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Raman scattering determination of carrier distribution in GaP diodes

S. Nakashima, H. Yugami,[a] A. Fujii, and M. Hangyo
Department of Applied Physics, Osaka University, Yamada-oka, Suita, Osaka 565, Japan
H. Yamanaka
Discrete Division, Matsushita Electronic Co. Ltd., Takatsuki, Osaka 569, Japan

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Using a Raman microscope we have studied Raman scattering from plasmon-LO-phonon coupled modes in the cross section of GaP diodes. The line shape analysis of the coupled mode has provided the thermal-equilibrium carrier concentration and mobility. Their distribution is determined from the spatial variation of the spectra. The carrier distribution thus obtained is consistent with that estimated from capacitance measurements. The result demonstrates that the Raman microprobe is a powerful method for determining the distribution of the carrier concentration and mobility in semiconductor devices without electric measurements using electrodes.

I. INTRODUCTION

The Raman scattering from plasmon-LO-phonon coupled modes has been observed mostly in zinc-blende-type semiconductors.[1] The frequency of the coupled modes varies noticeably with carrier concentration when the collision damping of the plasmon is small. In this case the carrier concentration can be easily estimated from the frequencies of the coupled modes. If the plasmon damping is large as in GaP, i.e., $\omega_p \tau < 1$, where ω_p is the plasma frequency and τ is the collision time of the free carriers, the plasmons and LO phonons are almost decoupled and then the free carriers cause a slight shift and broadening of the LO phonon band.[2-4] This fact has made it difficult to evaluate the carrier concentration precisely from Raman scattering data for semiconductors having overdamped plasmons.

Recently the use of an optical multichannel detector instead of a photomultiplier has enabled us to determine the frequency of Raman bands precisely because no mechanical scanning of wave number is needed. We have applied this technique combined with Raman microprobe to the determination of carrier and mobility distributions in GaP light emitting diodes (LED).

So far, the Hall measurement has widely been used to determine the carrier density and mobility in semiconductors. Recent Raman scattering studies have indicated that the analysis of the plasmon-LO-phonon coupled mode can be used to determine the carrier concentration in bulk semiconductors.[3,5,6] The Raman scattering determination of the carrier concentration has advantages; it requires no electrodes and magnets, and the spatial resolution amounts to about 1 μm if we use a Raman microprobe technique.

In this work Raman spectra of the cross section of GaP p^+-n-n^+ junctions have been measured by use of a scanning Raman microscope. The carrier concentration and mobility are determined from the line-shape fitting of the observed coupled modes using the spectrum at the depletion region as a reference. This procedure is analogous to the Raman difference spectroscopy. The spatial distribution of these quantities is obtained from the data at various points.

II. EXPERIMENT

A. Junction structure

The (111) surface GaP with electron concentration of $\sim 3 \times 10^{17}$ cm^{-3} was used as a substrate for liquid-phase epitaxial (LPE) growth. Details of the LPE method were described in Ref. 7. The n-epitaxial layer was grown from solution doped with sulfur. After the n-layer growth, sulfur was reduced with volatilization in vacuum. Then zinc was doped in the growth solution and p^+-layer was grown on the n-epitaxial layer. Total thickness of the LPE layer was 60 μm and the p^+ layer was 20-μm thick.

The value of N_D-N_A in the n-epitaxial layer estimated from capacitance measurements was about 5×10^{16} cm^{-3}. The epitaxial wafer was cut by a dicing saw and etched slightly to get smooth cross sections.

B. Raman measurements

The Raman spectra of the GaP LED's were measured at room temperature with a Spex double monochromator with 1.0-m focal length combined with an optical microscope. The incident laser beam was focused on a sample surface by means of an objective lens with a numerical aperture of 0.8. A focal spot size used was about 1 μm. The scattered light was collected by the same objective lens and directed into the spectrometer. The entrance slit was fixed at 150 μm. The dispersed Raman signals were detected with an optical multichannel detector (TN-6122) and stored in a microcomputer. The width of an element of the diode array was 25 μm and the spectral resolution of the system was about 0.6 cm^{-1}. The spectra were not corrected for the instrumental resolution.

The samples were mounted on an X-Y stage which was translated by micrometers. The spatial resolution of this system was 1 μm. The Raman spectra were observed at various points along the direction perpendicular to the p-n junction. The 488.0-nm line of an Ar^+ ion laser was used for the

[a] Present address: Research Institute for Scientific Measurements, Tohoku University, Katahira, Sendai 980, Japan.

