Raman Spectroscopy

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Mar 11, 95

Abstract

Theory of Raman scattering and an experimental setup are described. Raman Spectra of GaAs is explained.

1 Introduction

Raman scattering is an inelastic process in which an incident photon of energy $\hbar\omega_i$ interacts with the lattice via electrons to create (Stokes) or to destroy (AntiStokes) a phonon of energy $\hbar\omega_o$ and also create a photon of energy $\hbar\omega_s$.

$$\omega_s = \omega_i \pm \omega_o$$

Only those phonons having certain type of symmetry give rise to Raman scattering. The symmetry requirement imposes selection rules which are derived from group theory. For scattering of light in crystals, momentum is also conserved along with energy.

$$k_s = k_i + \mathrm{q}$$

q is crystal momentum. Magnitude of the scattering vector is in general given by

$$\mathrm{k} = 2\ \mathrm{Pi}\ \mathrm{n}/\lambda$$

where n is refractive index and λ is the wavelength of light in vacuum. The phonon wave vector can take any value lying in the Billouin zone(BZ). The maximum value being limited by the width of the BZ(Pi/d) where d is the lattice constant. In most Raman scattering experiments the wave vector inside the crystal is of the order of $10^{15}cm^{-}1$ and the wave vector conservation requires that wave vector of phonon created or destroyed is of the order of $10^{5}cm^{-}1$. This is small compared to (Pi/d) $10^{8}cm^{-}1$ and only the long wavelength phonons(phonons from the center of the BZ where q$\approx$ 0 are observed in first order Raman scattering. Phonons with large q are observed in second order Raman scattering.

2 Experimental Setup

A block diagram of the experimental setup used for backscattering Raman Spectroscopic studies (Fig1).

It consists of Light Source, Sample compartment, Double monochromator(DM) and Detection system [1].

2.1 Light Source

Laser used in Raman scattering experiments is an Ar ion laser(Innova 90-5, Coherent). It is a gas laser with CW o/p at various discrete wavelengths. The o/p of this laser is vertically polarized and has a natural linewidth of 4GHz($10^{-2}cm^{-}1$).

2.2 Sample Compartment

Laser beam is directed onto the sample by means of 2 mirrors . These mirrors are dielectric coated and reflect more than 99 percent of the incident light and maintain the polarization. The laser beam after reflection from these mirrors is focussed on the sample by means of a plano convex lens of focal length 15 cm, which gives a focussed spot of 75 microm in

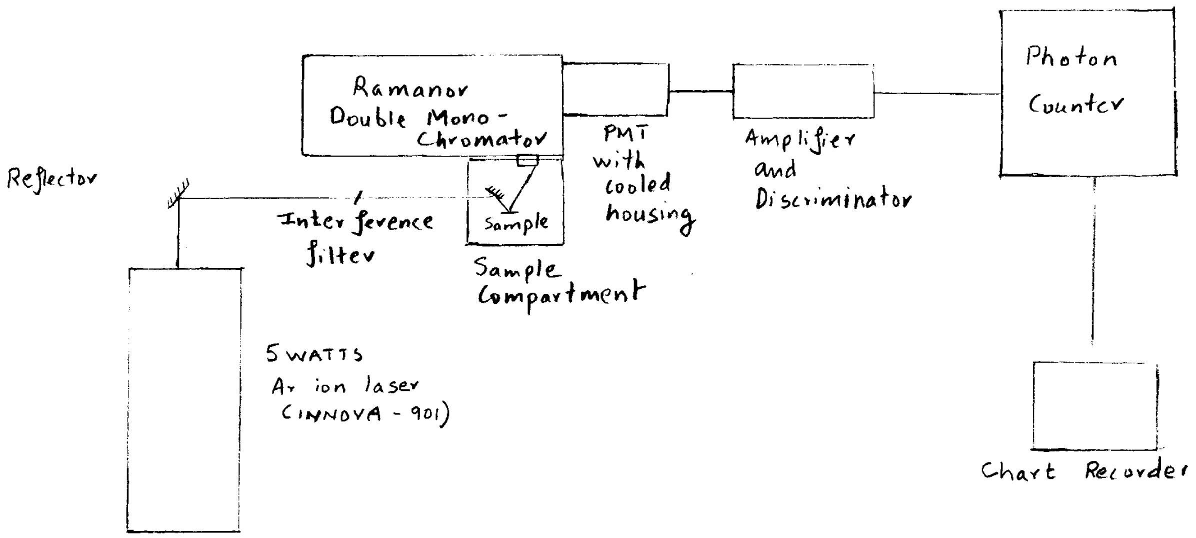

Fig 1 :- BLOCK DIAGRAM OF THE EXPERIMENTAL SET UP USED FOR RAMAN SCATTERING STUDIES

diameter for 514 nm line . Sample is mounted on aprecision x-y stage, which enables a tight focussing of the laser beam on the sample.

