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The influence of residual strain on Raman scattering in $In_xGa_{1-x}As$ single crystals

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Abstract

Micro-Raman scattering studies were performed on bulk $In_xGa_{1-x}As$ single crystal grown by the two-step multi-component zone melting method, with the aim to understand the influence of residual strain on the shifts in phonon frequencies in Raman spectra. 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}. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Residual strain; Raman scattering; InGaAs bulk crystal

1. Introduction

Ternary bulk $In_xGa_{1-x}As$ single crystal is a promising lattice-matched substrate for InGaAs-based laser diodes used in the next generation of optical communication systems. Homogeneous $In_{0.3}Ga_{0.7}As$ single crystals are specially required for laser diodes oscillating at $\lambda = 1.3$ μm. Several groups tried to grow bulk $In_xGa_{1-x}As$ single crystals using cooling liquid encapsulated Czochralski (LEC) [1], Bridgman [2], vertical gradient freeze [3], multi-component zone melting (MCZM) [4–6]. One can see from the InAs–GaAs quasi-binary phase diagram that it is difficult to grow an $In_xGa_{1-x}As$ crystal with homogeneous composition. Recently, one of the authors (SK) succeeded to grow $In_{0.3}Ga_{0.7}As$ single crystals using the two-step MCZM method [7], in which the composition of crystals was increased gradually 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. The crystal some times cracked during and after crystal growth. In order to reveal these polycrystallization and cracking issues, we have made the present micro-Raman measurements in the $In_xGa_{1-x}As$ single crystal grown by the two-step MCZM method and found that there exists a large amount of residual strain in the crystal.

2. Experiment

The samples examined in the present work were prepared from a 15 mm-diameter $In_xGa_{1-x}As$ single crystal grown by the two-step MCZM method [7]. The crystal was cut along the $\langle 111 \rangle$ growth direction in two pieces. The cut surface of one piece was mechanically polished and then chemically etched with 90% H_2SO_4:5% H_2O_2:5% H_2O so as to check single crystal region and to evaluate the compositional variation by energy dispersive X-ray (EDX) analysis. The EDX analysis was made along the center line of the piece. The other piece was sliced into semicircular wafers. The surfaces of the wafers were optically polished for Ra-

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man measurement. In one of the wafers, a cracked and chipped line was observed.

Raman scattering measurement was made at room temperature using a Ranishaw model 2000 micro-Raman system equipped with an argon-ion laser ($\lambda =$
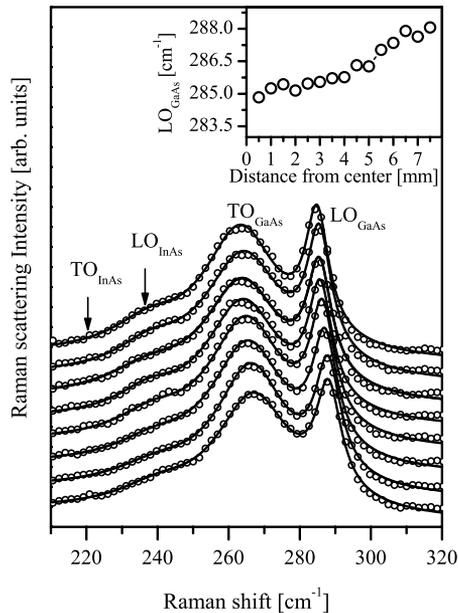