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excitation of the Raman scattering because a tail of photoluminescence prevented the Raman measurement when the 514.5-nm line was used. The use of the 488.0-nm line caused photocarrier generation, and so a laser power of less than 5 mW was used to avoid the generation of high-density carriers. The use of low laser powers was necessary for the n region and especially for the depletion region.

To check the drift of zero of the spectrometer the Raman spectrum of the depletion layer was observed before and after the measurement and the data were employed only when the drift was absent. The line shape fitting was made using a microcomputer by the Gauss–Newton method. The accuracy of the frequency determination in this method was ± 0.1 cm^{-1}.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Raman measurements

Raman scattering has been measured for the cross section of the GaP diode shown in Fig. 1. The observed spectra at typical points are shown in Fig. 2. Each spectrum is normalized with the peak intensity of the TO phonon band. The frequency and width of the TO phonon band do not vary with the position. However, the LO phonon band shows drastic change in the shape and intensity for different positions. It is weak and has an asymmetric shape in the p^+ and n^+ regions. At the position 22 μm apart from the edge (the outer surface of the p^+ region), the LO phonon band is sharp and its intensity is the strongest. This position corresponds to the depletion layer.

Figures 3 and 4 show the peak intensity of the LO phonon band normalized by the peak of the TO phonon band, and the bandwidth (FWHM), respectively, as a function of the position. The band width in the n region is about 1.5 cm^{-1}. This value is comparable with the result (1.2 cm^{-1}) of GaP with high resistance, which was obtained by using a Fabry–Perot interferometer.[3] The variation of the frequency of the coupled mode relative to that of the LO phonon at the depletion region is also shown in Fig. 5. As can be seen in these figures the peak intensity, bandwidth, and frequency of the LO phonon bands are strikingly different for the p^+, n, and substrate (n^+) regions. The above quantities have strong correlation. In the p^+ region the intensity is weak, the width is large, and the frequency is upshifted. In the n region the intensity is medium and the bandwidth is small. The intensity is strong and the frequency is lower at around the depletion layer.

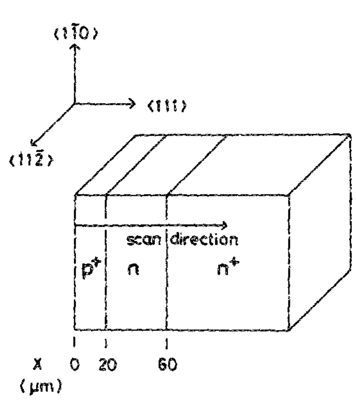

FIG. 1. The structure of GaP diode.

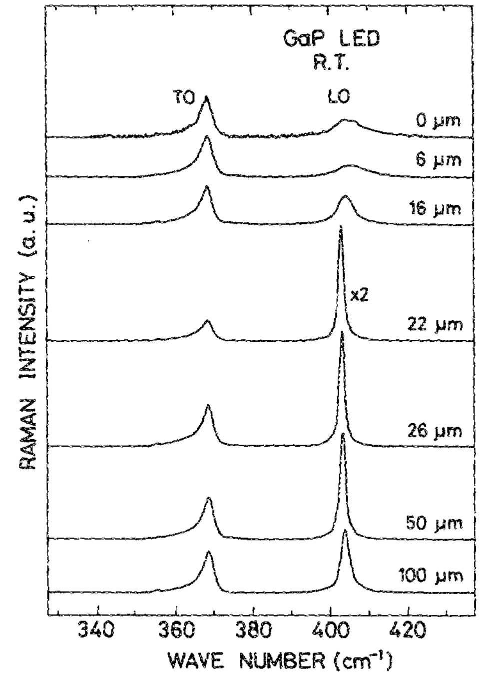

FIG. 2. Raman spectra at several points of the GaP LED cross section. The distance is measured from the outer edge of the P^+ region.

