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Invited

Raman Spectroscopy for Characterization of Semiconductor Materials and Surfaces

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Some examples of characterization of semiconductors with laser Raman spectroscopy are described. Stress in cap layer-GaAs structures was characterized from broadening of the LO phonon. Surface recombination velocity of InP was estimated based on LO-plasmon coupled mode. Instability introduced by annealing in superlattice was discussed also based on zone folding phonons and spectra corresponding to phonons from alloy semiconductors.

Laser Raman spectroscopy is a useful means for characterizing materials and structures of semiconductors because of following reasons.
(1) A very small area such as one with a diameter of about one micron can be characterized.
(2) Properties of semiconductor can be characterized without mechanical contact of any probe on a surface.
(3) A large variety of informations on semiconductors, such as structural and electronic properties, stress, and informations on impurities can be obtained.
(4) It is sufficient to measure at room temperature in an air atmosphere in most cases.
(5) Characterization through dielectric films can be done provided they are transparent to the laser beam used in the measurement.

1. Principle of laser Raman spectroscopy

Raman effect is phenomenon in which a part of scattered light includes components whose frequencies shifted from one of incident light. Main origins of the frequency shift are optical and acoustic phonons in semiconductor crystal. Other modes are also included in the scattered light if some conditions are satisfied as shown in Fig. 1. For example, stress in the surface region of semiconductor makes the width larger and/or introduces extra shift of phonon. Forbidden modes such as optical phonons corresponding to other point than Γ point and acoustic phonons in the case of zincblend structure are observed when disorder is introduced in the crystal for example by ion implantation. LO phonon-plasmon coupled mode is observed if a carrier concentration of semiconductor crystal is high such as $5\times10^{17}\,cm^{-3}$ for GaAs. Local modes are also observed if a concentration of impurities in lattice site is high.

Schematic diagram of a system used in the measurement of Raman spectra is shown in Fig. 2. Argon ion laser was used as a probe while other lasers may be used. A double monochrometer JRS-400D or a triple monochrometer JRS-400T, and a photomultiplier were used for detection of scattered Raman light. Region measured in the direction of depth is almost the penetration depth of the laser beam, that is about 110 nm for the argon ion laser with a wavelength of 514.5 nm.

2. Stress in cap layer-GaAs structures

Layers of dielectric materials such as SiO_2, Si_3N_4, and AlN are used as cap layers in annealing of ion-implanted GaAs. In general it is expected that stress exists in cap layer-GaAs structures if thermal expansion coefficient is different between a cap layer and semiconductor. Figure 3 shows Raman spectra from semi-insulating GaAs after annealing at 850°C for 2 h obtained through dielectric layers because they are transparent to the incident beam[1]. No ion had been implanted in order to study only the effects