Fig. 1. Raman spectra measured at intervals of 0.5 mm from center to edge in a semicircular wafer sample sliced from a 15-mm diameter $In_xGa_{1-x}As$ single crystal. The frequency positions of the LO_{GaAs} peaks are plotted in the inset.
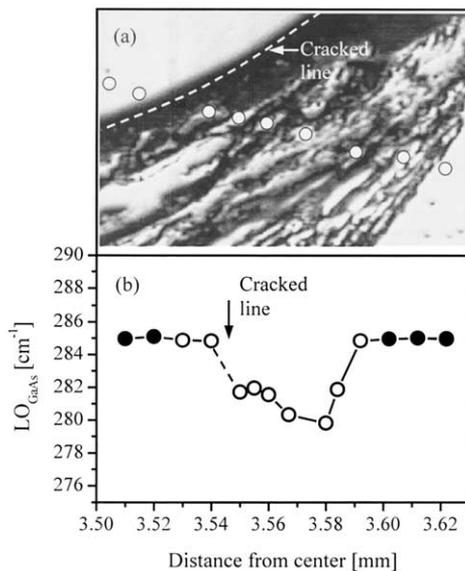

Fig. 2. (a) Microscope observation of a cracked region, in which a series of open circles across the cracked line indicate the points at which Raman measurements were performed. (b) The frequency positions of the LO_{GaAs} peaks measured across the cracked-line at the points indicated by open circles in the microscope image. The points indicated by closed circles are not shown in the microscope observation result.

514.5 nm). The incident light was focused to a spot of about 2 μm on the sample surface with a 50 × 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.

3. Results and discussion

Fig. 1 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. 1, strong peaks corresponding to GaAs-like LO and TO phonons and rather weak peaks corresponding to InAs-like LO and TO phonons are observed. These weak peaks are due to low content of InAs 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. In the inset of Fig. 1, the frequency positions of the LO_{GaAs} peaks are plotted as a function of distance from the center of the semicircular wafer sample. 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 $In_xGa_{1-x}As$ 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 evaluated successfully the composition in $In_xGa_{1-x}As$ polycrystals [8] 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 $In_xGa_{1-x}As$ samples, we have performed precise micro-Raman measurements in a microscopic region including a cracked-line on the sample. Fig. 2(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. 2(b), where the data denoted by open circles are taken at the points shown by the open circles in Fig. 2(a). The data points corresponding to the closed circles are not shown in Fig. 2(a). It is found from Fig. 2(b) that the LO_{GaAs} peaks measured on the
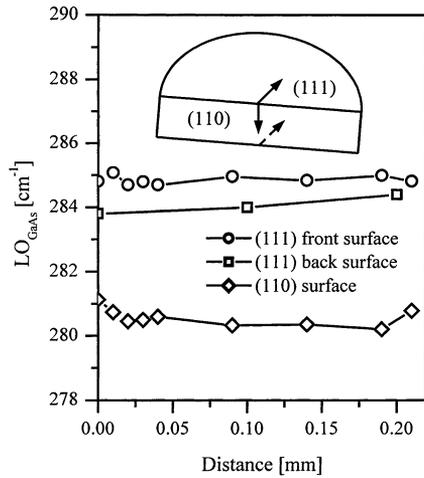
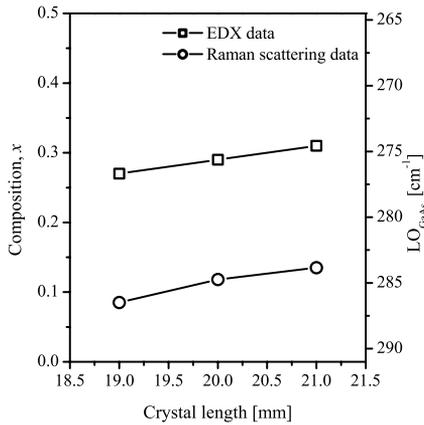Fig. 3. The frequency position of LO_{GaAs} peak measure along the arrowed directions of the sample.

Fig. 4. 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].

unchipped smooth surface remain almost at the same Raman frequency while the LO_{GaAs} peaks measured on the chipped rough 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. 1. 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 [9].

Fig. 3 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. 3. It is found from Fig. 3 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. 4, 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:

$$LO_{GaAs} = 291 - 53x \qquad (1)$$

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

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

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 a 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 [10]. 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 [11,12], 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.

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