B. Analysis

Raman scattering from plasmon-LO-phonon coupled modes has been widely studied. It arises from three mechanisms; charge density fluctuation (CDF), deformation potential (DP), and electro-optic (EO) mechanisms.[1,3,8] If the carrier damping is large, i.e., $\omega_p \tau < 1$, the contribution of the

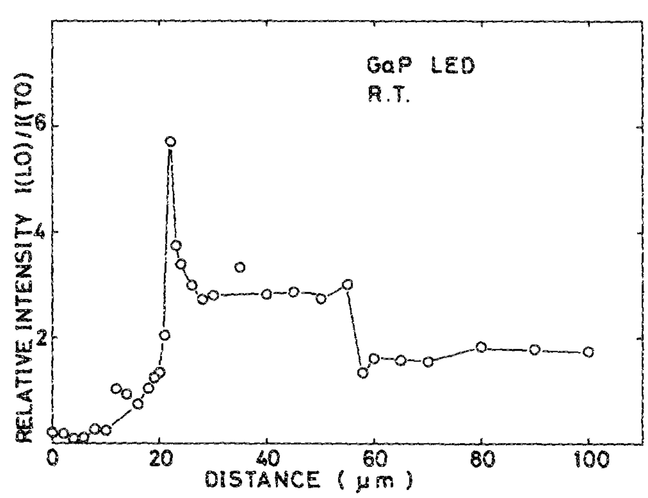

FIG. 3. The peak intensity of the plasmon-LO-phonon coupled mode as a function of the position. The intensity is normalized by that of the TO band.

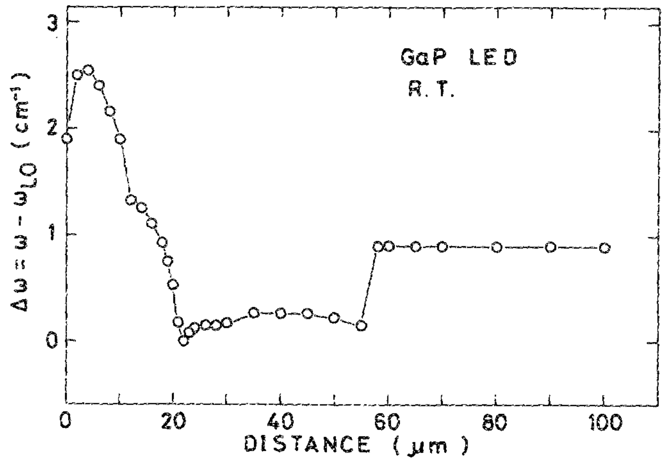

FIG. 4. The frequency shift of the plasmon-LO-phonon coupled mode relative to that of the LO phonon band at the depletion region.

CDF mechanism to the band shape can be neglected, because the CDF mechanism and EO and DP mechanisms do not interfere and the CDF mechanism gives a very broad background to the coupled mode in the case of $\omega_p \tau < 1$. In this case, the Raman scattering cross section due to the DP and EO mechanisms are given by

$$I = \frac{d^2S}{d\omega\, d\Omega} \propto (n_\omega + 1) A \,\mathrm{Im}\left(-\frac{1}{\epsilon(\omega)}\right), \qquad (1)$$

$$\begin{aligned} A = {} & 1 + 2C\,(\omega_t^2/\Delta)\,[\omega_p^2\gamma(\omega_t^2 - \omega^2) - \omega^2\Gamma \\ & \times (\omega^2 + \gamma^2 - \omega_p^2)] + C^2[\omega_t^4/\Delta(\omega_l^2 - \omega_t^2)] \\ & \times \{\omega_p^2[\gamma(\omega_l^2 - \omega_t^2) + \Gamma(\omega_p^2 - 2\omega^2)] \\ & + \omega^2\Gamma(\omega^2 + \gamma^2)\}, \end{aligned} \qquad (2)$$

$$\begin{aligned} \Delta = {} & \omega_p^2\gamma[(\omega_t^2 - \omega^2)^2 + (\omega\Gamma)^2 \\ & + \omega^2\Gamma(\omega_l^2 - \omega_t^2)(\omega^2 + \gamma^2)], \end{aligned} \qquad (3)$$

where ω_l and ω_t are the frequencies of the LO and TO phonons, γ is the plasma damping constant, Γ is the phonon damping constant, and n_ω is the Bose factor. The Faust–Henry coefficient C is taken to be -0.53 (Ref. 2) and the dielectric function ϵ is given by

$$\epsilon(\omega) = \epsilon_\infty\left(1 + \frac{\omega_l^2 - \omega_t^2}{\omega_t^2 - \omega^2 - i\omega\Gamma} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}\right). \qquad (4)$$

