# **Study of Microscopic Level Physics at Nanoscale Using Raman Scattering**

**M.Sc.** Thesis

By KM NEESHU



### DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE 2020

# **Study of Microscopic Level Physics at Nanoscale Using Raman Scattering**

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by KM NEESHU



### DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE2020



### INDIAN INSTITUTE OF TECHNOLOGY INDORE

#### CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled Study of Microscopic Level Physics at Nanoscale Using Raman Scattering in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2019 to June 2020 under the supervision of Dr. Rajesh Kumar, Associate Professor.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.



Signature of the student with date KM NEESHU

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the Supervisor of M.Sc. thesis with date Dr. Rajesh Kumar

KM NEESHU has successfully given her M.Sc. Oral Examination held on 22 02 20

Convener, DPGC

Signature(s) of Supervisor(s) of MSc thesis Date: 22/6/2020

Date: 22/06/2020 .

Member (Dr. Vinod) Signature of I

Date:

Date: 22106/2020

#### ACKNOWLEDGEMENTS

Above all, I would like to express my thankfulness and deepest gratitude to almighty **God, Lord Krishna** by whose grace and blessings, I would have been able to achieve this academic endeavor.

My deepest gratitude and indebtedness goes to my thesis supervisor **Dr. Rajesh Kumar** for giving me the possibility to do this interesting project and for his trustworthy advices and support through all the phases of the project. I am indebted to him for his some remarkable qualities, such as his depth of perception and lucid presentation, perhaps the best I have come across so far, will always continue to inspire me. The experience of working with him, I strongly believe, will have far-reaching influence in my future life.

I am also grateful to my **PSPC** members **Dr. Vinod Kumar and Dr. Suman Mukhopadhyay** for providing me guidance from time to time. I am thankful to and fortunate enough to get constant encouragement, support and guidance from all teaching staff of Physics department.

I am also thankful to all my lab mates ,specially **Devesh Pathak** and **Manushree Tanwar** for their cooperation, and my classmates for their support during my research work. I am extremely thankful to **Neeraj Singh** and my brother **Ankur Sharma** from the core of my heart for their motivations and valuable suggestions to overcome the difficulties during the course of my project work.

Finally last but not least, my sincere gratitude and feelings goes to my respected parents, Shri Rohtash Sharma & Smt. Neelam Sharma and my siblings, Tanu Sharma & Ashish Sharma, for their encouragement and support, which gave me confidence to materialize this research work.

KM NEESHU

Under the inspiration of Almighty God, the present thesis is dedicated to my parents and my siblings

#### Abstract

A comparison of experimentally observed Raman scattering data with Raman line-shapes, generated theoretically using phonon confinement model, has been carried out to understand the sensitivity of different Raman spectral parameters on quantum confinement effect. Size dependent variations of full width at half maximum (FWHM), Raman peak position and asymmetry ratio have been analyzed to establish the sensitivity of their corresponding physical counterparts (phonon life time and dispersion) in confined systems. The comparison has been done in three different confinement regimes namely, weakly, moderately and strongly. Proper reasoning has been assigned for such a variation after validation of the theoretical analysis with the experimental observations.

A moderately confined system was created by preparing 6 nm sized silicon nanostructures using metal induced etching. An asymmetrically broadened and red shifted Raman line-shape was observed which established that Raman width to be the most sensitive parameter. Raman spectral asymmetries induced by electron phonon interaction (Fano resonance) with quantum confinement effect have also been discussed for Si NSs. The methodology has been validated by studying the effect of similar microscopic perturbations, Fano coupling with quantum size effects on different Raman spectral parameters to know the sensitivity of different Raman spectral parameter. Sensitivity of a given Raman spectral parameters has been shown to be used as a tool to understand the role of external perturbations in a material.

#### LIST OF PUBLICATIONS

1. Neeshu, K.; Rani, C.; Kaushik, R.; Tanwar, M.; Pathak, D.; Chaudhary, A.; Kumar, A.; Kumar, R. Size Dependence of Raman Line-Shape Parameters Due to Confined Phonons in Silicon Nanowires. *Advances in Materials and Processing Technologies* **2020**, *0* (0), 1–8. https://doi.org/10.1080/2374068X.2020.1740876

2. Kaushik, R; Rani, Chanchal; Neeshu, Km; Tanwar, Manushree ; pathak, D; Chaudhary, Anjali ; Siraj, Fouzia; Jha, H; Kumar, Rajesh, Brain Tumor Detection and Grading using Raman Scattering: Analogy from Semiconductors for Solving Biological Problem (communicated).

## Contents

1 Introduction 1
1.1 Raman Spectroscopy 3
1.2 Silicon 4
1.3 Techniques to Prepare Silicon Nanostructures
2 General Overview 7
2.1 Overview of Silicon7
2.1.1 Crystal Structure 7
2.1.2 Optical Properties
2.2 Effect of Reduce Dimensions 11
2.2.1 Energy Gap Enhancement12
2.3 Raman Scattering 13
2.3.1 Raman Scattering in Solids 14
2.3.2 Raman Scattering in c-Si 17
2.3.3 Raman Scattering from Nano Crystalline Semiconductor18
2.4 Raman Study of Electron-Phonon Coupling
3 Experimental Methodology and Sample Details 23
3.1 Sample Preparation 23
3.1.1 Metal Induced Etching Method 23
3.1.2 Mechanisms24
3.2 Instruments' Details26
3.2.1 Scanning Electron Microscope
3.2.1.1 Signals Generated 26
3.3 Raman Spectroscopy27
3.4 Experimental Details

- 4 Confinement of Phonons in Low Dimensional Silicon 33

6 Conclusion and Future Scope 59

#### LIST OF FIGURES

2.1 Silicon crystal structure	8
2.2 Energy band diagram of Si	9
2.3 Interband transitions	10
2.4 Enhancement in energy band gap with size	12
2.5 Diagram of stokes and anti-stokes component of scattered li	ght 13
2.6 Raman scattering processes in terms of interactions	16
2.7 Raman spectrum of c-Si	17
2.8 Raman spectra for c-Si (bulk)	19
2.9 Raman spectra for Si nanowires (4nm)	20
3.1 Schematic diagram of step by step formation of SiNWs	25
3.2 Schematic diagram of Raman Spectrometer	28
3.3 (a) Surface morphology of Si NSs	30
3.3 (b) Raman spectrum of Si NWs along with theoretical fitting	g 31
using PCM	
4.1 Raman line-shapes as a function of Si NWs size	35
4.2 Shows various definitions of Raman parameters	38
4.3 Theoretical Raman line-shapes as a function of Si NSs size	40
generated using PCM	
4.4 Raman shift, FWHM and asymmetry ratio as a function of	41-42
size for two degree of confinement	
4.5 Rate of change of Raman line shape parameters as a function nanocrystallite sizes for two degree of confinement	n of 44
4.6 FWHM, asymmetry ratio and Raman shift as a function of s	ize for 46
one degree of confinement	

4.7 Rate of change of Raman line shape parameters as a function of47 nanocrystallite size for one degree of confinement.

5.1 Diagram representing Fano resonance	51
5.2 Theoretical Raman line shapes for heavily doped n-type c-Si	52
and p-type c-Si	
5.3 Theoretical Raman line shapes generated for different values	55
of Fano coupling parameter for donor type	
5.4 Rate of change of variation of width and Raman peak shift	56
as a function of Fano parameter for donor type	
5.5 Theoretical Raman line shapes and rate of change of variation	57
of width and Raman peak shift as a function of Fano parameter for	
acceptor type	

#### ACRONYMS

Acronym	Meaning
NSs	Nanostructures
PL	Photoluminescence
MNPs	Metal Nanoparcticles
Si NWs	Silicon Nanowires
Si NSs	Silicon Nanostructures
MIE	Metal Induced Etching
РСМ	Phonon Confinement Model
FWHM	Full Width at Half Maximum
c-Si	Crystalline Silicon
n-Si	Nano Silicon
a-Si	Amorphous Silicon
c-Si-N	n-type Crystalline Silicon
c-Si-P	p-type Crystalline Silicon

# Chapter 1

## Introduction

Nanotechnology [1] is one of the leading research areas which the whole world is focused at. Nanotechnology products in the market today are mostly gradually improved products. Nanotechnology attracts the attention of media, researcher, industry and public too [2, 3] because it provides great potential in improving the well-being of humankind [4]. In other words, nanotechnology is amalgam of state of the art in biotechnology, medical sciences, physics, chemistry, engineering and many more disciplines and interdisciplinary areas [4].

Due to the increased interest in it an obvious question tihat comes in mind is what exactly is nanotechnology and what makes it so important? It could not be and need not be define properly because it is highly converged topic in nature and diversified in applications so it can not confined within a single discipline. That's why; one of the problems facing by this technology is the confusion about how to define Most revolve around the study and control of nanotechnology. phenomena and materials at length scales below 100 nm. The most important requirement for the nanotechnology definition is that the nano structure has special properties, which are depend on the size of structures and cannot observed in the bulk form that are exclusively due to its nanoscale proportion. For example inert material like platinum become catalyst, opaque substance like copper become transparent, insulating/semiconducting silicon (Si) becomes conductor and transforms to a direct band gap material from an indirect one [4]. Fascinating things

about nanotechnology is due to display of unique phenomenon at nanoscale. Today from agriculture to aerospace research impact of nanotechnology is being felt.

First observations and size measurements of nanoparticles were made during the first decade of the 20th century [5, 6]. They are mostly related with Richard Adolf Zsigmondy [6], using dark-field ultra-microscope he made a comprehensive study of gold sols and other nanomaterials with sizes less than 10 nm.

Materials of very low dimensions interact and assemble into structures which exhibit properties different from its bulk form enabling one to tailor properties such as vibrational, electronic and optical etc. [7-9], by simply varying the size of the material in the range of nanometers. This is based on the number of dimensions of a material, which are outside the nanoscale range. Accordingly, in zero dimensional (0D) nanomaterials all the dimension are measured within the nanoscale; in one-dimensional nanomaterials (1D), one dimension is outside the nanoscale; in twodimensional nanomaterials (2D), two dimension are outside the nanoscale. In nanostructures, most of the electronic and vibrational properties are different compared to that of the bulk crystal, mainly due to the quantum confinement effect. Due to the reduced size, the De-Broglie wavelength of elementary excitations within nanostructures is in the order of the dimension of nanostructures. In fact, interest in the nanostructures is triggered by the discovery that their physical properties (electronic, optical, and thermodynamically) are different from those of the corresponding bulk material due to quantum confinement effect. Quantum confinement effect is one of the most significant effects in the current era of nanomaterials leading the research field in nanoscience and nanotechnology.

