

Raman Scattering in Low Dimensional Semiconductors: Theoretical Aspects

¹Goutam Kumar Paul and ²Sujit Kumar Bera

¹Assistant Professor, ²Associate Professor

¹Department of Physics,

¹Hooghly Mohsin College, Hooghly - 712101, West Bengal, India

²Department of Physics,

²Tamralipta Mahavidyalaya, Tamluk - 721636, Purba Medinipur, West Bengal, India

Abstract: Raman scattering is one of the most informative experimental techniques that allows one to observe elementary excitations of solids by the frequency shift between incident and scattered photons on a sample. In this work the theoretical basis of Raman scattering have been presented in a very lucid manner and its applicability towards low dimensional semiconductors have been focused.

Index Terms: Raman scattering; Low dimensional semiconductors; phonon-phonon interaction; electron-phonon interaction; FWHM.

I. INTRODUCTION

Raman scattering is has proven to be one of the most powerful non-invasive techniques and becoming a widely used tool for the characterization of semiconducting materials down to nanometer scale [1] because of the fact that it is very much sensitive to crystal sizes below a few hundred angstroms. It can give information on the crystal and electronic structures, strain, temperature, phonon-phonon, and electron-phonon interaction [2]. In the particular case of semiconductor nanostructures [3, 4], Raman scattering provides additional information related to surfaces. Through a careful and detailed analysis of the first order Raman spectrum, accurate determination of the shape and size microcrystalline grains in a thin semiconducting film is possible. In this context it may be mentioned that, First order Raman spectra are sensitive to some other factors including surface strain, surface vibrations, mixed amorphous/microcrystalline phases in the samples and also intra-grain defects. Compared to the First order Raman Spectra, Second order Raman spectra are more sensitive to microcrystalline effects. The shape and size of the crystallites are directly related to the line shape, asymmetry and broadening of the Raman spectra. Thus, a lot of scientifically important information including compositional information as well as electronic structure can be extracted by properly analyzing the Raman spectra of the specimen under experiment. In this work we have described the theoretical aspects of Raman scattering with a special emphasis on the low dimensional semiconducting systems.

II. DETAILS OF THE PROCESS

Raman scattering allows one to observe elementary excitations of solids by the frequency shift between incident and scattered photons on a sample. From the viewpoint of quantum mechanics the first step in a Raman Process is the absorption of a photon. This leads to an intermediate electronic state, which may interact with elementary excitations (i.e. *phonons*) via several mechanisms, and elementary excitations are created or annihilated. Finally, photon with up-shifted or down-shifted frequency is scattered from the sample.

We know that, the energy of lattice vibration is quantized. The quantum of acoustic or vibrational energy is called *phonon*, which is considered as discrete particle and used especially in mathematical models to calculate thermal and vibrational properties of solids. All kinds of lattice vibrations are composed of *phonons*: thermal vibrations in crystals are *thermally excited phonons*; sound waves are *acoustic phonons* and the excitation of the optical branch results in *optical phonons*.

Raman scattering is basically an interaction of light with the optical modes [5] of lattice vibration. In the scattering process, the incident phonon gives a part of its energy ($h\nu_i$) to the lattice in the form of a phonon of energy ($h\nu_0$) and emerges with a lower energy ($h\nu_s$).

$$h\nu_s = h\nu_i - h\nu_0 \quad (1)$$

This down-converted frequency shift is the Stokes-shifted scattering. Another way of viewing this interaction is that the incident photon excites a phonon, while the semiconductor re-emits the remaining energy of the exciting photon. The exciting photon can raise an electron to a virtual level from which the scattered radiation is emitted. In semiconductors the absorption of photons by excitation across the band gap leads to intermediate states in the form of electron-hole pairs which are scattered and which recombine. However, if the exciting photon has energy greater than the band gap energy, the transition is to a real state and a much stronger excitation results.

If the lattice of the semiconductor is already in an excited state i.e., it already has an appreciable density of phonons, then the scattering process can result in the emission of a more energetic photon.

$$h\nu_s = h\nu_i + h\nu_0 \quad (2)$$

These up-shifted frequency shifts are the anti-Stokes-shifted scattering modes.