The plasma frequency ω_p is given by

$$\omega_p^2 = 4\pi n e^2/\epsilon_\infty m^*,$$

n and m^* are the carrier density and effective mass of electrons (holes), respectively. The effective masses of the electron and hole are defined as follows[9,10]:

$$\frac{1}{m_e^*} = \frac{1}{3}\left(\frac{2}{m_t^*} + \frac{1}{m_l^*}\right), \qquad (5)$$

$$\begin{aligned} \frac{1}{m_h^*} = {} & \frac{1}{m_{lh}^*}\,\frac{1}{1 + (m_{hh}^*/m_{lh})^{3/2}} \\ & + \frac{1}{m_{hh}^*}\,\frac{1}{1 + (m_{lh}^*/m_{hh}^*)^{3/2}}, \end{aligned} \qquad (6)$$

where $m_t^* = 0.254 m_0$, $m_l^* = 1.7 m_0$, $m_{hh}^* = 0.55 m_0$, and $m_{lh}^* = 0.13 m_0$. The mobility μ is related to the damping constant γ with the following equation:

$$\gamma = |e|/m^*\mu.$$

Using the carrier density and mobility as adjustable parameters, we performed the line-shape fitting of the calculated coupled mode to the observed ones. In this fitting procedure a precise value of the LO phonon frequency is required to determine the accurate carrier concentration. However, GaP crystals with low carrier concentration less than about 10^{16} cm^{-3} were not available. Hence, we employed the value of ω_l at the depletion layer (403 cm^{-1}) which shows the strongest Raman intensity as the frequency of pure GaP. This frequency is 0.12 cm^{-1} lower than that of a GaP crystal with carrier concentration of 2×10^{16} cm^{-3}. The damping

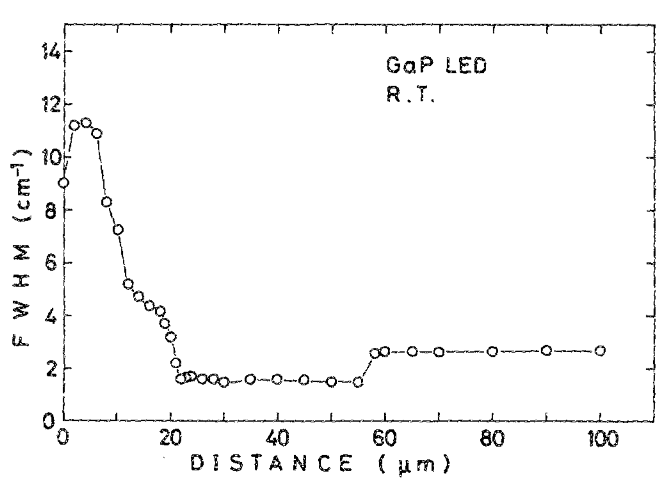

FIG. 5. The band width (FWHM) of the coupled mode is plotted as a function of the position.

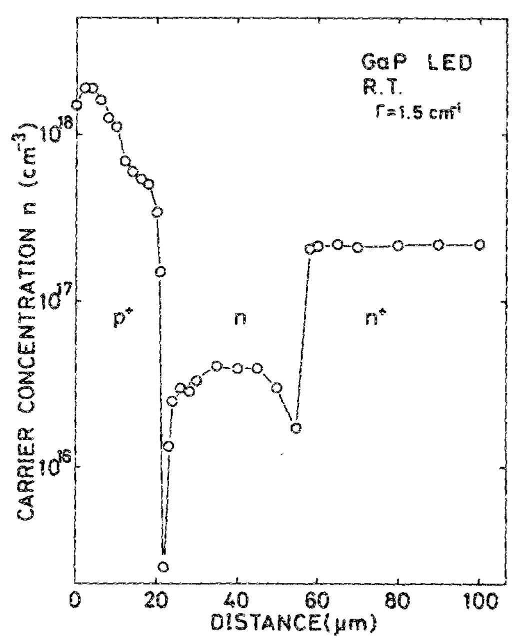

FIG. 6. The carrier concentration profile of the GaP diode determined from the Raman microprobe measurement.

constant of the LO phonon Γ is fixed at 1.5 cm $^{-1}$. The fitting parameters μ and n are adjusted so as to reproduce the line shape and also the intensity. The fitting of the intensity is important especially for low carrier concentrations.

The carrier concentration determined from the fitting is plotted as a function of the distance in Fig. 6. The distribution of the carriers is close to that expected from the growth condition. At around the depletion layer the carrier concentration does not show a steplike distribution. Because the estimated width of the depletion layer is about 1 μm at the zero bias voltage, such distribution reflects a nonuniform impurity profile due to the diffusion of Zn impurities of the p^+ region into the n region during the epitaxial growth. At the boundary between the substrate and n region the carrier concentration is decreased. This decrease may be due to the charge compensation induced by contaminations during the growth, because the growth of both n and p layers was made with the same crucible.