#### **1.1 RAMAN SPECTROSCOPY**

Raman spectroscopy has proved to be a very versatile tool for the detailed analysis of semiconductor nanostructures due to its sensitivity towards nanoscale perturbations in the systems which can be clearly distinguished by appropriately analyzing the Raman line-shape. Raman Spectroscopy, since its discovery in 1928, remains one of the most effective and easiest techniques when it comes to investigate quantum confinement effect [10, 11]. Raman spectroscopy provides a fast and convenient method to analyze the vibrational properties of solids.

Raman spectrum contains information about a solid through the response of solid's phonons to the incident photons by means of scattering. In an attempt to understand the significant variation in Raman line shape parameters with respect to the size, various theoretical models have been developed. Most of the models are based on the confinement of phonons in nano dimensional systems which show interesting variations for the case of 1-D, 2-D and 3-D confinement. Raman spectroscopy monitors the subtle changes taking place at the quantum level in a sensitive and precise way which helps the researchers to gain an exact analysis and understanding of the nanoscopic phenomena. For example, in case of crystalline silicon (c-Si) the Raman line-shape is a sharp and symmetric Lorentzian line peaked at 520 cm-1 owing to the participation of the zone centered phonons due to momentum conservation rule which in case of nanocrystalline silicon is not conserved and hence the line shape is a superposition of the spectrum arising from the phonons other than the zone centered ones thus containing a special set of information regarding confinement of phonons in the nanocrystal. The Raman line shape when examined appropriately gives a wholesome analysis of the perturbations at the confined regime. The interpretation of line shape can be done using line-shape parameters like Raman shift, Full Width at half Maximum (FWHM), and asymmetry ratio. One needs to carefully examine all these

parameters in order to understand the subtle changes at the nanoscopic level which are otherwise not appreciated using other microscopic technique due to the resolution limit.

#### **1.2 Silicon**

Silicon (Si) is the second most abundant element in the Earth's crust after oxygen and the gift of the nature to the mankind. Crystalline silicon is extremely important semiconductors. In the present scenario, the Si nanostructure has a very important role in nano-electronics [12-14], energy conversion [15–17], optoelectronics [18–20], energy storage [21], chemical or biological sensors and bionic models [21–24]. Si nanostructures are the most significant material for current semiconductor industry. Extensive studies on Si thin films [25], nanotubes [26,27], porous structures ,nanowires (NWs) [28], and nanoparticles [29–31] has been carried out over the past few decades due to their unique physical properties and various applications ranging from biophysics, electronics and medical sciences etc. [32].

Silicon, the backbone of IC industry, has not seen any competition when it comes to application in semiconductor industry. Applications of Si are restricted in the field of optically active material, due to its indirect energy band gap. However Si with reduced dimensionality becomes a light emitter and opens a possibility of its application in optoelectronics also. To use silicon nanostructures in device applications [2, 3] in an efficient manner, it is important to understand the size dependent properties and Raman line-shape parameters. There are still many properties of this material which is unexplored and thus still is an area of research interest. Visible photoluminescence (PL) at room temperature is another reason for the increased research activity in the area of Si NSs [33, 34]. However origin of the PL at room temperature has been a subject of extensive research since its discovery [35]. As being an indirect band gap material, Si in its bulk form restricts the emission of light [36] even at low temperatures. So many studies have been carried out by several research groups worldwide to understand the mechanism of this emission. But till now the mechanism for emission of visible PL from Si NWs is still in infant state and highly debatable research topic. However Several studies explains that the visible emission is due to the quantum confinement effect on the carriers or due to the strong oxide layer formed on the top of the nanostructures [37,38] with quantum confinement being the most acceptable one for the NSs.

Miniaturization process converts c-Si into a direct band gap material. Si NSs plays an important role in the fabrication and improvement in efficiency of solar cell [14]. As the size of Si becomes comparable to its Bohr's exciton radius, various properties get modified compared to its bulk counterpart. Presence of quantum confinement effect enables Si NSs to be used in new applications. The quantum confinement effect provides the flexibility to tune optical, chemical, electrical and thermal properties of Si.

## 1.3 TECHNIQUES TO PREPARE SILICON NANOSTRUCTURES

There are large variety of techniques that have been developed to fabricate Si nanostructures such as electron beam lithography, epitaxial growth, chemical vapor deposition and many simple chemical etching techniques. Amongst various techniques used for fabrication of Si nanostructures, metal induced etching, also known metal assisted chemical etching, is one of simplest and cheapest method for synthesis of semiconductor nanostructures.In this method, firstly metal nanoparticles are deposited on a clean semiconductor surface. After the metal coating step, wafers (containing metal nanoparticles) are transferred into etching solution. After a particular time of etching, silicon nano structures get fabricated on the semiconductor surface.

## Chapter 2

# Overview and Theoretical Background

#### 2.1 Overview of Silicon

Silicon [39], the second most abundant element in the Earth's crust, (~ 25.7% of the crust by mass), is the backbone for electronics and IC industry. It is commonly found in nature as Si dioxide (SiO<sub>2</sub>). It has crystalline structure same as that of diamond form of carbon. It shows many chemical and physical properties similar to carbon. Highly purified Si, doped with arsenic, phosphorus and boron, is the basic material which generally used in transistors, computer chips, Si diodes and various other electronic circuits. Three stable isotopes of the Si:  $^{28}$ Si (92.2 %),  $^{29}$ Si (4.7%) and  $^{30}$ Si (3.1%).

#### 2.1.1 Crystal Structure of Si

Si is a non-metallic element. It belongs to the fourth group of element in the periodic table having four electrons in its outermost shell. Each Si atom shares its valence electrons with each of four adjacent Si atoms.

Crystal structure of silicon shown in fig.2.1.It has diamond like crystal structure, described as being built from two interpenetrating fcc lattices which are displaced with respect to each other along the body diagonal of the cube by one fourth of the length of the diagonal. Crystal structure of

silicon derived from the fcc lattice although the structure is not a close packed one.



Fig.2.1 Crystal structure of Si [39].

It is a FCC lattice with a basis containing two identical atoms. In c-Si, useful model for practical purpose is to consider each Si atom to be at the centre of a tetrahedron with its four nearest neighbours at the four corners of the tetrahedron. The lattice parameter of c-Si is 0.543 nm and tetrahedral angle is 109.2°.

### 2.1.2. Optical Properties of Si

In bulk form, Si is an indirect band gap solid. The energy band structure of Si reported by Cardona and Pollak [40] shown in fig.2.2. It is clear from fig.2.2 that in case of c-Si, the maxima of valence band is located at the centre of the Brillouin zone and the minima of conduction band is located at X point along the  $\Delta$  direction which makes it indirect band gap material. Band gap of c-Si is 1.1eV. C-Si cannot emit light due to indirect nature of

band gap. For light emission to take place efficiently, radiative recombination of the electron-hole pairs needs the participation of phonon to conserved momentum, which makes the process less favourable. Unlike other semiconductors like GaAs and InP, in which the maxima of valence band and minima of conduction band are located at the same k point which makes them a direct band gap materials. In these materials, the radiative recombination is more probable then c-Si because no mediating phonon is required.



Fig.2.2 Energy band diagram of Si [40].

The schematic representation of indirect and direct band gap transition is shown in fig.2.3. It is clear from fig.2.3 that in an indirect band gap for transition to take place both photons and phonons involves at a time. According to quantum mechanics there are two different processes, first order and second order process. The first order process takes place through direct transition with no role of phonons whereas in the second order process indirect transitions is involve in which a photon must be destroyed and a phonon must be either created or destroyed.



Fig.2.3 Interband transitions in (a) direct band gap and (b) indirect band gap [41]

In fig.2.3 (a) shown interband transitions in direct band gap and in fig. 2.3(b) indirect band gap solids, where the vertical arrow represents the photon absorption while wiggly arrow represents the emission or absorption of a phonon [41].

#### **2.2 Effect of Reduced Dimensionality**

When the size of a material is reduced from a macroscopic size to a very small size, then the changes in the properties of nanomaterials can be observed. In low-dimensional systems physical properties (electronic, optical, and thermodynamically) are different from those of the corresponding bulk material, mainly due to quantum confinement effect [41, 42]. The changes in properties of the material take place when the De-Broglie wavelength of elementary excitations within nanostructures is in the order of the dimension of nanostructures.

When the confining dimension is large enough then the de Broglie wavelength of the particle, the particle behaves as free particle within the confined area. When the confining dimension is decreased and reaches the order of the De-Broglie wavelength, the electronic and vibrational states of particle modified due to the overlap of the wave functions reflected from the boundaries. This is defined as the "*quantum confinement*" [43, 42]. The effect of reduction in size or dimension of the semiconductor, known as quantum confinement effect. Quantum confinement effect leads to confinement of electrons and phonons in one or more directions. Due to quantum size effect, the electronic and optical properties of the semiconductors can be tailored for novel device applications. A variety of quantum structures can be fabricated, depending upon the degree of confinement, with modulated properties. Some major properties that change with size of the low-dimensional semiconductors are discussed below.

### 2.2.1 Energy Gap Enhancement

A reduced dimension of the semiconductor is reflected in modification of electronic energy gap. Band gap increases with decrease in size due to electron confinement at Nano-scale. Energy gap of the low dimension structure is enhanced due to quantum size effect shown in fig.2.4. This enhancement in energy band gap can be understood using the analogy to the problem of a particle within a potential box.



Fig.2.4 Enhancement in energy band gap with size [42]

#### 2.3 Raman Scattering

The phenomenon of inelastic scattering of light is known as Raman scattering. When a monochromatic light beam illuminates a solid, gas or liquid, small fraction of light is scattered in all directions. Scattered light almost consists of same frequency as incident, known as Rayleigh scattering. In addition to this there are some other frequencies below and above than the incident also present, known as Raman lines [43] (having higher and lower energies than the energy of incident). The lines on the lower frequency side of the exciting line are called 'Stokes' lines, whereas those on the higher frequency side are called 'anti-Stokes' lines. Observation of lower and higher frequency components along with the incident frequency in the scattered radiation is known as the Raman effect and this type of scattering is called Raman scattering.