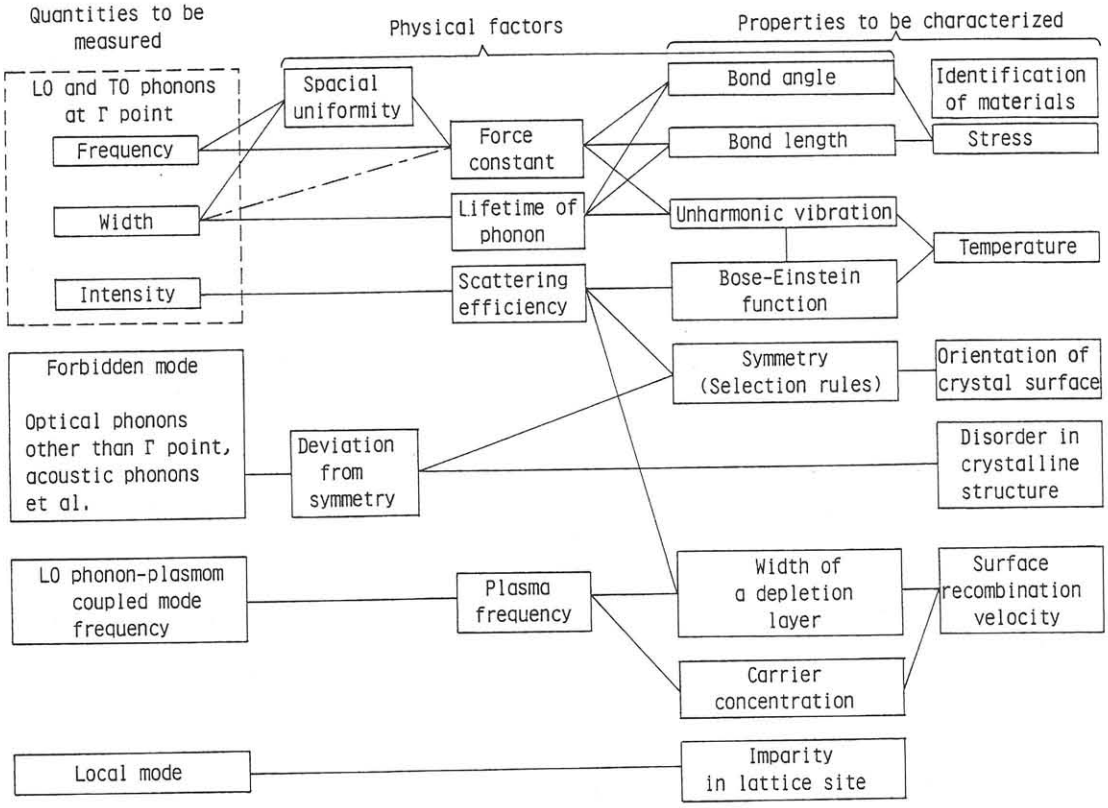

Fig. 1 Quantities to be measured, physical factors determining Raman spectra, and properties to be characterized.

of difference in thermal expansion coefficients without effects of structural disorder. Width of the LO phonons observed from GaAs with SiO_2 or Si_3N_4 cap layer are larger than that from GaAs with AlN. Difference in the thermal expansion coefficient is larger between SiO_2-GaAs or Si_3N_4-GaAs than between AlN-GaAs. Figure 4 shows a relation between LO phonon width and resistivity of GaAs after annealing at 850°C for 2 h. Resistivity of GaAs had been about 10^8 Ωcm before annealing. Amount of (resistivity) x (thickness of a thermally converted layer) is plotted in the ordinate because the thickness can not been estimated accurately. It is apparent that decrease in resistivity during annealing becomes larger with increase in LO phonon width, that is, increase in stress in a cap layer-GaAs structure.

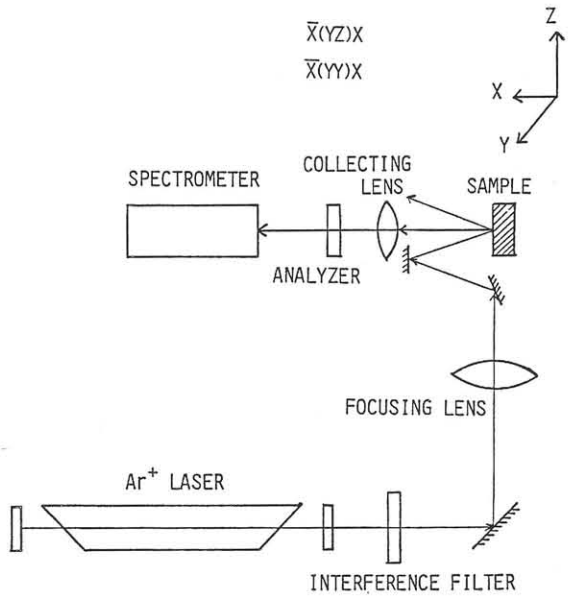

Fig. 2 Schematic diagram of a system used in the measurement of Raman spectra.

3. Surface recombination velocity

Figure 5 shows the typical Raman spectra from n-InP with a carrier concentration of $2.7 \times 10^{17} cm^{-3}$ obtained with different laser powers. In order to keep constant the amount of Raman light detected by the photon counting system, the product of incident power and integration time were kept constant. Peaks at 346 and 340cm^{-1} have been assigned to the LO and TO phonons of InP, respectively. The reason for appearance of the TO phonon from a (100) surface is that a 90°

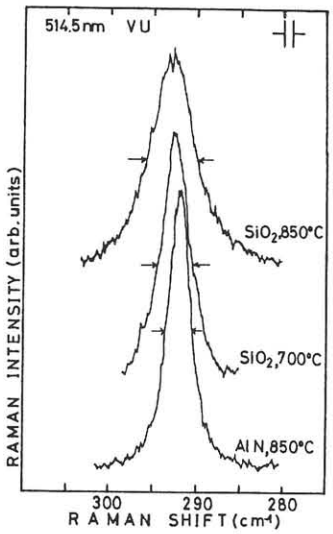

Fig. 3 Raman spectra from SI GaAs after heat treatment with SiO_2 or AlN.