Normally, the intensity of the anti-Stokes modes is much weaker than that of the Stokes components, because there are few phonons to be absorbed compared to the density of phonons that can be emitted, the probability of absorption being lower than

the probability of emission by a factor of $e^{\frac{h\nu_0}{kT}}$. However, the phonons resulting from Stokes-shifted process (phonon-emission) can subsequently participate in the anti-Stokes process (phonon-absorption). Hence, at strong excitation, the Stokes and anti-Stokes components can be nearly equal.

In addition to the conservation of energy, momentum must also be conserved in the photon-phonon interaction. The momentum of a photon ($k = \frac{2\pi}{\lambda}$) is very small compared to the range available to phonons (up to $q = \frac{2\pi}{a}$, a being the lattice spacing).

Because the interaction involves two photons and one phonon the momentum of the phonon is restricted to small values, extending at most to twice the momentum of a photon.

So, the conservation conditions are

$$h\nu_{s1} = h\nu_i \pm h\nu_0 \quad (3a)$$

$$k_{s1} = k_i \pm q \quad (3b)$$

(- ve sign applies for Stokes shift and + ve sign applies for anti-Stokes shift).

Here, $\eta\vec{q}$ is the crystal momentum vector of the elementary excitation and \vec{q} is the wave vector of the phonon.

It may be noted here that the resulting photon of energy $h\nu_{s1}$ can in turn interact with the lattice to produce a second photon of still lower energy:

$$h\nu_{s2} = h\nu_{s1} - h\nu_0 = h\nu_i - 2h\nu_0 \quad (4)$$

This cascade process can be repeated m times, emitting

$$h\nu_{sm} = h\nu_i - mh\nu_0 \quad (5)$$

However, the intensity of the interaction decreases as the order of the process increases. *The intensity of the multiphonon shifted radiation is enhanced when its energy coincides with the energy of an exciton.*

Since $|k_i|$ and $|k_s|$ in the visible range of the spectrum are small compared to reciprocal lattice vectors, only *elementary excitations* (i.e. *phonons*) with $|\vec{q}| \approx 0$ participate in Raman processes, i.e., only states close to the *Brillouin zone* center can be observed.

Due to electron-photon and electron-phonon [6] interactions the Raman intensity and its resonance behaviour depends on the underlying electronic structure. For a theoretical description of these effects in the vicinity of critical points it is usually sufficient to consider the term, which leads to the strongest resonances. For the first order Stokes Raman process, the Raman intensity (I) may be expressed as follows:

$$I \approx \left| \sum_{\mu_i, \mu_j} \frac{\langle F|H|\mu_j\rangle \langle \mu_j|H_{EL}|\mu_i\rangle \langle \mu_i|H|I\rangle}{(\eta\omega_s - E_{\mu_j} + i\Gamma_{\mu_j}) \cdot (\eta\omega_i - E_{\mu_i} + i\Gamma_{\mu_i})} \right|^2 \quad (6)$$

The initial and final states of the system are given by $|I\rangle$ and $|F\rangle$ respectively. The summation extends over all possible intermediate states $|\mu\rangle$ with energies E_μ and broadenings Γ_μ . Resonances of the Raman intensity occur whenever the energy denominators in the above equation become small for a suitable choice of $\eta\omega_i$ or $\eta\omega_s$. In semiconductors this is the case for excitation at band gaps and other critical points of the electronic structure. Resonances of $\eta\omega_i$ with E_μ are called *incoming* and those of $\eta\omega_s$ with E_μ are called *outgoing*.