**Fig.2.5** Diagram of lower frequency (stokes) and higher frequency (anti -stokes) components along with the incident frequency in the scattered radiation [43]

#### 2.3.1 Raman Scattering in Solids

In the Raman scattering [43, 44], certain amount of energy is lost or gained by an incident photon. This energy (lost or gain by incident photon) uses in order to create or annihilate elementary excitations (usually phonons) of the solid, resulting scattered photon of a different energy. For energy conservation in first order Raman scattering (one phonon participation), transfer of energy to the elementary excitation involved. The amount of energy transferred corresponds to the elementary excitation involved is given by

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\omega_p \tag{2.1}$$

Here  $\omega_i$  and  $\omega_s$  are incident and scattered frequency of photon and  $\omega_p$  is frequency of phonon. In eq 2.1, "minus" and "plus" sign stands for a phonon excitation (Stokes process) and annihilation (anti-Stokes process) respectively. According to momentum conservation, momentum  $\hbar k_p$  of the vibrational excitation is related to the momentum of the incident photon  $\hbar k_i$  and scattered photon  $\hbar k_s$  is given by

$$\hbar k_i = \hbar k_s \pm \hbar k_p \tag{2.2}$$

For Si (homopolar semiconductor), the electron lattice interaction is due to the excitation of phonons, which perturb the potential acting on the electrons by the displacement of atoms. The scattering of one photon by n phonons is governed by the momentum conservation rule given by

$$\sum_{p=1}^{p=n} \hbar k_p = \hbar k_i \pm \hbar k_s \approx 0$$
(2.3)

According to eq 2.3, momentum conservation allows the first-order Raman scattering for the phonon  $k \approx 0$  (only vibrations from the centre of Brillouin zone). Since  $k_i$  and  $k_s$  (~105 cm<sup>-1</sup>) are negligible in comparison to the width of the Brillouin zone (~3x10<sup>8</sup> cm<sup>-1</sup>),due to this only. Long wavelength phonons can be active in first order spectrum (in any one phonon process). This is the selection rule of the first-order Raman scattering for phonons. First-order Raman scattering is shown in fig.2.6(a).

In Second-order Raman scattering, is either a line spectrum or a continuous spectrum, in which two phonon participate [44]. Second-order Raman line spectrum arises due to two successive first-orders Raman scattering as shown in Fig. 2.6 (b), where the frequency shift is the sum or difference of Raman shifts occurring in the first-order Raman spectrum. Second-order Raman line scattering is the result of wave-vector conservation in two successive first-order Raman scattering.

The second-order continuous Raman spectrum is in which a pair of phonons participates in a single event as shown in fig. 2.6(c). According to wave vector conservation, the wave-vectors of two phonons should be equal and opposite.



**Fig. 2.6** Raman scattering processes in terms of interactions  $H_{E-L}$  (Electron-Lattice interaction Hamiltonian),  $H_{E-R}$  (Electron-Radiation interaction Hamiltonian),  $\omega_i$  (frequency of incident photon),  $\omega_p$  (frequency of vibrational excitation) and  $\omega_s$  (frequency of scattered photon). (a) first-order Raman scattering process and (b), (c) shows second-order Raman scattering.[45]
#### 2.3.2 Raman Scattering in Crystalline Si

Phonon frequencies present in the c-Si can be obtained from the phonon dispersion curve. Fig. 2.7 shows the Raman spectrum of c-Si. c-Si has a first-order Raman active peak with Lorentzian line-shape centred at 520.5 cm<sup>-1</sup> with natural line width of 4 cm<sup>-1</sup> at room temperature. Second-order Raman scattering [46] is shown in Fig. 2.7 in the frequency range 200–500 cm<sup>-1</sup> and 550 –1000 cm<sup>-1</sup>. A kink at 230 cm<sup>-1</sup> and the peaks at 300 cm<sup>-1</sup> and 435 cm<sup>-1</sup> are associated with the second order transverse acoustic (2TA) phonons (see Fig. 2.7) from the critical points at L, X and near  $\Sigma$  directions, respectively.



Fig.2.7 Raman spectrum of c-Si.

Weak scattering at 460 cm<sup>-1</sup> is associated with Raman scattering involving phonons along and near  $\Sigma$  direction. The features at 610 cm<sup>-1</sup> and 820 cm<sup>-1</sup> in the two phonon Raman spectra are contributed by two acoustic and optic phonons in the  $\Sigma$  direction, respectively. Scattering in the range 900-1050 cm<sup>-1</sup> is identified with second-order transverse optic (2TO) phonon overtones from the critical point at X, while shoulders at 940 cm<sup>-1</sup> and 975 cm<sup>-1</sup> are associated with 2TO phonon overtones at W and L point respectively [7-9].

### 2.3.3 Raman Scattering from Nano Crystalline Semiconductor

Raman spectroscopy is a powerful and sensitive tool to provide in-depth information on the structural modification caused by formation of nano structures. It is a useful tool for obtaining information about structural quality at the atomic scale of a material, because it depends on lattice excitations. Raman spectrum of a solid contain information about the response of solid's phonons to the incident photons by means of scattering. Raman spectroscopy is also sensitive to perturbation to electronic state of the solid.

Normally in crystalline materials in the bulk form, the Raman

scattering is limited to near zone centered phonons due to spectroscopic selection rule [47], which result in a symmetric Lorentzian line-shape spectrum(fig.2.8) and the peak of the spectrum at a frequency corresponding to the zone center phonon. This can be understand using Heisenberg uncertainty principle  $\Delta k.\Delta x \approx 1$  where  $\Delta x$  and  $\Delta k$  are the uncertainties in the position and wave vector respectively. In crystalline material, the region over which the spatial function extends is infinite, which leads to  $k\approx 0$  selection rule for first-order Raman scattering. However, in nano materials and disordered semiconductors, the phonons are confined to the small volume, which leads to relaxation of  $k\approx 0$  selection rule for first-order Raman scattering, and cause the peak shifted asymmetric broadening in the Raman spectra [5, 6]. Therefore, not only the zone-centre phonons  $k \approx 0$  but away from the zone centre with k > 0 also take part in the Raman scattering process.

The interpretation of the spectrum can be done by calculating width, peak position and symmetry of the spectrum. Any deviation from a given value of the width, peak position (or shift in peak position) and asymmetry indicates perturbation by any external condition. For example, in silicon nanostructures (SiNSs), asymmetrically broadened and red-shifted Raman spectra (fig. 2.9) are observed because the general spectroscopic selection rule gets relaxed and phonons other than the zone centered also contribute due to confinement of phonons.



Fig. 2.8 Raman spectra for c-Si (bulk)

Since the optical phonon dispersion relations in most semiconductors have negative dispersion, the Raman spectra exhibit peak shift to lower frequency side and broadening of the peak width fig. 2.9.



Fig.2.9 Raman spectra for Si nanowires (4nm).

#### **2.4 Raman Study of the Electron-Phonon** Coupling

In heavily doped c-Si, Raman line-shape exhibits asymmetry and peak shift [48–51]. Such changes in the Raman line-shape can be explained with the Fano-type [52] interaction model based on a discrete continuum interaction. It was Ugo Fano [52], who suggested the first theoretical explanation of observed asymmetric profiles in some of the Rydberg spectral atomic lines and proposed a formula (also known as the Beutler-Fano formula) that predicts the shape of spectral lines based on a superposition principle of quantum mechanics. Fano's interpretation of these "strange line-shapes" of spectral absorption lines is based on the interaction of a discrete excited state of an atom with a continuum sharing the same energy level which results in an interference phenomenon. The resulting line shape is produced by the interference between the discrete and continuum states. Using this model, the observed Raman line-shape of heavily doped c-Si has been explained as a result of electron-phonon interaction i.e. the interference between the discrete phonon state and continuum of electronic states present due to heavy doping. When doping in Si is of the order of 10<sup>19</sup> cm<sup>-3</sup>, the semiconductor behaves like a degenerate semiconductor.

In addition to confinement effect, Fano resonance [53–55] (electronphonon interaction) is another factor that can induce asymmetry in Raman spectral line shape [56–58]. In contrary to phonon confinement effect where the broadening occurs in Raman line shape only in pre maximum side, the presence of Fano effect results in increased half width in the premaximum side and post-maximum side for heavily doped n-type and ptype Si respectively meaning that it depends on the nature of the system.

# **Chapter 3**

# **Experimental Methodology** and Sample Details

In this chapter, experimental details, characterization techniques used and methodology adopted for the research work is discussed. The sample preparation technique and details of the method used for research work has also been provided in the current chapter.

#### **3.1 Sample Preparation**

The samples containing Si NSs used in the present study have been prepared using metal induced etching (MIE). Details of the method used are as follows.

#### **3.1.1 Metal Induced Etching Method**

There are large variety of techniques have been developed to fabricate Si NSs such as electron beam lithography, epitaxial growth, chemical vapor deposition and many simple chemical etching techniques. Amongst various techniques used for fabrication of Si nanostructures, metal induced etching(MIE), also known metal assisted chemical etching, is one of simplest and cheapest method for synthesis of semiconductor nanostructures with the ability to control various parameters (as diameter, length, orientation, cross-sectional shape of nanostructures) [21,59,60]. It is a two-step method in which, firstly metal nanoparticles( mainly silver or gold) are deposited on a clean semiconductor surface by dipping the wafer in a solution containing appropriate metal salt dissolved in acid.

Size and distribution of metal NPs deposited on the wafer depends on concentration of the solution and deposition time.

After the metal coating step, wafers (containing metal nanoparticles) are transferred into etching solution. After a particular time of etching, NSs get fabricated on the semiconductor surface.

#### **3.1.2 Mechanisms**

The steps involved in SiNSs preparation are discussed below. The materials and chemicals used are Si wafer,  $AgNO_3$ , HF,  $HNO_3$ ,  $H_2O_2$  and distilled water (DI).