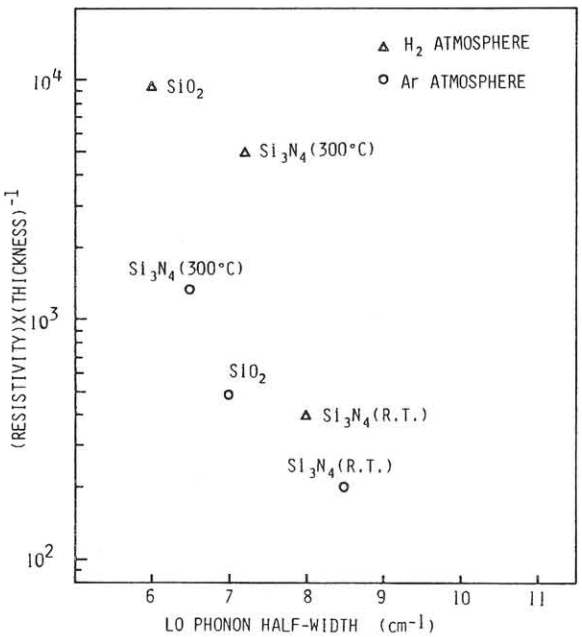

Fig. 4 Relation between a half-width of the LO-phonon line from SI GaAs heat treated in an atmosphere of H_2 or Ar with a SiO_2 or Si_3N_4 cap layer, and sheet resistivity of the surface region.

scattering geometry was used in the measurement and not that the screened LO phonon, i.e., L^+-mode, appeared at the frequency of the TO phonon since an increase in intensity of the TO phonon with a large laser power was not observed as is shown in Fig. 5. The LO phonon originates from a surface depletion layer which is present on a natural (100) surface exposed to air. A broad peak is based on the L^+ mode from InP. The increase in frequency with that in laser power is due to excess carriers optically excited at the surface by an incident laser beam. In order to make clear the relation between the incident laser power and concentration of the excess carriers, the frequency ω^+ was plotted against the equilibrium concentration of the carriers in n-InP samples as shown in Fig. 6.

The concentration of the excess carriers Δn was calculated from the frequency ω^+ by subtracting the equilibrium carrier concentration from the total carrier concentration deduced from the L^+ mode frequency[2]. For example, Δn was about $0.9\sim2.7\times10^{17}\ cm^{-3}$ when the power density was $5\times10^2\ W/cm^2$.

It was assumed that a concentration Δn of the optically excited excess carriers near the surface was determined by diffusion, surface recombination, and bulk recombination process such as through traps[2]. The surface recombination velocity was estimated as $1\sim8\times10^3$ cm/s for samples denoted above if the bulk lifetime is larger than 10^{-7} s. Surface recombination velocity of GaAs was estimated at least 10^{-7} s.

4. Thermal instability in superlattices

Thermal instability means here disappearance of periodicity or production of alloys. The former is detected by disappearance of zone folding optical phonon and the latter can be said from appearance of a new peak in Raman spectra corresponding to an alloy semiconductor.

Figure 7 shows Raman spectra from GaAs-InAs strained superlattice after thermal annealing. A peak at $260cm^{-1}$ is known as zone folding optical phonon. Its intensity decreased by thermal annealing at 450°C for 10 minutes and could not be observed after annealing at 500°C. Zone folding phonon from GaAs-AlAs, however, disappeared after annealing at a relatively high temperature such as 750°C. Frequency of GaAs LO phonon from GaAs-InAs superlattice which had shifted to higher one before annealing from that of bulk crystal varied with annealing to that of

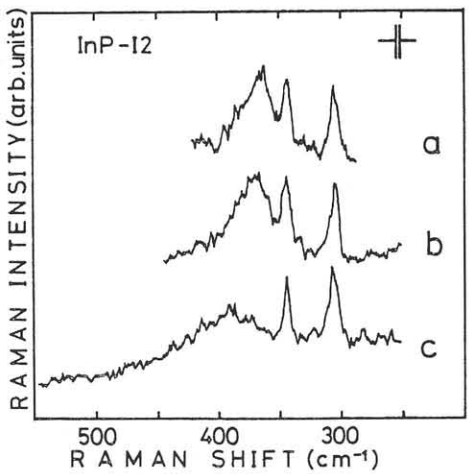

Fig. 5 Raman spectra from n-InP obtained with different powers. Products of a laser power and an integration time were (a)5x50, (b)10x25, and (c)50 mW x 5s.