In *super lattices* and *quantum wells* made from semiconductors one finds significant changes in the electronic structure and the lattice-dynamical properties as compared to the bulk. Varying band gaps of the different constituents cause periodic potentials across samples. The simplest case is the Kronig-Penney square well potential for electrons and holes [7]. For sufficiently high or thick barriers the electronic states are confined in isolated potential wells. The wave functions in the well plane can be regarded approximately as standing waves which, however, penetrate somewhat into the adjacent barrier material. In the limit of infinitely high barriers the energies E of these states are given by

$$E = \frac{\eta^2}{2m^*} \left(n \frac{\pi}{d} \right)^2 \quad (7)$$

where, d is the layer thickness and m^* is the effective mass of the carriers. The index $n = 1, 2, 3, \dots$ labels the number of half wavelengths in the wave function of a confined state; $n \left(\frac{\pi}{d} \right)$ can be regarded as a wave vector. For even (odd) n the wave functions have odd (even) parity with respect to the center of the well. While the continuous bulk dispersion is split into discrete levels along the direction of potential modulation, the movement of carriers in the well plane is free. For finite barriers the wave functions confined to individual wells penetrate into the neighbouring material. In analogy to the superposition of electronic states and the formation of bands in connection with the transition from single atoms to a bulk crystal, the mini-bands of a SL (super lattice) form when the overlap between single QW (quantum well) functions increases.

In Raman spectra taken on perfect single crystals only optical phonons close to the Γ point of the Brillouin zone are observed, because of momentum conservation. The full width at half-maximum (FWHM) of such a Raman peak is reciprocally related to the lifetime of the phonon. The wave function of a phonon in an infinite perfect crystal is given by

$$\phi(\vec{q}_0, \vec{F}) = u(\vec{q}_0, \vec{F}) \exp(-i\vec{q}_0 \cdot \vec{F}) \quad (8)$$

where, \vec{q}_0 is the phonon wave vector and $u(\vec{q}_0, \vec{F})$ is a Bloch function of the crystal periodicity.

For nanocrystalline semiconductors the momentum will no longer be a good quantum number, because a phonon can no longer be described by a plane wave, but described by a wave packet localized in the microcrystal. As a result, not only $q = q_0$ phonons but also phonons with a certain momentum near the center of the Brillouin zone can also contribute to the first order Raman scattering. In other words, the wave vector selection rule during the Raman scattering process is partially broken down by the phonon confinement. Since the phonon dispersion curves are not flat, the Raman peak will shift, broaden and become asymmetric by the phonon confinement. This effect can be described by a weighting function $W(\vec{F}, L)$ for the phonon amplitude. Here L is the critical distance in nanocrystals corresponding for example to the diameter of the spheres or columns. For the later nanocrystal type its length is considered to be infinite. The resulting wavefunctions for phonons in nanocrystals are then given by [8]:

$$\psi(\vec{q}_0, \vec{F}) = W(\vec{F}, L)\phi(\vec{q}_0, \vec{F}) = u(\vec{q}_0, \vec{F})\psi'(\vec{q}_0, \vec{F}) \quad (9)$$

The wavefunction $\psi'(\vec{q}_0, \vec{F})$ can now be expressed in a Fourier series:

$$\psi'(\vec{q}_0, \vec{F}) = \int C(\vec{q}_0, \vec{q}) \exp(-i\vec{q} \cdot \vec{F}) d\vec{q} \quad (10)$$

The corresponding Fourier coefficients are

$$C(\vec{q}_0, \vec{q}) = \frac{1}{(2\pi)^3} \int \psi'(\vec{q}_0, \vec{F}) \exp(i\vec{q} \cdot \vec{F}) d\vec{F} \quad (11)$$

The phonon wavefunctions in nanocrystals can be expressed as a superposition of the eigenfunctions found for perfect single crystals. Therefore phonons out of an interval of \vec{q} vectors centred around \vec{q}_0 will contribute to the Raman scattering spectra. The Raman scattering intensity can be calculated using the following relation:

$$I(\omega) \propto \int \frac{|C(\vec{q}_0, \vec{q})|^2}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_0}{2}\right)^2} dq \quad (12)$$