#### Si wafer cutting and cleaning

The p and n-type Si wafers were cut using a diamond tip glasscutter. Si substrates were cleaned using ultrasonic bath to remove inorganic impurities present on the surface. Substrates were cleaned in acetone and iso-propanol (IPA) for 10 minutes respectively each followed by washing with DI water.

#### Surface treatment (to remove oxide layer)

After cleaning, the Si wafer were washed with 5% HF solution to remove the oxide layer formed on the surface of Si wafer due to exposure to air. After washing with HF, further washed with DI water to remove unnecessary fluoride ions present on the surface of the Si wafer.

#### **Metal Deposition**

Si NSs have been prepared using MIE [17, 33, 61] technique in the current study. MIE is mainly a two steps process as discussed earlier. After removing oxide layer, Si wafers were then dipped in solution

containing HF and AgNO<sub>3</sub> to deposit Ag nanoparticles (AgNPs) and then rinsed with distilled water. The deposition of MNPs plays an important role to determine the diameter of Si nano wires (Si NWs).

#### **Etching process**

After the metal deposition step, wafers (containing metal NPs) are transferred into etching solution for porosification. A typical etching solution containing hydrofluoric acid (HF) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). After a particular time of etching, porous Si/Si NSs get fabricated on the wafer surface. Etching time decides the length of SiNWs.

#### **Removal of Ag-NPs**

The etched Si wafer is dipped in the HNO<sub>3</sub> for two min to remove the metal nano particles present inside the pores. After the treatment HNO<sub>3</sub>, strong oxide layer is formed on the surface of SiNWs. The sample were further transferred to the HF solution and then washed with DI water to remove the oxide layer from the surface of Si NWs. Fig.3.1 displayed the schematic diagram of steps involved in the MIE technique.



**Fig.3.1** Schematic diagram of step by step formation of Si NWs. (1) Cleaned Si wafer, (2) MNPs deposited Si wafer, (3) etched Si wafer, (4) increase etching time and (5) Si NWs after removal of MNPs.[45]

#### 3.2 Instruments' Details

#### **3.2.1 Scanning Electron Microscope**

Scanning electron microscopy (SEM) is a non-destructive technique for imaging surfaces to understand the morphology. The SEM contains a focused beam of high-energy (ranging from 0.2 keV to 50 keV). Electrons with significant amounts of kinetic energy, when they interact with surface of sample generate a range of signals. These signals that are obtained from the electron-sample interactions give information about the sample's surface.

#### **3.2.1.1 Signals Generated**

When electron interacts with matter, this interaction leads to emission of X-rays, secondary electrons, backscattered electrons etc. In case of SEM, secondary electrons and backscattered electrons used for the generation of images. Secondary electrons and backscattered electrons are discussed below

#### **Secondary electrons (SE)**

When the electron beam hits the specimen, the emission of the valence electrons of the constituent atom in the sample known as secondary electrons. The energies of secondary electrons are very small generally less than 50 keV. SEs are extremely abundant and SE yield depends on the accelerating voltage.

#### **Backscattered electrons (BSE)**

Backscattered electrons are generated by elastic scattering and BSE yield depends on atomic number of the specimen. The energies of backscattered

electrons are higher than 50 keV, so BSE contain information from a relatively deep region. The BSE are sensitive to the composition of the specimen.

#### **X-Rays**

X-rays are generated when electrons in the inner shells are excited. Energies of the X-rays correspond to the energy difference between the shells involved in the transition. X-rays are basically used for elemental analysis in SEM.

#### **3.3 Raman Spectroscopy**

Raman scattering [43,62] has now become one of the widely used versatile spectroscopic tools. It uses for many propose such as to study crystal structure, crystal defects, chemical composition. It also uses to investigate different physical phenomena taking place at microscopic levels like confinement, defect states etc. Raman spectroscopy can provide qualitative as well as quantitative key information easily and quickly and also specifying the structure and chemical composition of the probed material. The Raman spectroscopy provides a convenient method to analyze the rotational, vibrational and other low frequency modes in the samples. Raman spectroscopy depends on inelastic scattering of monochromatic light (usually laser in the visible, near infrared or near ultraviolet range). The experimental set-up of a Raman spectrometer is shown in Fig. 3.2.



Fig. 3.2 Schematic diagram of Raman Spectrometer.

In Raman spectroscopy when laser light interacts with phonons, molecular vibrations or other excitations in the system, due to inelastic scattering of photon the energy of the laser photons being shifted .

This energy shift gives information about the vibrational modes in the system [7, 63]. In the Raman scattering, a sample is illuminated with a laser beam then electromagnetic radiation from the illuminated spot is collected with a lens and passed through a monochromator. Elastically scattered radiation at the wavelength corresponding to the incident laser beam (Rayleigh scattering) is filtered out, while the rest of the collected light is dispersed onto a detector. The scattered light is analyzed to see the components available in the signal. In order to record the light intensity as a function of energy (in wavenumber units), a charge-coupled device (CCD) detector is used. In this work Horiba LabRAM HR micro Raman spectrometer was used for recording the Raman signals of Si NSs.

#### **3.4 Experimental Details**

A commercially available (Vin KarolaTM) Si wafer (n- type) with resistivity ~0.1 $\Omega$ -cm has been used to fabricate the SiNSs using by metal induced etching (MIE). For MIE, first Ag nanoparticles (AgNPs) were deposited on cleaned Si wafers by dipping them into a solution containing 4.8 M HF and 5 mM AgNO<sub>3</sub> for 60 s at room temperature. The AgNPs deposited samples were then kept for etching in a solution containing 4.6 M HF and 0.5 M H<sub>2</sub>O<sub>2</sub> for 45 minutes at room temperature. Etched wafers were then transferred to HNO<sub>3</sub> to remove the AgNPs after the etching process. The samples were then dipped into HF solution to remove any oxide layer induced by nitric acid used in above step. A Supra55 Zeiss scanning electron microscope (SEM) has been used to study the surface morphologies of these samples.

The sample prepared after porosification of Si wafer using metal induced etching looks to have uniform porosity (Fig. 1(a)) with an average pore size of less than a micron. The porous looking morphology is actually a result of an assembly of well aligned wire like structures clubbed together as can be seen using the cross-sectional SEM images (Fig.3.3 (a)).

#### Neeshuetal.Adv.Mater.Proc.Technol.2020, https://doi.org/10.1080/2374068X.2020.1740876,



**Fig. 3.3** (a) Surface morphology of Si NSs in top view and cross-sectional view (inset)

These pores are approximately a few tens of microns long as obtained after 45 min. of etching. These wires are known to be consisting of smaller nanostructures of sizes in the range of a few nanometers and are capable of exhibiting confinement effects.

Raman spectroscopy is a promising tool to study the perturbation due to quantum confinement effect. In case of c-Si the Raman spectrum corresponds to a sharp and symmetric Lorentzian Raman line shape owing to the participation of the zone centered phonon governed by the momentum conservation rule in a c-Si. This is not the case for SiNWs where the asymmetry induced in zone boundaries leads to the violation of the momentum conservation rule and phonons apart from the zone centered one (governed by dispersion relation) start participating in the scattering process in lieu of which the Raman line shape encompasses asymmetry, broadening and Raman shift. This perturbation was first modeled by Richter et al. and later modified by Campbell and Fauchet in order to acquire a wholesome study from Raman scattering of confined systems[40, 64].



**Fig. 3.3 (b)** Raman spectrum (discrete points) along with theoretical fitting (solid line) using phonon confinement model; inset shows various definitions of Raman parameters.

The red shift, asymmetry and broadening are quantified through peak position ( $\omega_0$ ), asymmetry ratio ( $\alpha$ ) and full width at half maximum (FWHM or  $\gamma$ ) respectively. All of these parameters can be matched with theoretically generated Raman line shape function, given by PCM to estimate the nanocrystallite size. The fitting of the experimentally observed Raman scattering data (discrete blue points) using PCM (solid red line) has been shown in Fig. 3.3 (b). The best fit between the experimental and theoretical data yields a nanocrystallite size of 6 nm when a two dimensional confinement is considered.

## **Chapter 4**

# **Confinement of Phonons in Low Dimensional Silicon**

In this chapter the behavior of confined phonons, present in low dimensional Si, using Raman scattering has been reported. The effect of phonon confinement on Raman spectra of Si is analyzed in terms of the Raman spectral line-shape. An analytical model for Raman parameters are analyzed carefully mainly within the framework of PCM [40,64]. A theoretical model (PCM) has been presented which is used to analyze qualitatively in this chapter to extract any subtle physics taking place at these nanostructures measure. The results presented in this chapter are published.

## 4.1 Raman Scattering from Low Dimensional Solids (Theoretical background)

Raman spectroscopy provides a fast and convenient method to analyze the nature of zone centered optical phonon in solids. A Raman spectrum contains information about a solid through the response of solid's phonons to the incident photons by means of scattering. Theoretical background of Raman scattering from a-Si and *c*-Si has already discussed in chapter 2. Raman spectrum of Si NSs shows different nature as compared to c-Si because in the Si NSs optical phonon's frequency is likely to change from its bulk form due to the quantum confinement effect. Thus, the Raman spectral line-shape function for the Si NSs must be modified, from a typical Lorentzian function (for c-Si), through the change in optical phonons frequency. At nanoscales, the deviation of vibrational properties of the crystalline materials in the Raman spectra is due to the breakdown of translational symmetry at its grain boundaries of that material [65, 67]. As the size of materials is reduced to the order of its Bohr's exciton radius, the effect of optical phonon confinement is more pronounced [68-70] and strongly reflected in Raman scattering.

Raman spectroscopy is one of the most promising tools to categorize the phase the material such as crystalline, amorphous or nanocrystalline [71,64,67]. The first-order Raman spectrum provides an easiest and effective method to analyze the vibrational properties of crystalline semiconductor as well as amorphous semiconductors. NSs of semiconducting material are mainly quasi-crystalline phase of materials; Raman spectra of NSs are present in the intermediate range between the spectra of the crystalline and amorphous nature of that material.

In order to understand the vibrational properties in Si NSs for one or more degree of confinement lots of researches have been done using Raman spectroscopy [72,73]. Usually all the results show an asymmetrically broadened and red-shifted Raman spectra from Si NSs.



