces were sliced into wafers perpendicular to the growth length. These wafers were also etched for examining their etching images and were polished for Raman and PL measurements. After certain growth length in increasing composition region, the etching images of the wafers indicate the formation of polycrystallization. Therefore, these wafers were considered in our study, which were obtained from the growth lengths of 19, 20, 21, and 22 mm, and named as wafers A, B, C, and D, respectively. In addition to polycrystallization, a chipped region adjacent to a cracked line was also found in one of the wafers.

Raman scattering measurements were made at room temperature using a Ranishaw model 2000 micro-Raman system equipped with an argon-ion laser ($\lambda=514.5$ nm). The incident light was focused to a spot of about 2 μm on the sample surface with a 50 \times objective lens and the scattered light was collected by the same objective lens. Typical slit width used was about 100 μm . Low laser power was used to prevent the local heating of the sample.

Using a PL mapping system equipped with a 20 mw He-Ne laser and a cooled InGaAs detector, PL measurements were also performed at room temperature. The optical arrangement is similar to that of Raman scattering. The wafers were scanned by computer-controlled X-Y-translational stages. Peak position of PL spectrum was determined by line-shape fittings.

3. Results and discussions

3.1 Polycrystallization characterization

Figure 1 shows the etching images of wafers A, B, C, and D. The etching image obtained from the wafer B shows a small dark

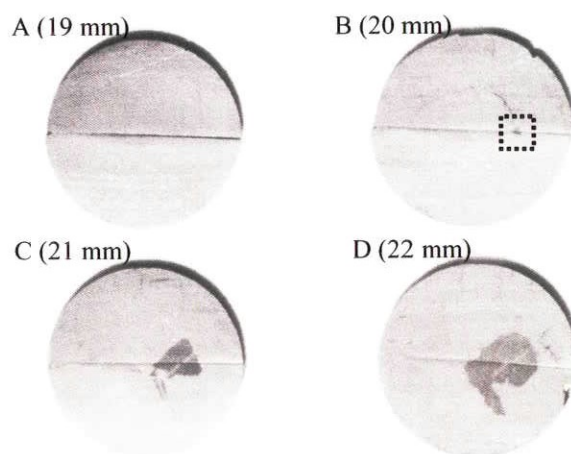


Fig. 1 Etching images of the wafers sliced at the different growth length of the crystal. A small dark region shown inside the dotted square found to increase in size with growth length. The crystallinity in this region appears to be changed with respect to the surrounding.

region within the crystal, which is enclosed by dotted lines to emphasis its position. This region was found to increase in size with increasing growth length, as seen in the etching images of the wafers C and D. The wafers obtained after the wafer D at longer growth lengths show that this region further increases in size. However, such dark region was not found in the etching image of the wafer A, which is adjacent to the wafer B. Therefore, etching results obtained from the wafers indicate that the dark region was initiated from the wafer B, and increased in size with growth length. Such dark regions in etching images typically indicate polycrystalline region. In order to confirm this, and to further characterize these regions, the wafers were investigated by Raman scattering and PL measurements.

The first order Raman spectrum from a semiconductor typically contains LO and TO phonons [8]. 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 [8-10] 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 and appearance of these phonons are strongly influenced by the alloy composition and crystal orientation. Figure 2 shows some of Raman spectra, which were measured from the front surface near and across the dark region of the wafer B. The inset in Fig. 2 shows an enlarged view of the investigated region of the wafer where Raman spectra were measured at a lateral interval of 50 μm . The spectra shown from top to bottom in Fig. 2 correspond, respectively, to the points shown in the inset from left to right, represented by the letters a to j. It is observed in Fig. 2 that the GaAs-like phonons (TO_{GaAs} and LO_{GaAs}) are stronger than the InAs-like phonons (TO_{InAs} and LO_{InAs}) in Raman spectra due to low In-content in the wafer. It is also observed in Fig. 2 that Raman spectra measured in the dark region show random shift in phonons peak positions, where some