where $\omega(q)$ is the phonon dispersion relation, Γ_0 is the natural line width. Equation represents a weighted integration of phonon Lorentzians. The weighting function influences the line shape of the phonon Raman peaks via the Fourier coefficients $C(\vec{q}_0, \vec{q})$. The type of weighting function which has to be used can only be chosen by physical arguments. $C(\vec{q}_0, \vec{q})$ is actually the Fourier transform of a phonon confinement function. An optical phonon dispersion relation is taken as $\omega(q) = \omega_0 - 120(q/q^*)^2$ where, $q^* = \frac{2\pi}{a}$, $L =$ diameter of the nanocrystals [9] and the Fourier coefficient $C(\vec{q}_0, \vec{q})$ is calculated to be [10],

$$|C(\vec{q}_0, \vec{q})|^2 = \frac{4L^2}{(2\pi)^4} \cdot \frac{\sin^2(qL/2)}{q^2(4\pi^2 - q^2L^2)^2} \quad (13)$$

Using the Fourier coefficients given by equation (13) in equation (12) the variation of intensity with photon wave vector can be obtained. Analyzing the line shape of Raman scattering intensity distribution, one can have an estimate of the size of crystallites, dispersion in the crystallite size etc. in low dimensional semiconducting thin films. Small physical dimensions of the scattering crystallites in the low dimensional systems lead to a downshift and broadening of the first order Raman line. Moreover, the exact shape of the microcrystal is related to the asymmetry and width of Raman spectra and also the amount of shift. Thus by analyzing the line shape of Raman spectra recorded for the given sample the interior of the crystals can be explored.

III. CONCLUSIONS

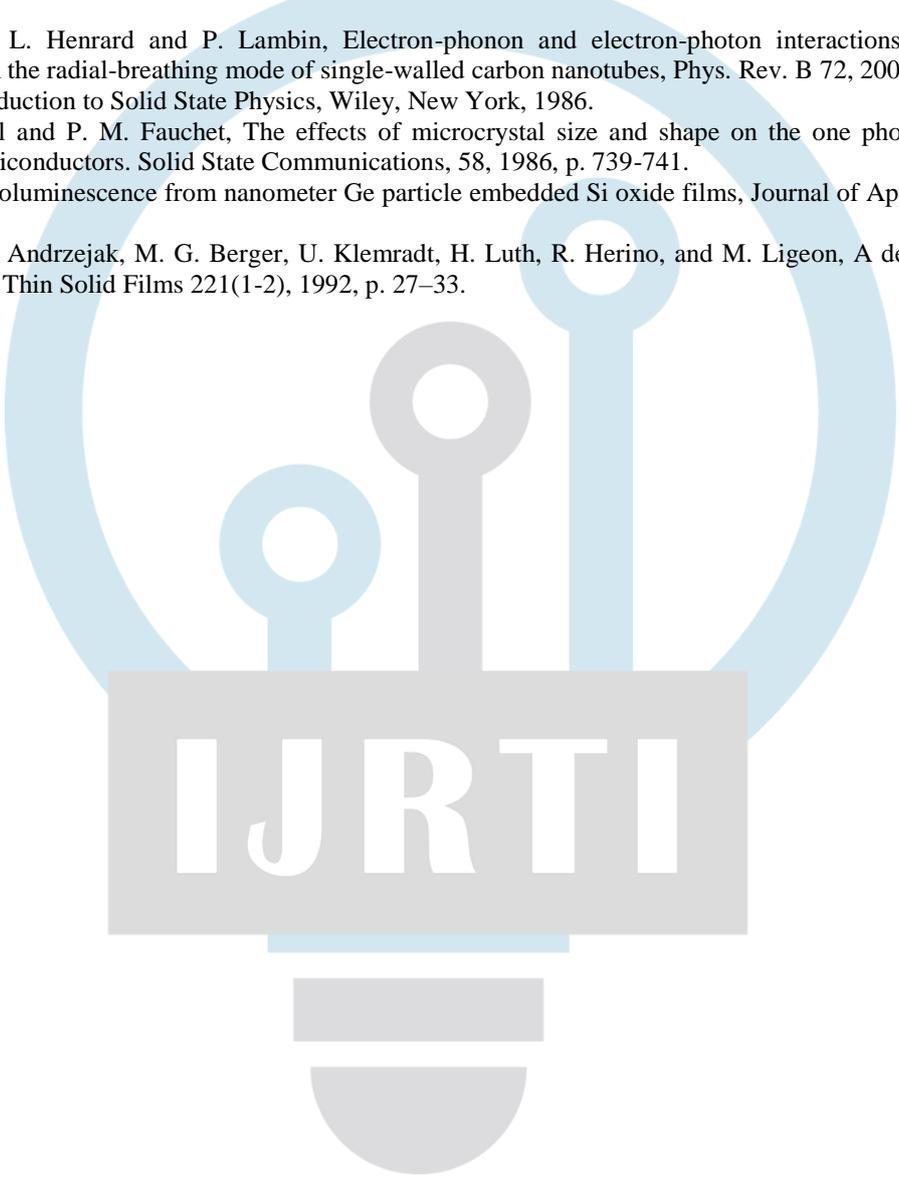
Raman scattering from low dimensional semiconductor crystallites can make significant changes in the first order Raman band, due to sized-induced relaxation of the wave vector selection rule. The Raman scattering technique can be successfully applied to micro-sized and nano-sized materials to obtain valuable information about crystallization of ultra thin amorphous films, phase separation in supersaturated solutions, the presence of amorphous and crystalline phases in nanostructured materials, nanocrystal size and shape, grain size distribution and lattice contraction. Resonance Raman scattering allows one to extract more reliable information, and to investigate the electronic structure of low-dimensional semiconductors. In this communication we have explained in detail the theoretical basis of Raman scattering and its applicability for extracting information of the crystallites including composition in low dimensional semiconducting materials.