Fig.4.1 Raman line-shapes as a function of Si NWs size [39].

#### **4.2 Phonon Confinement Model**

In crystalline materials in the bulk form, only zone centered phonons contribute to the Raman scattering due to spectroscopic selection rule, result in a symmetric Lorentzian line-shape spectrum peaked at a frequency corresponding to the zone center phonon. The PCM describes well the observed Raman line-shape from the Si NSs. Richter *et al.* [40] proposed a very intuitive PCM for confined phonons in the Si NSs of spherical shape with diameter L. The plane wave function of the phonon in NSs is restricted within the finite size of NSs. The wave function of a phonon with wave vector  $k_0$ , in a crystal is defined in polar co-ordinates as [64],

$$\Phi(k_0, r) = u(k_0, r) \cdot e^{-ik_0 \cdot r}$$
(4.1)

where  $u(k_0, r)$  having the same periodicity as of the lattice. In case of a finite crystal of dimension L, phonons are restricted to crystal volume.

Phonons inside the Si NSs can be described by the following weighting functions  $W(\mathbf{r}, \vec{L})$  [64].

$$\Psi\left(\mathbf{k}_{0},r\right) = W\left(r,\vec{\mathbf{L}}\right)\varphi\left(\vec{\mathbf{k}}_{0},r\right)$$
(4.2)

Using eq. (4.1) in the eq. (4.2)

$$\psi(\vec{k}_0, r) = \psi'(\vec{k}_0, r) u(\vec{k}_0, r)$$
(4.3)

Where

$$\psi'(\vec{k}_0, r) = W(r, \vec{L}) e^{-i\vec{k}_0.r}$$
(4.4)

Richter *et al.* [40] chose the  $W(r, \vec{L})$  to a Gaussian form exp (-2r<sup>2</sup>/L<sup>2</sup>), with amplitude of 1/e at the boundary of the finite crystal. For line-shape Raman spectrum,  $\Psi'(\vec{k}_0, r)$  might be expanded in a Fourier series as

$$\Psi'(\vec{k}_0, r) = \int \mathcal{C}(\vec{k}_0, k) e^{-i\vec{k}_0 \cdot r} d^3k$$
(4.5)

Where the corresponding Fourier coefficient  $C(k_0, k)$  is given

$$C(\vec{k}_{0},k) = \frac{1}{(2\pi)^{3}} \int \psi'(\vec{k}_{0},r) e^{-i\vec{k}\cdot r} d^{3}r$$
(4.6)

Thus, the phonon wave function in a finite crystal is no longer an Eigen function of the phonon wave vector  $k_0$  but rather a superposition of the Eigen functions with k vectors around k = 0. For a spherical finite crystal, the Fourier coefficients are given as  $|C(\vec{k}_0, k)|^2 \sim exp$  (-k<sup>2</sup>L<sup>2</sup>/4), where  $k_0$  is assumed to be 0. Thus intensity of the first-order Raman scattering, can be written as [64]

$$I(\omega) = \int \frac{|C(\vec{k}_0, k)|^2}{[\omega - \omega(k)]^2 + (\frac{\gamma}{2})^2} d^3k$$
(4.7)

where  $\omega(k)$  is the phonon dispersion function for the optical branch of c-Si and  $\gamma$  is the natural line width of Raman spectrum of c-Si. The dispersion relation  $\omega(k)$  of the optical phonons in a Si NSs can be taken as  $\omega(k) = \sqrt{A + B \cos \frac{\pi q}{2}}$ , where A=171400 cm<sup>-2</sup> and B = 100000 cm<sup>-2</sup>.

Different weighting functions, namely *exponential*, *Gaussian and sinc* respectively have been proposed for the Fourier coefficients. It is found that the Raman line-shape are explained very well using the relation  $|C(0, k)|^2 = exp [-(k^2L^2/4a^2) \text{ for Si NSs [173]}.$  Therefore the Raman line shape for a given size L is:

$$I(\omega) \alpha \int \frac{\exp\left[-\frac{k^2 L^2}{4a^2}\right]}{[\omega - \omega(k)]^2 + \left(\frac{\gamma}{2}\right)^2} d^n \vec{q}$$
(4.8)

Where, *k* is expressed in the units of  $2\pi/a$ , *a* being the lattice constant, 0.543 nm. The parameter *L* stands for the average size of the nanocrystals.  $\gamma$  being the line width of the Si optical phonon in bulk c-Si (~ 4 cm<sup>-1</sup>) and '*n*' shows the degree of confinement and may take values 2 or 3 for 2-dimensional or 3-dimensional confinement, respectively.

#### **4.3 Effect of Size on Raman Line Shape**

In the bulk form of c-Si, the Raman scattering is limited to near zone centered phonons due to spectroscopic selection rule and result in a symmetric Lorentzian line-shape spectrum peaked at a frequency corresponding to the zone center phonon. Whereas in silicon nanostructures (Si NSs), asymmetrically broadened and red-shifted Raman spectra are observed because the general selection rule gets relaxed and phonons other than the zone centered also contribute due to confinement of phonons in a crystallite of finite dimension.

Any deviation from a given value indicates perturbation of the phonon by an external condition. There are three key observations, which are used to identify any external perturbation of the phonon.

Asymmetry ratio: It is given as the ratio of half width at pre maximum to that of half width at post maximum. For the case of c-Si the symmetric nature of the Raman line-shape may be explained on the basis of the single phonon participation at k=0 .On the contrary for the case of Si NWs the

participation of the different phonons (as described by the dispersion relation).For the case of Transverse optical phonons (TO) the participation of the lower energy phonons due to confinement effect leads to an symmetry in the lower energy side of the maximum.

**FWHM**: The width and symmetry of the spectrum, normally quantified through full width at half maximum or FWHM, depends (inversely) on the lifetime and dispersion respectively of the phonons involved in the scattering. The natural line width for the c-Si is 4 cm<sup>-1</sup> which for the case of SiNWs gets increased due to the resultant spectrum is now a superposition of spectra from phonons ranging from k=0 to k=1.



Fig.4.2 shows various definitions of Raman parameters.

Raman shift: The participation of the single phonon at the zone center generates a sharp and symmetric Raman spectrum peaked at 520 cm<sup>-1</sup> which in case of SiNWs is subjected to the participation of range of

phonons due to the violation of momentum conservation rule and hence the Raman spectrum for the case of TO phonons acquire a red shift.

The Raman line shape contains a wealth of information which, when interpreted in an appropriated manner gives detailed analysis of the perturbations in the system. To understand the Raman line-shape envelope few parameters like asymmetry ratio, FWHM, Raman shift must be interpreted carefully for all sizes. It is interesting here to observe that the deviation of  $\omega$ , $\alpha$  and  $\gamma$  from those of the bulk counterparts are not equal in terms of their values apparently meaning that the effect of quantum confinement is not of same order on the three parameters and it is expected that one (or may be couple) of these will get affected more than and prior to the rest. To understand which of these gets affected first, the size dependent Raman line-shapes, generated by PCM, have been analyzed closely as discussed below. Fig. 4.3 shows the theoretical Raman line-shape function, predicted by PCM, as a function of nanocrystallite size (between 20 nm to 3 nm) confining the phonons in two dimensions (nanowires).



**Fig. 4.3** Theoretical Raman line-shapes as a function of Si NSs size generated using phonon confinement model considering two-dimensionally confined system.

It is very clear that the Raman line-shape, which is symmetric (with asymmetry ratio, of unity) and centered at 521 cm<sup>-1</sup> with FWHM of ~ 4 cm<sup>-1</sup> for crystalline Si deviates from its bulk Raman line-shape on decreasing nanocrystallite size. It is quite clear from the above discussion that if one wants to interpret the Raman line-shape parameters in an appropriate manner, the line-shape parameters needs to be understood clearly. The extent of confinement can be easily interpreted using Bohr exciton radius which for the case of silicon is ~5 nm. It is worth mentioning here that the Raman line-shape remains more or less like the bulk line-shape till the crystallite size as low as 20 nm which is four time the Bohr's exciton radius value for Si hence showing little confinement effect.

On further decreasing the size till 11 nm, the Raman line-shape starts showing some deviation from the bulk line-shape, this is expected as this is the "weak confinement" size regime. On further decreasing the sizes a rapid variation in line-shape can be appreciated when the sizes are comparable to 5 nm which also happens to be the Bohr's exciton radius value. The Raman line-shape gets extremely asymmetrically broadened and red shifted with peak positioned at 515.5 cm<sup>-1</sup> carrying a FWHM of 35 cm<sup>-1</sup> and asymmetry ratio of 5 in the strong confinement regime for sizes ~ 3 nm. From fig. 4.3, one can notice that different Raman line-shape parameters respond to the confinement effect differently in the different confinement regimes. The same has been analyzed qualitatively below to extract any subtle physics taking place at these nanostructures.

In order to understand the onset of transition from bulk to nano, FWHM explains the broadening in the Raman spectrum arising due to confinement effect. Similarly, other line shape parameters like Raman shift and asymmetry are plotted as a function of size for two degree of confinement.





**Fig.4.4** Raman shift,FWHM and asymmetry ratio as a function of size for two degree of confinement.

A size dependent variation of different Raman line-shape parameters for two degree of confinement (Fig. 4.4 ) reveals that the three parameters vary in different ranges with the common size variation in the range of 20 nm to 3 nm. It is evident that the variation by values (or the numbers) is maximum for FWHM which varies from 5 to 35 cm<sup>-1</sup> (seven times or 600%) whereas the variation is minimum for peak position which varies from 521 to 515.5 cm<sup>-1</sup> (nearly ~1%). On the other hand, the asymmetry ratio varies moderately between the values 1 to 5 (five times or 400%) while changing the size in the same above-mentioned range (20 nm to 3 nm).

For better understanding, derivatives of all the parameters have been taken and its variation as a function of size is shown in Fig. 4.5. For better comparison, negative derivative has been used for peak position as it shows opposite behavior to that from asymmetry ratio and FWHM.

Fig. 4.5 clearly shows that FWHM varies most rapidly in comparison to the other two which vary nearly at the same rate as a function of size. It can be understood that though the confinement of same physical entity, phonons, and its manifestation in FWHM, A.R and peak shift is different.