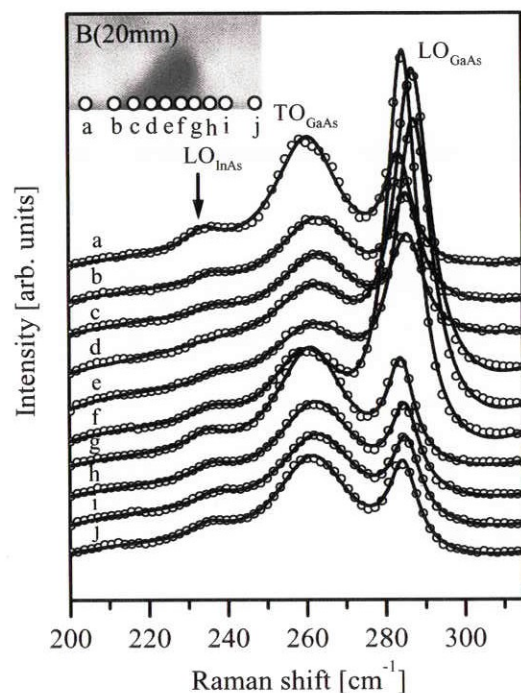


Fig. 2 Raman spectra measured near and in polycrystalline region of the wafer B corresponding to the measurement points shown in the inset

spectra also show drastic change in intensity ratio between TO_{GaAs} and LO_{GaAs} phonons. Since LO_{GaAs} phonons are stronger in the spectra, we will consider this phonon for further discussion. The exact peak positions of phonons were determined by the best line-shape fitting with Lorentzian components and a proper background.

Figure 3(a) shows the variation of LO_{GaAs} peak positions and relative intensity ratio $\text{LO}_{\text{GaAs}}/\text{TO}_{\text{GaAs}}$ as a function of distance from the center of the wafer. The measurement points a and j are at about 2.85 and 4.15 mm distance, respectively, from the center. The peak positions and relative intensity ratio shown in Fig. 3(a) were measured near and in dark region from the front surface of the wafer B, where left and right hand scales correspond to the LO_{GaAs} peak position and $\text{LO}_{\text{GaAs}}/\text{TO}_{\text{GaAs}}$ intensity ratio, respectively. It is observed in Fig. 3(a) that Raman peak positions measured in the dark region show random shift in the higher frequency side, with some part (measurement points d and e) showing a shift as high as 2 to 3 cm^{-1}

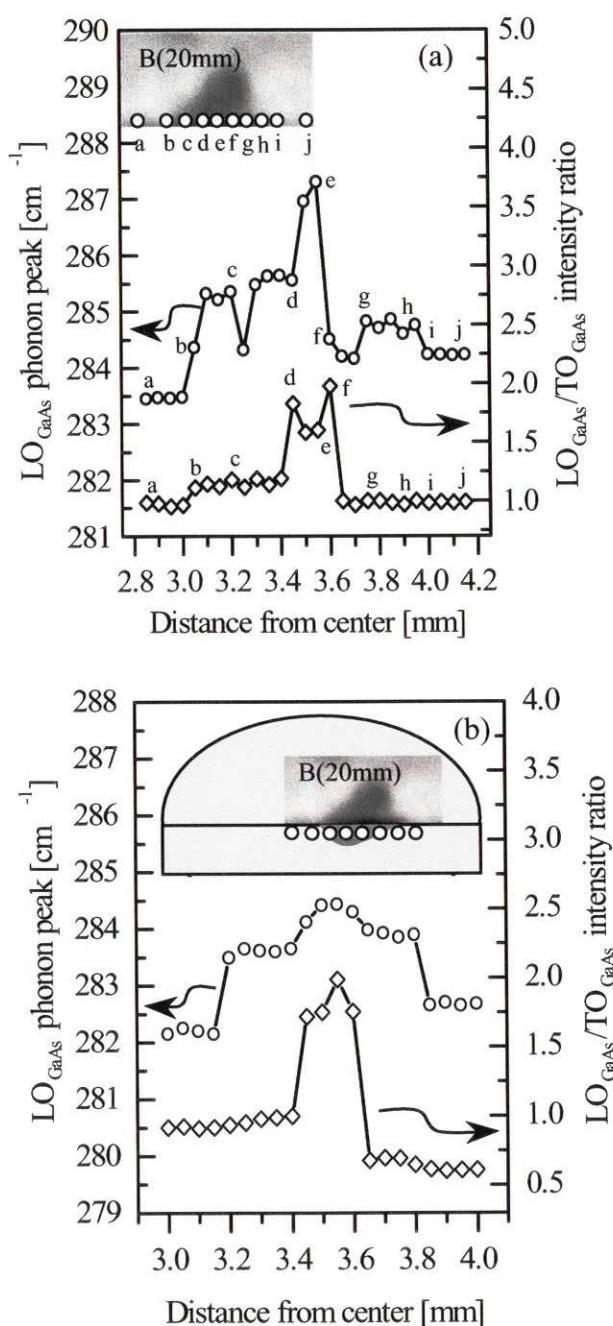


Fig. 3(a) and (b) LO_{GaAs} phonon peak positions and LO_{GaAs}/TO_{GaAs} intensity ratio measured from the front and side surfaces of the wafer B.

compared to the peak positions measured outside the dark region. In Fig. 3(a), it is also found that Raman peak positions measured at the right side out of the dark region show a shift of about 0.75 cm⁻¹ compared to the peak positions measured from the left side of the dark region.