A small mirror of diameter 5 mm is used in front of the objective lens in ordrer to fold the laser beam pependicular to the sample surface. In all these experiments, the reflected beam from the sample is kept away from the objective lens by tilting the sample slightly to avoid the stray light entering the spectrometer.

2.3 Double Monochromator(DM)

The scattered light from the sample is analyzed by the Ramanor DM. The scattered light is focussed on to the enterance slit of the DM by means of an objective lens (F/1.8 aperture). The spot on the enterance slit is viewed through a periscope attached to the spectrometer for better allignment. This DB is fitted with two identical concave holographic gratings of 2000 grooves/mm , corrected for astigmatism and coma. The gratings have an aperture of f/8 with a focal length of 1 m and are blazed for 5000 A.The throughput of the spectrometer is high when light is polarized perpendicular the grating groove. Holographic grating eliminates ghosts and gives high stray light rejection, which is desired for samples having poor quality surfaces and surface defects. The spectrometer was calibrated with low pressure CdHg lamp and also with Ar ion laser plasma lines with accuracy of better than 0.5 cm^{-1}. Resolution of the spectrometer was checked by recording fine structure of 459 cm line of CCl_4 which was better than 1 $cm^{-}1$ using a 30 microm slit width. The response of the spectrometer for different incident photon energies is given by the throughput curve.

2.4 Detection System

The scattered light is analyzed by DM is focussed onto the cathode of Hamamatsu R942-02 photomultiplier tube(PMT). PMT has GaAs photocathode of small cathode area (10mm by 10mm) suitable for low level light detection , as it provides high signal to noise(S/N) ratio. Spectral response of this tube covers wide spectrum from 160-930 nm,with almost flat response from 300 to 800 nm. It was operated at 1825 Volts to optimize both gain and S/N ratio . S/N ratio is further improved by reducing dark current (due to thermionic emission of photocathode of PMT) by keeping PMT in a housing cooled by thermoelectric effect. O/p of PMT is in the form of weak discrete photoelectric pulses . These pulses are then amplified before being fed to the discriminator. The amplifier Discriminator unit permits individual photoelectron pulses seperated by as little as $10^{-}8$ secs to be resolved . Amplification factor is 350. A small coaxial cable is used to connect the PMT to the Amplifier Discriminator combine to avoid interference from external radio frequency signals. A compatible photoncounter (EG and G, model 1101) is used to count the photon pulses over time intervals adjustable from 1sec to 9990 secs. use of D to A convrter is made and analog signal is recorded on a strip chart recorder. The chart recorder speed and the speed of the steppor motor in DM are synchronized for direct reading of Raman intensity vs wavenumber shift.

3 Experimental Results

We now discuss the experimental results got for crystalline GaAs. In polar semiconductors like GaAs which is of Zinc Blende type ,the long wavelength optical phonons at the centre of BZ (Γ point) have Γ_{15} symmetry and are split into TO and LO phonons by the macroscopic electric field associated with the crystals. Hence in polar semiconductors this additional long range interaction has to be induced on the RS mechanism. In GaAs scattering by LO or TO phonons is decided by the orientation of the crystal and polarization vector. For example for $\prec 100 \succ$ GaAs ,in backscattering geometry only LO phonons are allowed, However, in most experiments, a small TO phonon is also observed probably because of misalignment of sample from true backscattering geometry.