**Fig. 4.5** Rate of change of Raman line shape parameters as a function of nanocrystallite size for two degree of confinement.

To understand the reason a closer analysis is required before any conclusion can be drawn. The FWHM is known to be the manifestation of phonon life time in a solid which means that it is the life time (of the confined phonons) which appears to be the most sensitive to the confinement effect. On the confinement scale, due to higher sensitivity, the FWHM starts responding to size variation as early as in the weakly confinement regime. On the other hand, the asymmetry and peak shift mainly depend on the nature of phonons' dispersion relation. The effect of confinement on the peak position and asymmetry is not appreciable until the moderate to strong confinement regime is attained. This is the regime when the Raman selection rule is relaxed sufficiently so that the phonons sufficiently away from the zone center start taking part in Raman scattering. Another factor that affects  $\omega$  and  $\alpha$  is the slope of the phonon dispersion curve which, for Si is flat near the zone center. The regime after which the phonon dispersion curve's flatness ceases, appreciable change in  $\omega$  and  $\alpha$  is visible of course compromised by the weak weighting factor

term. It is interesting to notice that simply looking variation of different Raman line-shape parameters ( $\omega$ , $\alpha$  and  $\gamma$ ) in fact contains several subtle physics about the confined phonons at nanoscale including the phonon life time and phonon dispersion nature and degree of confinement.

Variation of different Raman parameters with respect to size is very simplistic way to put it as it is difficult to ascertain that all of the parameters (asymmetry, peak and broadening) will get affected equally or differently in a given confined system. It would be interesting to understand the behavior of each of these parameters and thus the physical quantity responsible for this, on the quantum confinement effect. In order to understand the onset of transition from bulk to nano, FWHM explains the broadening in the Raman spectrum arising due to confinement effect. Similarly, other line shape parameters like Raman shift and asymmetry are plotted as a function of size for one different degree of confinement.

A size dependent variation of different Raman line-shape parameters for one degree of confinement (fig. 4.6) reveals that the three parameters vary in different ranges with the common size variation in the range of 20 nm to 3 nm same as we observed in the case of two degree of confinement. It is evident that the variation by values (or the numbers) is maximum for FWHM which varies from 4 to 8 cm<sup>-1</sup> (two times) whereas the variation is minimum for peak position which varies from 520 to 520.8 cm<sup>-1</sup>. On the other hand, the asymmetry ratio varies moderately between the values 1 to 2.5 while changing the size in the same above-mentioned range (20 nm to 3 nm).



**Fig. 4.6** FWHM, asymmetry ratio and Raman shift as a function of size for one degree of confinement.

For better understanding, derivatives of all the parameters have been taken and its variation as a function of size is shown in Fig. 4.7. For better comparison, negative derivative has been used for peak position as it shows opposite behavior to that from asymmetry ratio and FWHM. Fig. 4.7 clearly shows that FWHM varies most rapidly in comparison to the other two which vary nearly at the same rate as a function of size.



**Fig.4.7** Rate of change of Raman line shape parameters as a function of nanocrystallite size for one degree of confinement.

#### Summary

A comparison of experimentally observed Raman scattering data with Raman line-shapes, generated theoretically using phonon confinement model, has been studied out to understand the sensitivity of different Raman spectral parameters on quantum confinement effect. An asymmetrically broadened and red shifted Raman line-shape was observed which established that all the parameters get affected.

It is interesting here to observe that the deviation of peak shift, asymmetry ratio and FWHM from those of the bulk counterparts are not equal in terms of their values apparently meaning that the effect of quantum confinement is not of same order on the three parameters and it is expected that one (or may be couple) of these will get affected more than and prior to the rest. To understand which of these gets affected first, the size dependent Raman line-shapes, generated by PCM, have been analyzed closely for one and two degree of confinement.

An experimentally observed Raman scattering data and its comparison with theoretical phonon confinement model reveals that phonon life time is the most sensitive quantity to get affected by the confinement effect in Si NSs prepared by metal assisted etching. In terms of sensitivity, the relaxation of Raman scattering selection rule follows the phonon life time. In the one hand, the phonon life time starts getting affected even in the weakly confinement systems whereas the latter needs moderate to strong confinement effects to get manifested in the Raman line-shape.

The above observations is seen experimentally in following manner, a broadening (due to phonon life time) in the Raman line-shape starts appearing even in the regions where Raman peak shift and asymmetry ratio remains in the latent stages to be visible only in the strong confinement effect.

# **Chapter 5**

## **Electron phonon interaction in silicon nanostructures**

In this chapter, interaction of electrons with optical phonons has been reported with their manifestation in Raman spectra in nanocrystalline Si. Raman spectral asymmetries induced by electron phonon interaction (Fano resonance) with quantum confinement effect has also been discussed for Si NSs. The effect of microscopic perturbations, Fano coupling with quantum size effects analyzed to know the sensitivity of different Raman spectral parameters.

### 5.1 Electron Phonon Interaction (Fano Resonance)

In a quantum mechanical study of self-ionization states of atoms, in 1961 Ugo Fano discovered a new type of resonance which now known by his name i.e. Fano resonance [52,74]. The Fano resonance exhibits a distinctly asymmetric shape rather than Lorentzian resonance [75,76]. Fano resonance is properties of the system, observed when system contains a discrete energy state lies within a continuum of energy states. Fano resonance is the interference of the waves associated with transitions between discrete states which is lying in the continuum and the continuum of states. Interference of discrete auto ionized state of atom with continuum result a asymmetric line shape. As above discussed, the Fano effect is caused by interference of waves, and interference can be constructive as well as destructive, so resonance (due to constructive interference) and antiresonance [52] (due to destructive interference) both are observed simultaneously in the Fano spectrum.

This type of phenomenon may be observed in variety of systems including solid materials, molecules, and atoms and in nanostructure also. Semiconductor can be an example to see this effect because semiconductors have discrete energy states phonons( having discrete energies) can interact within a continuum of states, which provided by the electronic states under special conditions like heavy doping on quantum confinement effect. Ugo Fano used a perturbation method to explain the appearance of asymmetric resonances. Fano obtained the formula for the shape of the resonance profile [77] of a scattering cross section, which is given by eq 5.1.

$$I(\omega) = \frac{(q+\varepsilon)^2}{(1+\varepsilon^2)}$$
(5.1)

Where q is the phenomenological shape (Fano parameter) and  $\epsilon$  is the reduced energy which is the ratio of difference in frequency to the half width of the line shape and is given by eq. 5.2. The amplitude of 'q' provides the measure of electron phonon interaction (inversely) with a smaller value of '|q|' meaning strong electron-phonon interaction.

$$\in = \frac{\omega - \omega_0}{\gamma/2} \tag{5.2}$$

There are various techniques to study the possible Fano interaction in a system. In the present study, Raman spectroscopy has been used to study the Fano resonance in Si NSs.



Fig. 5.1 Diagram representing Fano resonance.[79]

#### 5.1.1 Fano Resonance in Crystalline Si

The electron-phonon coupling in well-tailored c-Si, in terms of interference between optical phonons and electronic continuum results in an asymmetric Raman line-shape. In the heavily doped (>1×10<sup>19</sup> cm<sup>-3</sup>) Si wafer [80] manifestation of the Fano interference is one of the well-studied properties. The origin of Fano resonance in semiconductor materials is the interference of phonons with continuum of states created due to photo excitation or heavy doping. The asymmetry induced by Fano resonance in the Raman line-shape depends on the doping type. Electronic continuum is created in valence band in heavily doped p-type semiconductor is due to transition of light hole to heavy hole while in case of heavily doped n-type it is created in conduction band [57]. Asymmetric broadening in the Raman spectrum (lower half width ( $\gamma_L$ ) is more than the upper half width in ( $\gamma_H$ )) produces due to Fano resonance, resulting from interference between discreet phonon and valence band electronic continuum (in n-type system while other way round in p-type due to

interference between phonon and valance band continuum). As a result Raman peak may dominate over the other in any of the spectral half-width either towards upper or lower frequency side.



**Fig. 5.2** Theoretical Raman line shapes obtained using Eq. 5.1 for (a) heavily doped n-type c-Si (c-Si-N) (b) heavily doped p-type c-Si (c-Si-P)[80].
As already discussed, Fano resonance is an interference which must possess constructive as well as destructive interference. If the Fano resonance is absent or very weak, then an antiresonance dip (destructive interference, minimum spectral intensity) cannot observe in Raman lineshapes (fig. 5.2). This is an important indication of presence of Fano resonance in a system. The theoretical Raman line-shapes, shown in fig.6.2, have been generated using well established general Fano-Raman line shapes equation (eq. 5.1) which takes care of Fano resonance for both n-and p-type semiconductor by appropriately choosing the sign of Fano parameter (q). An increase in lower (or higher) half width can be seen on decreasing the negative (or positive) value of q. In both the cases, a deviation from symmetry is evident on increasing the Fano coupling (decreasing |q| value).

### 5.1.2 Fano Resonance in Quantum Confined Si

As discussed in chapter 4, the Raman line shape encompasses asymmetry, broadening and Raman shift due to quantum confinement effect. It would be interesting to see how these Raman line shape parameters affected by the introduction of Fano resonance in the same system where quantum confinement effect is already present. Fano resonance resulted due to inter sub-bands transitions in semiconductor quantum wells.

The interplay between Fano and quantum confinement effects is debatable unless it is investigated clearly. All the reports on Fano interaction lack a clear theory as well as experiment on the mechanism of electron-phonon interaction in the Si NSs. There are several attempts made to investigate the presence of Fano interaction in low dimensional systems. Still a depth study is required to understand the Fano interaction and its implications and dependence on other parameters like size of the NSs, excitation laser power density and temperature etc. An attempt has been made to understand the combine effect of Fano and quantum confinement effect. A comprehensive theoretical Raman line shape function has been generated with appropriate modification in the general Fano line-shape to incorporate quantum confinement effect and weighting function, which have been extensively used to study this type of effect.