Since etching images indicate that the dark region was initiated from the wafer B, the origin of the dark region should be inside this wafer. In order to investigate the origin of the dark region, Raman spectra were measured from the side surface of the wafer B, as shown by the schematic in Fig. 3(b). Figure 3(b) shows LO_{GaAs} peak positions, which were measured from the side surface of the wafer B. The symbols indicated by circles in the schematic indicate some of the measurement points. Similar to Fig. 3 (a), Fig. 3(b) also shows that LO_{GaAs} peak positions measured in the dark region from the side surface shifted to the higher frequency side compared to the outside of the dark region. As shown in Fig. 3 (b) that LO_{GaAs} peak positions measured in the dark region show about 1.5 to 2.5 cm⁻¹ higher shift compared to the peak positions measured from out side of the dark region. It is also observed in Fig. 3 (b) that the phonon positions measured at the right side out of the dark region are shifted by about 0.7 cm⁻¹ compared to the phonon positions measured from the left side of the dark region. The shifts in optical phonons are induced due to the absolute change in composition under the relaxation of strain, which was found in previous study [11]. However, residual strain in In_xGa_{1-x}As single crystals is induced due to the change in lattice constant by the compositional inhomogeneity. In presence of strain, the observed phonon peak positions in Raman spectra give an additional shift with composition, which was found in another recent study [12]. The existence of compositional inhomogeneity in local area of the dark region was confirmed from the random fluctuation of LO_{GaAs} peak positions. Further, the variation of phonon peak positions measured from both sides out of the dark region also indicates existence of compositional inhomogeneity in both sides of the dark region. Therefore, the observed Raman peak positions have the influence of strain. However, if we consider the relative shifts in phonon peak positions, then the additional shifts in phonon positions contributed by strain will not make any

influence on the results discussed here. Raman peak positions measured from both sides out of the dark region indicate that In-content has been decreased from the left to the right side of the dark region. However, in the dark region, random shifts in peak positions in higher frequency direction indicate that dark region has lower In-content compared to the out side of the dark region, and it has been changed drastically inside the dark region.

Figure 3 (a) and (b) also show relative intensity ratio LO_{GaAs}/TO_{GaAs} measured in the dark regions from the front and side surfaces of the wafer B, respectively. It is observed in Fig. 3(a) that the relative intensity ratio between LO_{GaAs} and TO_{GaAs} phonons measured from outside of the dark region is almost same, however, it starts changing slightly from the boundary of the dark region. Some small regions inside the dark region show drastic change in relative intensity ratio as shown in Fig. 3 (a). Such regions are indicated by the letters d, e and f in Fig. 3(a), which corresponding to the measurement points shown in the inset. It is well established [8] that due to the selection rules, the intensity ratio between LO and TO phonons strongly depends on the crystal orientation. The change in phonon intensity in Raman spectra occurs for significant change in crystal orientation. For slight change in crystal orientation, Raman scattering is not so sensitive. Since relative intensity ratio LO_{GaAs}/TO_{GaAs} measured from both sides of the dark region is almost same, these regions can be considered as single crystal region. However, due to the slight change in intensity ratio at the boundary of the dark region, it can be considered that polycrystallization has been started from the boundary of the dark region. Inside the dark region, since some small regions show a significant change in intensity ratio, which is about two times compared to the out side of the dark region, crystal orientation in these regions has been changed significantly and dark region has been strongly polycrystallized. Similar results are also found from the side surface of the wafer B as shown in Fig. 3 (b). However, such change in intensity of phonons

was not found in Raman spectra measured from the wafer A, which indicates polycrystallization was initiated from certain part of the wafer B.