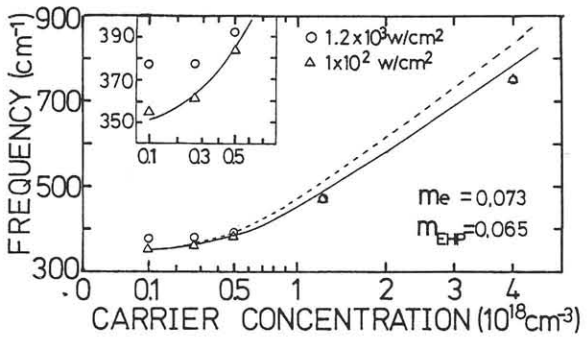

Fig. 6 Frequency ω^+ of the L^+ mode from InP with various carrier concentrations. Δ and O are the measured frequency with a laser of a lower power density 10^2 and a higher power density 1.2×10^3 W/cm^2, respectively. A solid line and a dashed line are the calculated frequency corresponding to the equilibrium carrier concentration and the optically excited carrier concentration, respectively.

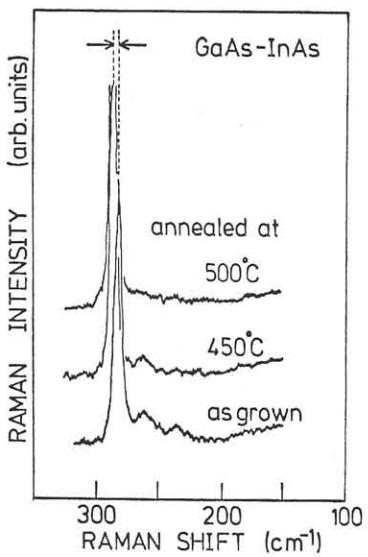

Fig. 7 Raman spectra from GaAs-InAs strained superlattice after thermal annealing.

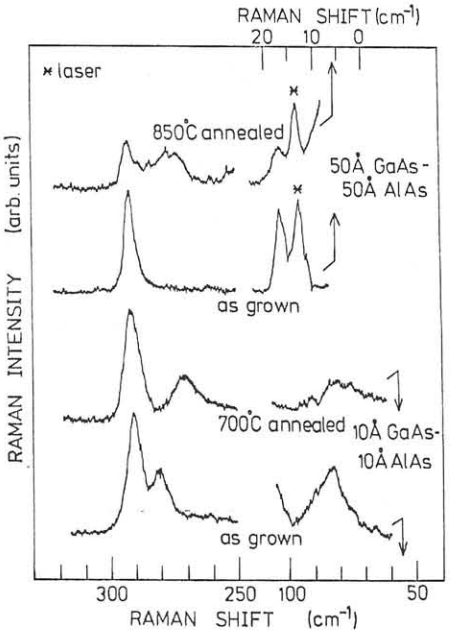

Fig. 8 Raman spectra from GaAs-AlAs superlattices with different periods obtained after annealing.

bulk GaAs probably due to decrease in stress.

Zone folding acoustic and optical phonons from 10Å GaAs-10Å AlAs superlattice disappeared and a new peak corresponding to bulk $Ga_{0.5}Al_{0.5}As$ appeared by thermal annealing at 700°C while the phenomenon was observed after annealing at 850°C for the 50Å GaAs-50Å AlAs superlattice as shown in Fig. 8.

Following results were obtained from the change of Raman spectra with annealing. (1) Instability was produced by thermal annealing at a lower temperature for GaAs-InAs strained superlattice than that at which alloying occurred in GaAs-AlAs strain-free superlattice. (2) Alloying was observed by thermal annealing at a lower temperature for a GaAs-AlAs superlattice with a shorter periodicity than that at which alloying was detected for a superlattice with a larger periodicity.

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1) T. Nakamura, A. Ushirokawa, and T. Katoda, J. Appl. Phys., 38, 13 (1981).
2) T. Nakamura and T. Katoda, J. appl. Phys., 55, 3064 (1984).