Raman Spectromicroscopic Study to Understand Microscopic Level Physics in Low Dimensional Semiconductor

Ph. D. Thesis

By

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Submitted in partial fulfilment of the requirements for the award of the degree of

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By

Manushree Tanwar



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INDIAN INSTITUTE OF TECHNOLOGY INDORE

I hereby certify that the work which is being presented in the thesis entitled "Raman Spectromicroscopic Study to Understand Microscopic Level Physics in Low Dimensional Semiconductor" in the partial fulfilment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2018 to January 2022 under the supervision of Dr. Rajesh Kumar, Professor, Discipline of Physics, IIT Indore. 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.

18 February 2022 signature of the student with date Manushree Tanwar

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

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05 July 2022

Signature of Thesis Supervisor with date

Professor Rajesh Kumar

Dedicated to My Family & Teachers



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Abstract

Any technological advancement requires a sound knowledge of physical process and phenomena taking place in a material that is used in a particular technological evolution. Quantum size (or confinement) effect¹ (QCE) is one of the main phenomena that enabled the scientific revolution to fabricate novel materials including Silicon nanostructures (SiNSs) which became the backbone of recent device development. Due to QCE, a material starts showing new properties which depend strongly on size in such a way that it becomes more prominent with decrease in size and are thus interesting to analyse.

Various methods of fabricating SiNSs include electrodeposition, laser induced etching, chemical vapor deposition and many others, out of which metal assisted etching (MACE) is one of the most economical and simplest techniques. The SiNSs fabricated using MACE have interesting perturbations in their vibrionic, electronic and optical properties, due to the effect of QC. Along with, in heavily doped SiNSs, the matching of energies of electronic continuum with discrete phonon, gives rise to electron-phonon interaction, also called as Fano resonance. Raman spectroscopy, being a sensitive and non-destructive tool, can detect the subtle scale phenomena and is thus indulges in the analysis of such systems. The perturbations in SiNSs are manifested in terms of various Raman line-shapes, when analysed through theoretical Raman line-shape models, yields interesting interplays of two physical phenomena for example QCE & Fano resonance.

This research work comprises of study to establish absorption spectroscopy as an easier and efficient technique for estimation of mean size and size distribution (SD) in SiNSs. This has been done by analysing a diffuse reflectance spectral line-shape by means of the proposed line-shape function developed by incorporating the size dependence of band gap. The model has been used for consolidate size analysis of two SiNWs samples prepared by metal induced etching technique. The estimated size and SD has been compared with the results obtained using Raman spectroscopy, a well-established technique for this purpose

The research work reported here deals with the analysis of perturbed Raman line shape obtained from heavily doped p- & ntype SiNSs. Cross sectional Raman mapping which has been done to understand the role of MACE in perturbing the size at microscopic level, reveals an interplay of size and two distinct physical phenomena namely, QCE & Fano resonance, with each other. The nature of complexities that arise in nano-crystalline via several ways like preparation methods can be easily assessed using Raman spectro-microscopy due to non-destructive assessment of sample along with requirement of only small amounts.

To vividly understand the mechanism of etching that leads to formation of nano-crystalline Si, a cross-sectional Raman mapping has been done for the first time, that validates the time dependent etching mechanism in SiNSs. The interplay time dependent stay of different portions of wafer causes has been found to cause a inhomogeneity in SiNSs size leading to a presence of smaller sizes at the tip of the NSs as compared to the vicinity of the substrate. Presence of structural inhomogeneity and physical phenomena therein taking place at microscopic level is very difficult to identify simultaneously using a holistic technique. Raman microscopy has been developed here and established for this purpose and shown to successfully work on n- and p-type silicon nanowires, a wellknown system otherwise, prepared using chemical technique. A Raman microscopic image) not only shows the presence of inhomogeneity in the nanocrystallites' size but also quantifies the size and its effect on microscopic quantum phenomena. Raman image has been shown to be a good blend of microscopic and spectroscopic technique. Another observation is the reduced doping in case of heavily doped p- and n-type nanostructures near the tip of the nanowire due to zonal migration of dopant atom (boron and phosphorus in p- & n- type respectively) and hence causing change

in the Fermi level position. The size dependent electron-phonon interaction, which manifest itself in terms of asymmetrical Raman line shape has been analysed using cross-sectional Raman mapping. Perturbations in optoelectronic properties like band gap enhancement and PL from SiNSs have also been analysed by suitable theoretical modelling.

LIST OF PUBLICATIONS

(A) From thesis work

M. Tanwar, D. K. Pathak, C. Rani, S. Kandpal, T. Ghosh, P. Mondal,
 A. Chaudhary, and R. Kumar, *Inverse Size Dependent Fano Parameter in Silicon Porous Wires: Consequence of Quasi-Continuum Flattening*, J. Phys. Chem. C 125, 12767 (2021).

[2] **M. Tanwar**, D. K. Pathak, A. Chaudhary, A. S. Krylov, H. Pfnür, A. Sharma, B. Ahn, S. Lee, and R. Kumar, *Pseudo-Anomalous Size-Dependent Electron–Phonon Interaction in Graded Energy Band: Solving the Fano Paradox*, J. Phys. Chem. Lett. **12**, 2044 (2021).

[3] **M. Tanwar**, D. K. Pathak, A. Chaudhary, P. Yogi, S. K. Saxena, and R. Kumar, *Mapping Longitudinal Inhomogeneity in Nanostructures Using Cross-Sectional Spatial Raman Imaging*, J. Phys. Chem. C **124**, 6467 (2020).