Raman measurements were further performed in the dark region from the front and side surfaces of the wafer C. Figure 4 shows the LO_{GaAs} peak positions and relative intensity ratio LO_{GaAs}/TO_{GaAs} measured from the front surface of the wafer C. Similar to Fig. 3, left and right hand scales in Fig. 4 indicate LO_{GaAs} peak positions and LO_{GaAs}/TO_{GaAs} intensity ratio, respectively. The measurement points shown by the letters a and l in the inset are at about 0.5 and 4.9 mm distance, respectively, from the center, which indicates dark region is increasing in size with increasing the growth length. It is observed in Fig. 4 that the phonons in Raman spectra measured near the boundary of the dark region are shifted by about 2 cm^{-1} , compared to the nearby region. Besides the boundary of the dark region, some Raman spectra measured inside the dark region show a shift of about 3 cm^{-1} towards higher frequency direction, which indicates that there exists a lower composition compared to the nearby region. Such regions are indicated by the points f, g and h in Fig. 4, which correspond

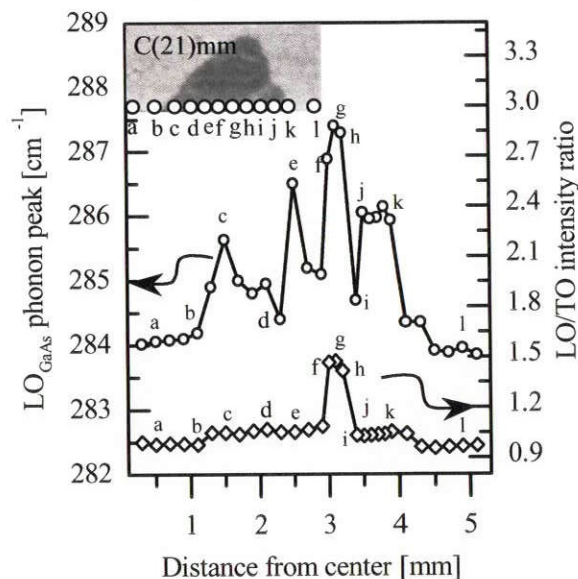


Fig. 4 LO_{GaAs} phonon peak positions and LO_{GaAs}/TO_{GaAs} intensity ratio measured from the front surface of the wafer C.

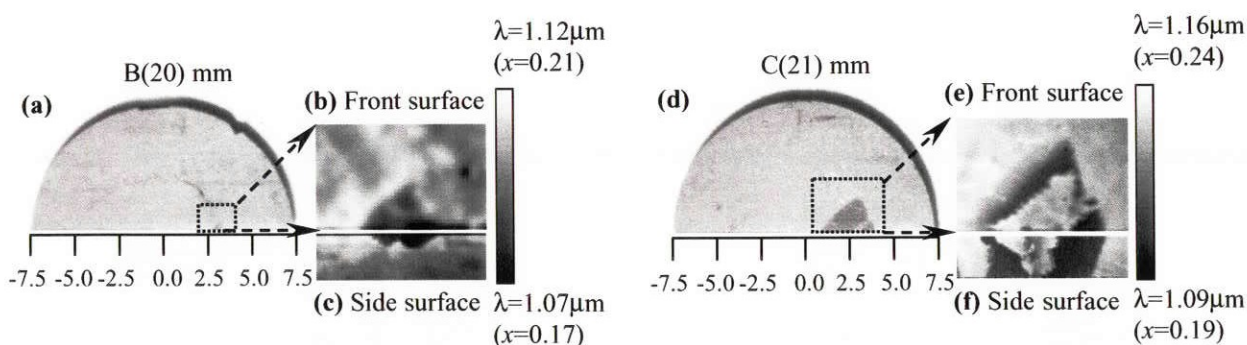


Fig. 5 2D mapping images of PL peak wavelength measured in the wafers of B and C. The PL measurements were made in the region surrounded by dotted lines in the etching images of (a) and (d), also shown are those made at the corresponding side surfaces.

to the measurement points in the inset of Fig. 4. Similar to Fig. 3, the relative intensity ratio shown in Fig. 4 indicates that the region outside of the dark region is single crystal region, however, crystal orientation in the dark region has been changed significantly and it has been polycrystallized. Similar results are also found from the side surface of the wafer C. From the experimental results, it is confirmed that the dark region has been strongly polycrystallized and which is initiated from the wafer B and its size is increasing with increasing the growth length. Our experimental results also indicate that, in the dark region, the relative intensity ratio has been changed drastically while Raman peak positions are shifted randomly in higher frequency direction; hence, there is a relation between the drastic fluctuation of composition and polycrystallization.