IV. ACKNOWLEDGEMENT

The authors gratefully acknowledge Prof. A. K. Pal, USIC, Jadavpur University for his guidance and constant inspiration.

REFERENCES

- [1] P. M. Fauchet, I. H., Critical Review of Raman Spectroscopy as a Diagnostic Tool for Semiconductor Microcrystals, MRS Online Proceedings Library 164, 1989, p. 259-264.
- [2] A. Cantarero, Review on Raman scattering in semiconductor nanowires: I. theory, J. of Nanophotonics, 7(1), 2013, p. 071598 1-28.
- [3] C. M. Lieber, Semiconductor nanowires: a platform for nanoscience and nanotechnology, MRS Bulletin 36, 2011, p. 1052 – 1063.
- [4] P. Yang, R. Yan, and M. Fardy, Semiconductor nanowire: what's next?, Nano Lett., 10, 2010, p. 1529 - 1536.
- [5] A. Yu. Boikov, S. V. Karpov and S. V. Mikushev, Appearance of polar optical modes in Raman scattering in semiconductor nanocrystals, Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques 2, 2008, p.37-41.
- [6] V. N. Popov, L. Henrard and P. Lambin, Electron-phonon and electron-photon interactions and resonant Raman scattering from the radial-breathing mode of single-walled carbon nanotubes, Phys. Rev. B 72, 2005, p. 035436 1-10.
- [7] C. Kittel, Introduction to Solid State Physics, Wiley, New York, 1986.
- [8] I. H. Campbell and P. M. Fauchet, The effects of microcrystal size and shape on the one phonon Raman spectra of crystalline semiconductors. Solid State Communications, 58, 1986, p. 739-741.
- [9] S. Y. Ma, Photoluminescence from nanometer Ge particle embedded Si oxide films, Journal of Applied Physics 84, 1998, p. 560.
- [10] H. Münder, C. Andrzejak, M. G. Berger, U. Klemradt, H. Luth, R. Herino, and M. Ligeon, A detailed Raman study of porous silicon, Thin Solid Films 221(1-2), 1992, p. 27–33.

A large, light blue watermark logo is centered on the page. It features a stylized lightbulb shape with a circular top and a semi-circular base. Inside the circle, there are three vertical stems of varying heights, each topped with a small circle. A grey rectangular box is superimposed over the middle of the logo, containing the text 'IJRTI' in white, bold, sans-serif capital letters.

IJRTI