To see the combination of Fano and quantum confinement effect on Raman line shape the following equation has been used, which is a wellaccepted approach for this purpose.

$$I(\omega) = \int_0^1 \exp(-k^2 L^2 / 4a^2) \frac{(q+\varepsilon')^2}{(1+\varepsilon')^2} d^n k$$
 (5.3)

Where  $\varepsilon' = [\omega - \omega(k)]/(\gamma/2)$ , here  $\omega(k) = \sqrt{A + B \cos \frac{\pi q}{2}}$  is the optical dispersion relation used for Si where  $A=171400 \text{ cm}^{-2}$  and  $B = 100000 \text{ cm}^{-2}$ ,  $\gamma$  is the natural line width ( $\gamma = 4 \text{ cm}^{-1}$ ), k is the wave vector of phonon.

The theoretical Raman line-shapes represented by eq.5.3 can be used as a general line-shape as it takes care of both the effects (Fano and nano combined effect) for both n- and p-type semiconductor nanomaterial by appropriately choosing the sign of Fano parameter (positive q for p-type material and negative q for n-type material).

A comparison of experimentally observed Raman scattering data with Raman line shapes, generated theoretically using phonon confinement model, has been discussed in chapter 4 to understand the sensitivity of different Raman spectral parameters on quantum confinement effect. In present chapter effect of Fano studied along with the quantum confinement effect and Raman line-shape parameters have been analyzed for the same. To see the combination of Fano and quantum confinement effect on Raman line shape parameters eq.5.3 has been used. To see the effect of Fano coupling on line-shape variation, the line-shape generated using different 'q' values between -3 to -10 have been analyzed (Fig. 5.3) representing a donor-type discrete-continuum Fano interference for a given crystallite size of 3 nm. The obtained theoretical line-shapes are broad and asymmetric (as compared to crystalline Si counterpart which is sharp and symmetric) in nature as a consequence of (the classic discrete-continuum) Fano interaction. Fig. 5.3 clearly shows that the Raman line-shape becomes more and more asymmetry when the absolute value of q reduces (due to increase in Fano coupling).



**Fig.5.3** Theoretical Raman line shapes generated using eq. 5.3 for different values of Fano coupling parameter q and crystallite size L = 3 nm.

It is apparent that with changing q values, the width as well as the peak position both changes but not at the same rate (with respect to 'q'). The rate of change of  $\gamma$  and  $\omega$  has been plotted as a function of q in fig. 5.4 which shows that the FWHM changes more rapidly as compared to the peak position. In physical terms, it means that the Raman spectral width is more sensitive to the micro level perturbation induced by donor type Fano coupling.



**Fig. 5.4** Rate of change of variation of width and Raman peak shift as a function of Fano parameter showing width being the fastest varying parameter for donor type Fano coupling system.

This behavior is similar to the one discussed in chapter 4, where Raman spectral width exhibits change without affecting the peak position which is expected to change only after the perturbation is of sufficiently large. This is also apparent from fig.5.4 where the peak position does not change until a large Fano coupling is present whereas the width starts responding to the perturbation relatively earlier.

Before concluding the above-mentioned observation, the Fano parameter dependent Raman spectral line-shape variation has been studied for an acceptor type discrete-continuum Fano coupling as shown in fig. 5.5(a) and corresponding rate of change of line-shape parameters has been shown in fig. 5.5(b).



**Fig. 5.5** (a) Theoretical Raman line shapes generated using Eq. 5.3 for different values of Fano coupling parameter q and crystallite size D = 3 nm, (b) Rate of change of variation of width and Raman peak shift as a function of Fano parameter showing width being the fastest varying parameter for acceptor type Fano coupling system.

However, this system is known to be complementary to the case discussed in Fig. 5.4, the sensitivity of the width remains prominent as compared to the peak position or asymmetry ratio here too. It further endorses the conclusions drawn above that Raman spectral line width ( $\gamma$ ) remains the most sensitive parameter which starts responding to even subtle perturbations whereas stronger perturbations are needed to be reflected in other Raman line-shape features like peak position.

Furthermore, to validate the above-said fact (the FWHM's sensitivity to subtle perturbation) another perturbation, of completely different in nature, the quantum confinement (or size-) effect, has also been discussed in chapter 4 in great details. In chapter 4, Raman line-shapes obtained corresponding to different Si nanowires size has been analyzed with no Fano effect. With decrease in size, effect on Raman peak position and FWHM becomes prominent (fig. 5.5(a)) with the latter varying more rapidly as evident from the derivative plot in Fig. 5.5(b).

### Summary

In summary, a theoretical approach has been adopted to understand the effect of perturbations induced by electron phonon (Fano resonance) interaction on Raman line shape parameters from nanocrystalline Si. The effect of microscopic perturbations, Fano coupling with quantum size effects, on different Raman spectral parameters also reveals Raman spectral width (phonon life time) to be the most sensitive parameter.

# **Chapter 6**

## **Conclusion And Future Scope**

### Conclusion

Raman line-shape analysis has been done from a very well-known semiconductor system, Si, where quantum confinement effect and electron-phonon (Fano) interaction have been used as known control perturbations and discussed one-by-one. One cannot find out the effect of quantum confinement on individual Raman line-shape parameters like peak shift, asymmetry ratio and line width. It cannot be ascertain that whether Bohr's exciton radius can be treated as the universal confinement regime. Main aim of the research project is to understand the sensitivity of different Raman spectral parameter towards the external perturbation and development of Raman as a better tool for material characterization especially in nanomaterials.

To understand the sensitivity of Raman spectral parameter, close study of the response of Raman parameters, FWHM, peak position and asymmetry ratio to the crystallite size and Fano with size has been done. Size and Fano parameter dependent variations of FWHM, Raman peak position and asymmetry ratio have been analyzed to establish the sensitivity of their corresponding physical counterparts (phonon life time and dispersion) in confined systems. The analysis helps in establishing different confinement regimes where the different parameters start responding to the confinement effect. Where the phonon life time, manifested as FWHM, is observed to be most sensitive parameter which can be observed in the weakly confined systems also.

Raman spectroscopy is one of the most suitable ways to investigate external perturbation effect especially that of phonons in nanostructures. A peak shifted and asymmetrically broadened Raman spectrum is treated as an indication of presence of external perturbations. It is interesting here to observe that the deviation of width, asymmetric ratio and peak position from those of the bulk counterparts are not equal in terms of their values apparently meaning that the effect of external perturbation is not of same order on the three parameters and it is expected that one (or may be couple) of these will get affected more than and prior to the rest. To understand which of these gets affected first, the variation of Raman lineshapes with size (generated by PCM) and with Fano parameter have been analyzed closely. First analysis has been done with quantum confinement effect, in this variation of different Raman line-shape parameters with size reveals that the three parameters ( $\omega, \alpha$  and  $\gamma$ ) vary in different ranges with the common size variation in the range of 20 nm to 3 nm. It is interesting to notice that simply looking variation of different Raman line-shape parameters, in fact contains several subtle physics about the confined phonons at nanoscale including the phonon life time and phonon dispersion nature and degree of confinement.

An experimentally observed Raman scattering data and its comparison with theoretical phonon confinement model reveals that phonon life time is the most sensitive quantity to get affected by the confinement effect in Si NSs. In terms of sensitivity, the relaxation of Raman scattering selection rule follows the phonon life time. In the one hand, the phonon life time starts getting affected even in the weakly confinement systems whereas the latter needs moderate to strong confinement effects to get manifested in the Raman line-shape. The above two observations is seen experimentally in following manner, a broadening (due to phonon life time) in the Raman line-shape starts appearing even in the regions where Raman peak shift and asymmetry ratio remains in the latent stages to be visible only in the strong confinement effect. Later a theoretical approach has been adopted to understand the effect of perturbations induced by electron phonon (Fano resonance) interaction on Raman line shape parameters from nanocrystalline Si. The effect of microscopic perturbations, Fano coupling with quantum size effects, on different Raman spectral parameters also reveals phonon life time to be the most sensitive parameter. Three different perturbations, quantum confinement effect, donor type Fano interference and acceptor type Fano interference reveal consistently that all these microscopic level perturbations can affect the Raman spectral widths even with their minimum possible presence. On the other hand, stronger perturbations are necessary to induce changes in the Raman peak position.

As the results have been validated using a nanostructured system where these subtle perturbations are observed to be inducing changes in the width as it is the most sensitive parameter to get affected by minimal perturbations. Effect of donor- and acceptor- type continuum-discrete interaction and quantum dimensional size on Raman spectral parameters confirms that spectral width is the most sensitive parameter to any subtle perturbations. On the whole, sensitivity of a given Raman spectral parameters can be used to understand the role of external perturbations in a material.

### Future Scope

Effect of other perturbations like strain, temperature will be studied along with the quantum confinement effect and Raman line-shape parameters will be analyzed for development of Raman as a better tool for material characterization especially in nanomaterials.

### References

[1] G. Gouadec and P. Colomban, Prog. Cryst. Growth Charact. Mater. **53**, 1 (2007).

[2]F. Priolo, T. Gregorkiewicz, M. Galli, and T. F. Krauss, Nat. Nanotechnol. 9, 19 (2014).

[3]A. L. Porter and J. Youtie, Nat. Nanotechnol. (2009).

[4]S. Joseph SJ, SR Vol4802 Febr. 2011 (2011).

[5]R. P. Feynman, J. Microelectromechanical Syst. 1, 60 (1992).

[6]R. Zsigmondy and J. Alexander, *Colloids and the Ultramicroscope: A Manual of Colloid Chemistry and Ultramicroscopy* ...(J. Wiley & sons, 1909).

[7]H. Weller, Curr. Opin. Colloid Interface Sci. 3, 194 (1998).

[8]V. H. Grassian, in *Nanoscale Mater. Chem. Environ. Appl.*(American Chemical Society, 2010), pp. 15–33.

[9]M. L. Brongersma, P. G. Kik, A. Polman, K. S. Min, and H. A. Atwater, Appl. Phys. Lett. **76**, 351 (2000).

[10] Raman CV. A new radiation. Indian J Physics, 1928; 2:387–398.

[11] Raman CV. Krishnan KS. A new type of secondary radiation. Nature. 1928;121:501–502.

[12]J. M. Rodríguez, I. Tobías, and A. Luque, Sol. Energy Mater. Sol. Cells **45**, 241 (1997).

[13]S. R. Wenham and M. A. Green, Prog. Photovolt. Res. Appl. 4, 3 (1996).

[14]Y. Jiang, X. Zhang, F. Wang, and Y. Zhao, RSC Adv. 5, 69629 (2015).