In order to confirm Raman results, PL experiments were performed in these wafers at spatial resolution of 20 μm . Figures 5(a) and (d) show the etching images of the semicircular wafers B and C, respectively, where the dotted lines and the scale in millimeter indicate the exact position of the polycrystalline region. Figures 5(b) and (c) show PL peak wavelength (composition) maps corresponding to the dotted area from the front and side surfaces of the wafers B, respectively. Figure 5 (e) and (f) show similar results for the wafer C. The spatial variations of PL maps indicate that there exists a drastic fluctuation of composition in the

polycrystalline region. In a previous study [13] carried out on epilayer, it was found that band gap energy is changed under the influence of strain, which is induced between the substrate and epilayer due to the change in lattice constant by the change in composition. Since the compositional inhomogeneity exists in the investigated samples, the measured PL peak wavelengths should have the influence of strain. As discussed earlier, if we consider the relative changes of PL peak wavelength then influence of strain on peak wavelength does not affect our results. The PL map shown in Fig. 5(b) shows drastic change in composition near the boundary of the polycrystalline region compared to the surrounding in agreement with Raman results. Similar results are also found in Fig. 5(e). Further, it is observed in Fig. 5(b) that the central part of the polycrystalline region shows slightly higher In-content compared to the boundary of the polycrystalline region. This In-rich part is found to increase in size with increasing the growth length as shown in Fig. 5(e). Figure 5(e) also indicates that some points inside the polycrystalline region show lower In-content in agreement with Raman results. Figure 5 (c) shows PL map obtained from the side surface of the wafer B. It is observed in Fig. 5 (c) that polycrystalline region has lower In-content compared to the surrounding. It is also found in Fig. 5(c) that the origin of polycrystalline region contains more GaAs, but close to the origin a tiny region shows more In-content compared to the surrounding. Figure 5(f) shows PL map

obtained from the side surface of the wafer C. The side surface map indicates that polycrystalline region is increasing in size with increasing the growth length in agreement with Raman results. The central part of the polycrystalline region contents more In compared to near the boundary, however, some points at the central region also show lower In-content. Besides the central region, surrounding of the polycrystalline region content more In compared to near the boundary.

In previous study [14], polycrystallization was found to initiate at the shoulder region in InP crystals grown by the LEC method due to the change in shape of growth interface. In the same study, beginning of oblique and perpendicular twin was also found, respectively, for higher ($150 \sim 200$ °C/cm) and lower (< 75 °C/cm) temperature gradient along the growth direction. Due to the purity of raw material and cone angle of the crystals, starting of polycrystallization was found at the shoulder region of InP crystal grown by the LEC method in the past [15], where it was also found that for the growth of twin free crystals, cone angle should be less than 19.68° . Further, due to dopant concentration and temperature gradient, polycrystallization was found to initiate in previous study [16] at the shoulder region in GaAs crystals grown by the horizontal bridgman method. In this study, polycrystallization was also initiated at the top surface in GaAs crystals due to the longitudinal temperature gradient. Since our experimental results show that the polycrystallization was initiated inside the crystal during the growth process, therefore, the causes related with the polycrystallization mechanism near the boundary of the crystal can be excluded from the crystal investigated at present. According to the experimental results, the origin of polycrystalline region has higher GaAs content compared to the surrounding. Inside a growing crystal, the GaAs rich region compared to the surrounding indicates that the GaAs rich grains were initiated to grow in the melt before the growth interface was reached in this region from the

seed crystal. As growth proceeded, these grains were embedded in the structure as a whole. We think these grains were initiated by the growth of small crystals in the solution, which could be due to supercooling or impurities in the melt, or other reasons. Originally, semiconductor melt has small kinematics viscosity compared to the thermal diffusivity, which causes local unbalance between temperature and compositional distributions. If such unbalance occurs in a saturated melt, local supercooling can easily occur compared to an unsaturated melt, which may cause polycrystallization. On the other hand, local supercooling is also induced due to the inhomogeneous distribution of InAs and GaAs by the convection. Local fluctuation of composition in $\text{In}_x\text{Ga}_{1-x}\text{As}$ crystal may also induce due to the constitutional supercooling, which is associated with growth and solidification rate of the crystal. Therefore, either convection-induced local supercooling or constitutional supercooling or impurities in the melt could be the cause of polycrystallization in the investigated crystal. Even in case of impurities in the melt, supercooling is the cause of polycrystallization, because higher GaAs content at the origin of polycrystallization indicates that polycrystalline region was initiated by supercooling. After beginning of polycrystallization, other effects can be triggered to increase it further with increasing the growth length.