Raman spectrum for GaAs crystal with $\prec 100 \succ$ orientation is shown (Fig2)[2]. The first order Raman spectrum consists of 2 peaks at 291 $cm^{-}1$ and 268 $cm^{-}1$, corresponding to LO and TO phonons respectively associated with the BZ center. Raman intensity is very weak in opaque materials like GaAs, because the laser light penetrates merely to the skin depth and the scattered light is strongly absorbed in crystals. Therefore the measurement of second order RS of GaAs is rather difficult. The second order RS generally consists of a structure between 50 and 250 $cm^{-}1$ with apeak at about 160 $cm^{-}1$, a structure between 300 and 400 $cm^{-}1$, and a very weak structure between 490 and 600 $cm^{-}1$. The fine structure between 300 and 400 $cm^{-}1$ is due to the combination of modes and was first reported by Tomoyuki Sekine etal. Weak structure between 400 and 490 $cm^{-}1$ is probably due to an overtone of longitudinal Acoustic(LA) and LO phonons. The structure between 300 and 400 $cm^{-}1$ consists off 2 small broad peaks at 335 $cm^{-}1$ and 371 $cm^{-}1$ the former being due to combination of TA and TO phonons and the later due to superposition of the overtone of the LA phonons and their combination. The structure between 490 and 600 cm^-1 is from the overtone of the optical phonon.

References

[1] P.Venkataraman, Thermal and anodic oxidation of GaAs and study of oxide and oxide to GaAs interface using Raman Spectroscopy, *MTech thesis*, 1989, IITD.

[2] R.Ashokan, Raman studies of implanted and pulse annealed GaAs, *Phd thesis*, 1986, IITD.

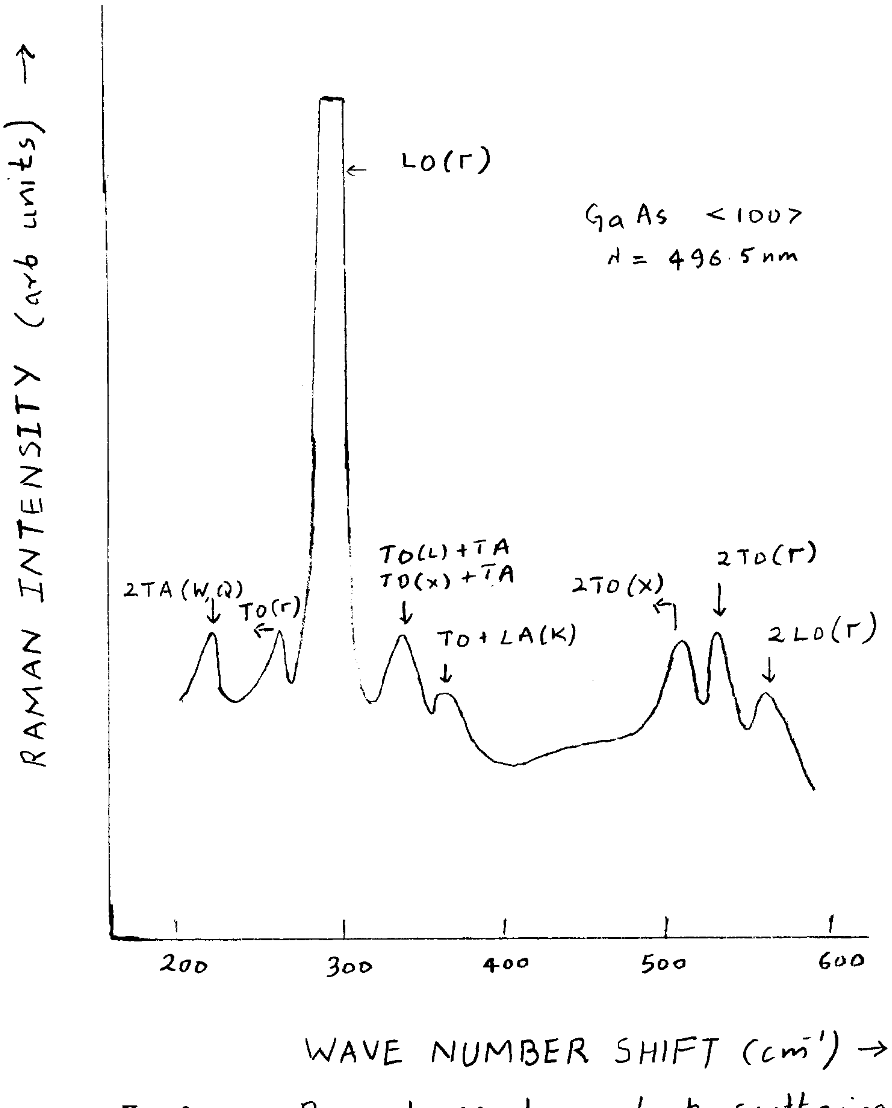

Fig 2 :- Room temperature back scattering Raman spectrum of <100> GaAs recorded with 496.5 nm line of Ar ion laser.