Simulations by a computer have indicated that for the region with high carrier concentration the determination of the concentration is insensitive to the value of the phonon damping and it is determined only from the peak frequency of the coupled mode. The estimated accuracy is 5% for $n \sim 10^{18}$ cm^{-3}, 8% for $n \sim 10^{17}$ cm^{-3}, and 50% for $n \sim 5\times10^{16}$ cm^{-3}. A comparison of the carrier concentration determined from the Raman scattering with that determined from the Hall measurement was made by Irmer *et al.*[3] for GaP crystals with carrier concentration ranging from 2×10^{16} to 5×10^{18} cm^{-3}. They have shown that the carrier concentration obtained from the Raman measurement is in close agreement with that obtained from the latter measurement. The agreement was also found in the results of the two measurements in β-SiC for which the carrier damping is large as in GaP and only the EO and DP mechanisms contribute to the coupled mode.[6]

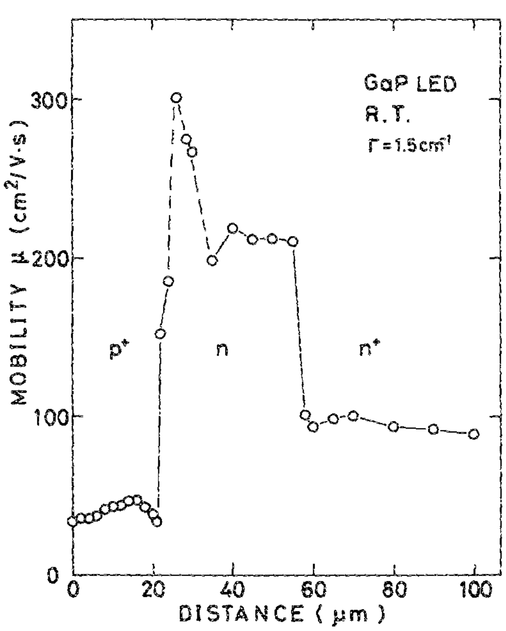

FIG. 7. The mobility profile of the GaP diode determined from the Raman microprobe measurement. The solid line is a guide for the eye.

The mobilities of electrons and holes determined from the fitting are shown in Fig. 7. The hole mobility in the p^+ region is about 40 cm^2/V s and does not show striking position dependence. The mobility in the n region is higher than that of the n^+ region. At places near the depletion layer, the fitted values are about 300 cm^2/V s which greatly exceeds the electron mobilities reported by Kao and Eknoyan.[11] The fitted value of the mobility is quite sensitive to the choice of the LO phonon damping Γ for low carrier concentrations. If we take $\Gamma = 1.45$ cm^{-1}, the fitted values lie below 200 cm^2/V s and the result for the n^+ region does not show noticeable change, but the computed mobility has a sharp peak near the depletion layer in the n region. Such mobility distribution is not conceivable. The protrusion of the mobility at the above places might be caused by fitting the bandshape without correction for the instrumental resolution, which will be important for narrow Raman bands.

Systematic studies have not been made as to whether the carrier mobility determined from the Raman measurement coincides exactly with that determined from the Hall measurement or not. However, Irmer *et al.*[3] reported that the agreement between the results of the two methods is good for GaP. For β-SiC the mobility determined from the Raman scattering agreed with that determined from the electric measurement for the concentration range lower than about 2×10^{17} cm^{-3}, but showed slight deviation for the higher concentration.[6] This deviation might be eliminated if different scattering mechanisms are taken into account in the determination of the Hall coefficient.[6] From these arguments it follows that the mobility determined from the Raman measurement is comparable with the result of the Hall measurement. The mobility profile obtained from the Raman microprobe measurement is not unreasonable and Raman scattering can be used as a tool for evaluating the carrier concentration as well as the mobility in a local area.

IV. CONCLUSION

A scanning Raman microscope system combined with a technique for precise frequency determination has been applied to the evaluation of the spatial distribution of the carrier density and mobility in GaP diodes. The carrier density and mobility have been determined from the fitting of the theoretical line shape to the observed spectra of the plasmon-LO-phonon coupled mode. The obtained result is in reasonable agreement with the distribution of doped impurities expected from the growth condition. The present study demonstrates that the Raman microprobe is a powerful tool for the characterization of semiconductors as well as the diagnostics of semiconductor devices.

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