3.2 Existence of residual strain

Figure 6 shows a series of typical first-order Raman spectra measured at an interval of 0.5 mm from the center to the edge in a semicircular wafer sample. In Fig. 6, strong peaks corresponding to GaAs-like phonons and rather weak peaks corresponding to InAs-like phonons are observed. These weak peaks are due to low In-content in the sample examined here. In order to estimate the exact peak positions and linewidths, we have made the best line-shape fitting with Lorentzian

components including a proper background. Since LO_{GaAs} peaks are sharp and intense, we mainly discuss them here. Figure 7 shows the frequency positions of the LO_{GaAs} peak as a function of distance from the center of the semicircular wafer sample shown in the inset, where arrow indicates the measurement direction. It is clearly found that they are not constant but differ by about 3 cm^{-1} between the one at the center and the one at the edge; that is, the composition is not homogeneous over the whole sample. If there is a compositional inhomogeneity in an $\text{In}_x\text{Ga}_{1-x}\text{As}$ single crystal, mechanical strain may be internally induced by the spatial variation of lattice constant due to the compositional inhomogeneity. In such a case, it is very difficult to evaluate the composition by separating the contribution of strain to the Raman shifts, although we have successfully evaluated the composition in $\text{In}_x\text{Ga}_{1-x}\text{As}$ polycrystals [11] in which the residual strain may be randomly distributed over the entire sample and hence averages out to zero at a particular point of the sample. In order to find out an evidence of the existence of strain in $\text{In}_x\text{Ga}_{1-x}\text{As}$ samples, we have performed precise micro-Raman measurements in a microscopic region including a cracked-line on the sample. Figure 8(a) shows an optical microscope picture of the microscopic region in which the cracked line is indicated by a dotted line. It is found that a part of the surface on one side separated by the crack becomes rough due to chipping associated with the cracking. Micro-Raman measurements were made on the chipped rough surface as well as on the unchipped smooth surface across the cracked-line. The LO_{GaAs} peaks measured across the cracked line are shown in Fig. 8(b), where the data denoted by open circles are taken at the points shown by the open circles in Fig. 8(a). The data points corresponding to the closed circles are not shown in Fig. 8(a). It is found from Fig. 8(b) that the LO_{GaAs} peaks measured on the unchipped smooth surface remain almost at the same Raman frequency while the LO_{GaAs} peaks measured on the chipped rough

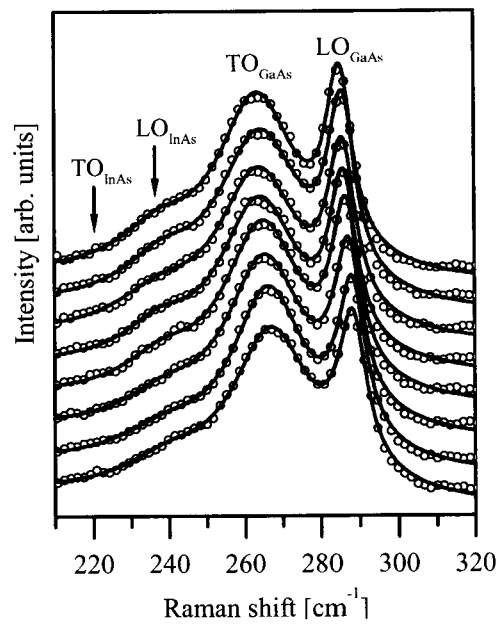


Fig. 6 Raman spectra measured at intervals of 0.5mm from center to edge in a semicircular wafer sample sliced from a 15 mm diameter $\text{In}_x\text{Ga}_{1-x}\text{As}$ single crystal.

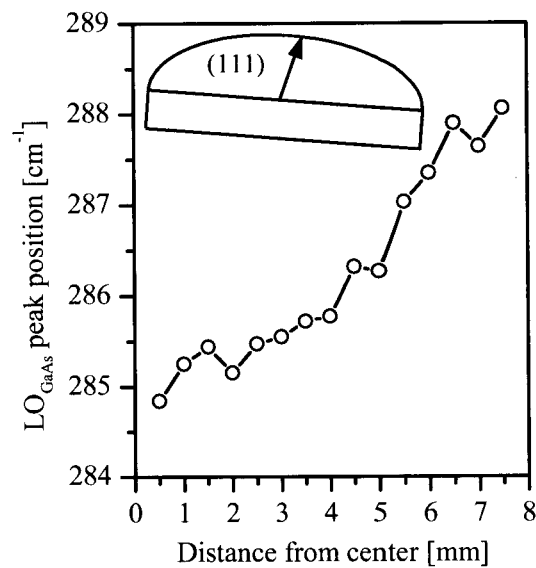


Fig. 7 Frequency positions of the LO_{GaAs} peak along arrowed direction of the sample.

surface are drastically changed. It should be noticed here that the drastic change of LO_{GaAs} peaks is 5 cm^{-1} at maximum and it is larger than the variation of 3 cm^{-1} from the center to the edge of the sample as shown in the inset of Fig. 6. It is noted again that the LO_{GaAs} peaks measured on the unchipped smooth surfaces

on both sides separated by the crack do not change but remain almost constant. It may be therefore concluded that the composition is nearly constant in the measured microscopic region of 100 micron square and the drastic change of 5 cm^{-1} on the chipped rough surface is related to residual strain existing in the sample. It is well known that the residual strain may be changed by cracking and /or chipping [17].