[15]S. Wippermann, Y. He, M. Vörös, and G. Galli, Appl. Phys. Rev. 3, 40807 (2016).

[16]X. Li, J.-H. Lee, A. N. Sprafke, and R. B. Wehrspohn, Semicond. Sci. Technol. **31**, 14009 (2016).

[17]K. Peng, A. Lu, R. Zhang, and S.-T. Lee, Adv. Funct. Mater. **18**, 3026 (2008).

[18]B. Tian, X. Zheng, T. J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, and C. M. Lieber, Nature **449**, 885 (2007).

[19]S. Mishra, H. Pandey, P. Yogi, S. K. Saxena, S. Roy, P. R. Sagdeo, and R. Kumar, Opt. Mater. **66**, 65 (2017).158

[20]O. Bisi, S. Ossicini, and L. Pavesi, Surf. Sci. Rep. 38, 1 (2000).

[21]K.Peng, X. Wang, and S.-T. Lee, Appl. Phys. Lett. 92, 163103 (2008).

[22]Zhang Baohua, Wang Haishui, Lu Lehui, Ai Kelong, Zhang Guo, and Cheng Xiaoli, Adv. Funct. Mater. **18**, 2348 (2008).

[23]K.-Q. Peng, X. Wang, and S.-T. Lee, Appl. Phys. Lett. **95**, 243112(2009).

[24]G. Zheng, F. Patolsky, Y. Cui, W. U. Wang, and C. M. Lieber, Nat. Biotechnol. 23, 1294 (2005).

[25]T. Takamura, S. Ohara, M. Uehara, J. Suzuki, and K. Sekine, J. Power Sources **129**, 96 (2004).

- [26]T. Song, J. Xia, J.-H. Lee, D. H. Lee, M.-S. Kwon, J.-M. Choi, J. Wu, S. K. Doo, H. Chang, W. I. Park, D. S. Zang, H. Kim, Y. Huang, K.-C.
- Hwang, J. A. Rogers, and U. Paik, Nano Lett. 10, 1710 (2010).
- [27]L. Li, Y. Yao, Z. Lin, Y. Liu, and C. P. Wong, in *Electron. Compon. Technol. Conf. ECTC 2013 IEEE 63rd*(2013), pp. 581–585.
- [28]K. W. Adu, H. R. Gutiérrez, U. J. Kim, and P. C. Eklund, Phys. Rev. B 73, (2006).
- [29]H. Kim, M. Seo, M.-H. Park, and J. Cho, Angew. Chem. Int. Ed. 49, 2146 (2010).
- [30]J. Theis, M. Geller, A. Lorke, H. Wiggers, A. Wieck, and C. Meier, Nanotechnology **21**, 455201 (2010).
- [31]T.M. Atkins, A. Y. Louie, and S. M. Kauzlarich, Nanotechnology 23, 294006 (2012).
- [32]B. S. Flavel, M. J. Sweetman, C. J. Shearer, J. G. Shapter, and N. H. Voelcker, ACS Appl. Mater. Interfaces **3**, 2463 (2011).
- [33]S. K. Saxena, P. Yogi, P. Yadav, S. Mishra, H. Pandey, H. M. Rai, V. Kumar, P. R. Sagdeo, and R. Kumar, Superlattices Microstruct. **94**, 101 (2016).
- [34]F. A. Harraz, A. A. Ismail, H. Bouzid, S. A. Al-Sayari, A. Al-Hajry, and M. S. Al-Assiri, Phys. Status Solidi A **212**, 1851 (2015).
- [35]M. Dovrat, Phys. Rev. B 75, (2007).
- [36]L. H. Lin, X. Z. Sun, R. Tao, Z. C. Li, J. Y. Feng, and Z. J. Zhang, J. Appl. Phys. **110**, 73109 (2011).
- [37]L. T. Canham, Appl. Phys. Lett. 57, 1046 (1990).
- [38]G. Ledoux, J. Gong, F. Huisken, O. Guillois, and C. Reynaud, Appl. Phys. Lett. **80**, 4834 (2002).
- [39]M. L. Schultz, Infrared Phys. 4, 93 (1964).
- [40]H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39**, 625 (1981). [41]A. M. Fox, *Optical Properties of Solids*(Oxford University Press, 2001).
- [42]F. Gonella and P. Mazzoldi, *Handbook of Nanostructured Materials andNanotechnology*(Academic Press, San Diego, 2000).
- [43]C. V. Raman and K. S. Krishnan, Nature 121, 501 (1928).
- [44]R. Loudon, Adv. Phys. 13, 423 (1964).
- [45]P. Yogi, S. Mishra, S. K. Saxena, V. Kumar, and R. Kumar, J. Phys. Chem. Lett. 7, 5291 (2016).
- [46]P. A. Temple and C. E. Hathaway, Phys. Rev. B 7, 3685 (1973).
- [47]S.-E. Cheon, H. Lee, J. Choi, A. R. Jeong, T. S. Lee, D. S. Jeong, K.-S. Lee, W.-S. Lee, W. M. Kim, H. Lee, and I. Kim, Sci. Rep. 7, 7336
- (2017).
- [48]V. Paillard, P. Puech, M. A. Laguna, R. Carles, B. Kohn, and F. Huisken, J. Appl. Phys. **86**, 1921 (1999).
- [49]J. Zi, K. Zhang, and X. Xie, Phys. Rev. B 55, 9263 (1997).
- [50]null Simonian, null Sproul, null Shi, and null Gauja, Phys. Rev. B Condens. Matter **52**, 5672 (1995).

[51]M. Chandrasekhar, J. B. Renucci, and M. Cardona, Phys. Rev. B 17, 1623 (1978).

[52]U. Fano, Phys. Rev. **124**, 1866 (1961).

[53]J. R. Lombardi and R. L. Birke, J. Phys. Chem. C 114, 7812 (2010).

[54]Q. Hao, B. K. Juluri, Y. B. Zheng, B. Wang, I.-K. Chiang, L. Jensen, V. Crespi, P. C. Eklund, and T. J. Huang, J. Phys. Chem. C **114**, 18059 (2010).

[55]C. L. Baldwin, N. W. Bigelow, and D. J. Masiello, J. Phys. Chem. Lett. **5**, 1347 (2014).

[56]D. M. Sagar, J. M. Atkin, P. K. B. Palomaki, N. R. Neale, J. L. Blackburn, J. C. Johnson, A. J. Nozik, M. B. Raschke, and M. C. Beard, Nano Lett. **15**, 1511 (2015).

[57]M. Jouanne, R. Beserman, I. Ipatova, and A. Subashiev, Solid State Commun. **16**, 1047 (1975).

[58]Y. Li, Y. Yi, V. Coropceanu, and J.-L. Brédas, Phys. Rev. B 85, (2012).

[59]K. Balasundaram, J. S. Sadhu, J. C. Shin, B. Azeredo, D. Chanda, M. Malik, K. Hsu, J. A. Rogers, P. Ferreira, S. Sinha, and X. Li, Nanotechnology **23**, 305304 (2012).

[60]B. M. Bang, H. Kim, H.-K. Song, J. Cho, and S. Park, Energy Environ. Sci. 4, 5013 (2011).

[61]A. Backes, A. Bittner, M. Leitgeb, and U. Schmid, Scr. Mater. **114**, 27 (2016).

[62]C. V. Raman, Curr. Sci. 74, 382 (1998).

[63]V. J. Cadarso, N. Chidambaram, L. Jacot-Descombes, and H. Schift, Microsyst. Nanoeng. **3**, 17017 (2017).

[64]I. H. Campbell and P. M. Fauchet, Solid State Commun. **58**, 739 (1986).

[65]Y. Chen, B. Peng, and B. Wang, J. Phys. Chem. C 111, 5855 (2007).

[66]M. Tanwar, P. Yogi, S. Lambora, S. Mishra, S. K. Saxena, P. R. Sagdeo, A. S. Krylov, and R. Kumar, Adv. Mater. Process. Technol. **0**, 1 (2017). [67]B. Li, D. Yu, and S.-L. Zhang, Phys. Rev. B **59**, 1645 (1999).

[68]M. Cardona and F. H. Pollak, Phys. Rev. 142, 530 (1966).

[69]K. W. Adu, H. R. Gutiérrez, U. J. Kim, G. U. Sumanasekera, and P. C. Eklund, Nano Lett. **5**, 409 (2005).

[70]K. W. Adu, Q.Xiong, H. R. Gutierrez, G. Chen, and P. C. Eklund, Appl. Phys. A **85**, 287 (2006).

[71]R. Kumar, G. Sahu, S. K. Saxena, H. M. Rai, and P. R. Sagdeo, Silicon 6, 117 (2014).

[72]K. W. Adu, H. R. Gutierrez, and P. C. Eklund, Vib. Spectrosc. **42**, 165 (2006).

[73]D. Abidi, B. Jusserand, and J.-L. Fave, Phys. Rev. B 82, 75210 (2010).

[74]E. Janzén, G. Grossmann, R. Stedman, and H. G. Grimmeiss, Phys. Rev. B **31**, 8000 (1985).

[75]S.-J. Xiong and Y. Yin, Phys. Rev. B 66, 153315 (2002).

[76]S. Bar-Ad, P. Kner, M. V. Marquezini, S. Mukamel, and D. S. Chemla, Phys. Rev. Lett. **78**, 1363 (1997).

[77]A. E. Miroshnichenko, S. Flach, and Y. S. Kivshar, Rev. Mod. Phys. **82**, 2257 (2010).

[78]S. K. Saxena, R. Borah, V. Kumar, H. M. Rai, R. Late, V. g. Sathe, A. Kumar, P. R. Sagdeo, and R. Kumar, J. Raman Spectrosc. **47**, 283 (2016). [79]P. Yogi, S. K. Saxena, S. Mishra, H. M. Rai, R. Late, V. Kumar, B.

Joshi, P. R. Sagdeo, and R. Kumar, Solid State Commun.

[80]S. K.Saxena, P. Yogi, S. Mishra, H. MohanRai, V. Mishra, M.

KamalWarshi, S. Roy, P. Mondal, P. R.Sagdeo, and R. Kumar, Phys.

Chem. Chem. Phys. 19, 31788 (2017).