Figure 9 shows another evidence about the existence of residual strain. Micro-Raman measurements were also performed along the growth direction on the side surface as well as along the radial direction, both on the front and the rear surfaces of a semicircular wafer sample as shown schematically in Fig. 9. It is found from Fig. 9 that there is a difference of about 1 cm^{-1} between the front and rear surfaces and the difference of about 4 cm^{-1} between the side surface and the front and rear surfaces. The former difference of about 1 cm^{-1} may be considered mainly to be due to the compositional variation along the growth axis whereas the latter difference of about 4 cm^{-1} is due to the existence of residual strain because if there were no existence of residual strain, the LO_{GaAs} peaks measured on the side surface would be located between those measured on the front and rear surfaces.

In order to estimate the contribution of residual strain to the LO_{GaAs} peaks, we have made Raman measurements in three different points whose compositions were already determined with the EDX method. The result is summarized in Fig. 10, where the EDX data are plotted with the composition scale shown at the left hand side while the Raman LO_{GaAs} data are plotted with the LO_{GaAs} scale shown at the right hand side. Here, both scales are adjusted to match the following equation;

$$\text{LO}_{\text{GaAs}} = 291 - 53x \quad (1)$$

where x is the composition. The above equation is deduced from extensive Raman measurements in polycrystalline $\text{In}_x\text{Ga}_{1-x}\text{As}$ materials [8], in which the strain effect is not observed. It is noted here that the present Raman scattering and EDX measurements

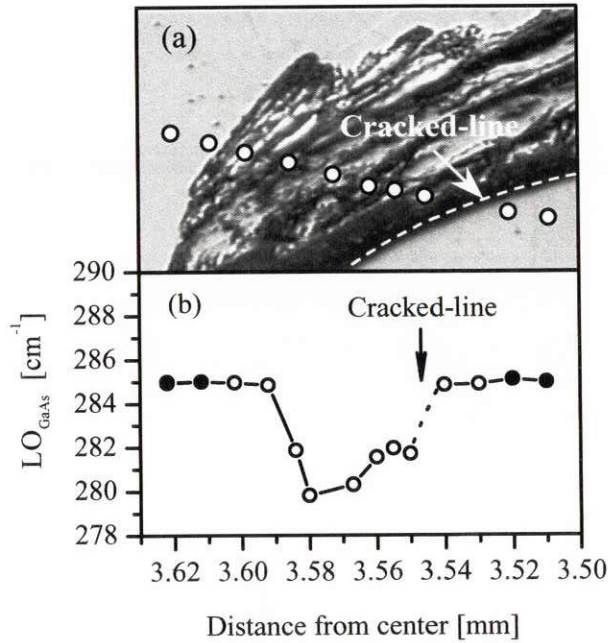


Fig. 8(a) Microscope observation of a cracked region, in which a series of open circles across the cracked line indicate the points at which Raman measurements were performed. (b) The frequency positions of the LO_{GaAs} peaks measured across the cracked-line at the points indicated by open circles in the microscope image. The points indicated by closed circles are not shown in the microscope observation result.

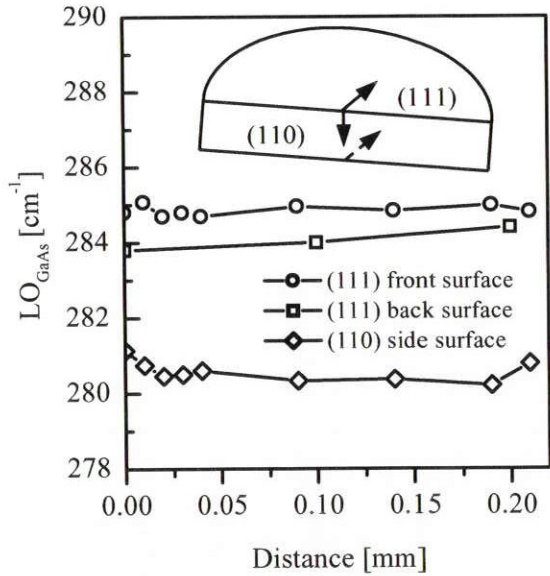


Fig. 9 The frequency position of LO_{GaAs} peak measure along the arrowed directions of the sample.

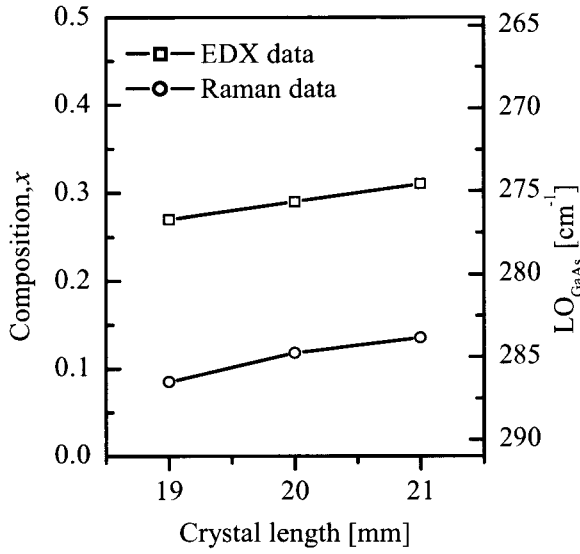


Fig. 10 Comparison of LO_{GaAs} peaks with the composition measured by EDX in three different points. The scale of LO_{GaAs} peak is shown at the right hand side, matched to the composition dependence of LO_{GaAs} peak; $LO_{GaAs} = 291 - 53x$. It should be noted that the composition dependence is confirmed in $In_xGa_{1-x}As$ polycrystals in which the strain effect is not observed [8].

were made at the same points on the samples. It is seen from Fig. 4 that the contribution of residual strain to the LO_{GaAs} peak observed here is about 9.5 cm^{-1} . If we take this strain effect into account, we may modify Eq(1) as follows;

$$LO_{GaAs} = 291 - 53x + \tilde{K}\epsilon_{ij} \quad (2)$$

where \tilde{K} is a constant related to the phonon deformation potential and ϵ_{ij} ($i, j = x, y, z$) is the strain. At the present stage, we do not know which strain component dominates the observed shift of 9.5 cm^{-1} . If we assume an uniaxial strain along the $\langle 111 \rangle$ growth direction, we may estimate the strain value to be of the order of 10^{-2} , using the phonon deformation potentials discussed by Anastassakis [18]. It may be presumed that the extremely large amount of residual strain causes cracking and polycrystallization during crystal growth. Although this shift of 9.5 cm^{-1} seems to be large for shift only due to strain,

we do not have any other independent experimental method to confirm this fact. However, in the case of epilayer [19,20], it has been found that the shift due to strain is as large as about 10 cm^{-1} for $x=0.3$. Further theoretical work to confirm our results is in progress.

4. Conclusions

Raman scattering and PL measurements were carried out with the aim to understand the polycrystallization mechanism in the bulk $In_xGa_{1-x}As$ crystal grown by the two-step MCZM method. From the etching image, a small dark region was found inside the ingot, which was initiated during the growth process after certain growth length. The crystal orientation in this region appears to be changed. Raman spectra measured from the dark region show random change in relative intensity ratio between LO_{GaAs} and TO_{GaAs} phonons, which proves that the crystal orientation in this region has been changed significantly and it strongly polycrystallized. Spatial variation of PL maps indicates existence of drastic fluctuation of composition near the boundary as well as inside the polycrystalline region, in agreement with the Raman results. Both PL and Raman results show existence of drastic fluctuation of composition at the origin of polycrystalline region, which could be due to the inhomogeneous distribution of InAs and GaAs in the local region caused by the supercooling. Therefore, we conclude that the local supercooling is the cause of polycrystallization in the investigated crystal, which could be occurred by convection or constitutional supercooling or impurity in the melt.

The existence of residual strain in the investigated crystal was further confirmed by Raman measurements. A continuous shift in LO_{GaAs} peak positions measured from center to edge of the sample demonstrates existence of compositional inhomogeneity in the sample. Compositional inhomogeneity could be the cause of residual strain in $In_xGa_{1-x}As$ single

crystal, which was confirmed by the precise Raman measurements both from a corner region and a chipped region adjacent with a cracked line. By comparing the Raman and EDX results, a large amount of residual strain was found in the crystal. The LO_{GaAs} peak positions measured from Raman scattering were found to be shifted by about 9.5 cm^{-1} with those estimated using the EDX compositions. This shift was originated due to the residual strain, which corresponds to a strain value of the order of 10^{-2} .

References

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