[4] **M. Tanwar**, D. K. Pathak, A. Chaudhary, S. K. Saxena, and R. Kumar, Unintended Deviation of Fermi Level from Band Edge in Fractal Silicon Nanostructures: Consequence of Dopants' Zonal Depletion, J. Phys. Chem. C **124**, 16675 (2020).

[5] **M. Tanwar**, A. Chaudhary, D. K. Pathak, P. Yogi, S. K. Saxena, P. R. Sagdeo, and R. Kumar, *Deconvoluting Diffuse Reflectance Spectra for Retrieving Nanostructures' Size Details: An Easy and Efficient Approach*, J. Phys. Chem. A **123**, 3607 (2019).

[6] **M. Tanwar** and R. Kumar, *Effect of Some Physical Perturbations and Their Interplay on Raman Spectral Line Shapes in Silicon: A Brief Review*, J. Raman Spectrosc. **52**, 2100 (2021).

(B) Beyond thesis work

[7] **M. Tanwar**, Shailendra K. Saxena, and Rajesh Kumar, *Raman Spectro-microscopy: A Tool to "See" Subtle Aspects in Science, Technology and Engineering*, J. Phys. Chem. C (Perspective) [Revision submitted].

[8] M. Tanwar, P. Yogi, S. K. Saxena, S. Mishra, D. K. Pathak, A. Chaudhary, P. R. Sagdeo, and R. Kumar, *Quantifying the Short-Range Order in Amorphous Silicon by Raman Scattering*, Anal. Chem. **90**, 8123 (2018).

[9] C. Rani, M. Tanwar, T. Ghosh, S. Kandpal, D. K. Pathak, A. Chaudhary, P. Yogi, S. K. Saxena, and R. Kumar, *Raman Spectroscopy* as a Simple yet Effective Analytical Tool for Determining Fermi Energy and Temperature Dependent Fermi Shift in Silicon, Anal. Chem. 94, 1510 (2022).

[10] C. Rani, M. Tanwar, S. Kandpal, T. Ghosh, D. K. Pathak, A. Chaudhary, and R. Kumar, *Predicting Raman Line Shapes from Amorphous Silicon Clusters for Estimating Short-Range Order*, J. Raman Spectrosc. n/a, (n.d.).

[11] A. Chaudhary, D. K. Pathak, **M. Tanwar**, J. Koch, H. Pfnür, and R. Kumar, *Polythiophene-NanoWO 3 Bilayer as an Electrochromic Infrared Filter: A Transparent Heat Shield*, J. Mater. Chem. C **8**, 1773 (2020).

[12] D. K. Pathak, A. Chaudhary, M. Tanwar, U. K. Goutam, P. Mondal, and R. Kumar, *Nickel Cobalt Oxide Nanoneedles for Electrochromic Glucose Sensors*, ACS Appl. Nano Mater. 4, 2143 (2021).

[13] D. K. Pathak, A. Chaudhary, **M. Tanwar**, U. K. Goutam, and R. Kumar, *Nano-Cobalt Oxide/Viologen Hybrid Solid State Device: Electrochromism beyond Chemical Cell*, Appl. Phys. Lett. **116**, 141901 (2020).

[14] A. Chaudhary, D. K. Pathak, S. Kandpal, T. Ghosh, **M. Tanwar**, and R. Kumar, *Raw Hibiscus Extract as Redox Active Biomaterial for Novel Herbal Electrochromic Device*, Sol. Energy Mater. Sol. Cells

215, 110588 (2020).

[15] S. Kandpal, T. Ghosh, M. Sharma, D. K. Pathak, **M. Tanwar**, C. Rani, R. Bhatia, I. Sameera, A. Chaudhary, and R. Kumar, *Multi-Walled Carbon Nanotubes Doping for Fast and Efficient Hybrid Solid State Electrochromic Device*, Appl. Phys. Lett. **118**, 153301 (2021).

[16] S. Kandpal, T. Ghosh, C. Rani, S. Rani, D. K. Pathak, M. Tanwar, R. Bhatia, I. Sameera, and R. Kumar, *MoS2 Nano-Flower Incorporation for Improving Organic-Organic Solid State Electrochromic Device Performance*, Sol. Energy Mater. Sol. Cells 236, 111502 (2022).

[17] S. Kandpal, T. Ghosh, C. Rani, M. Tanwar, M. Sharma, S. Rani,
D. K. Pathak, R. Bhatia, I. Sameera, J. Jayabalan, and R. Kumar, *Bifunctional Application of Viologen-MoS2-CNT/Polythiophene Device as Electrochromic Diode and Half-Wave Rectifier*, ACS Mater.
Au (2022).

[18] T. Ghosh, S. Kandpal, C. Rani, D. K. Pathak, **M. Tanwar**, A. Chaudhary, H. C. Jha, and R. Kumar, *Atypical Green Luminescence from Raw Cassia Siamea Extract: A Comparison with Red Emitting Tinospora Cordifolia*, ACS Appl. Bio Mater. **4**, 5981 (2021).

[19] T. Ghosh, S. Kandpal, D. K. Pathak, **M. Tanwar**, C. Rani, A. Chaudhary, and R. Kumar, *Aloe Vera Flower Extract as a Botanical Resistive Memory Element: A Natural Memristor!*, ACS Appl. Electron. Mater. **3**, 1556 (2021).

[20] A. Chaudhary, T. Ghosh, D. K. Pathak, S. Kandpal, M. Tanwar,
C. Rani, and R. Kumar, *Prussian Blue-Based Inorganic Flexible Electrochromism Glucose Sensor*, IET Nanodielectrics n/a, (n.d.).

[21] K. Neeshu, C. Rani, R. Kaushik, **M. Tanwar**, D. Pathak, A. Chaudhary, A. Kumar, and R. Kumar, *Size Dependence of Raman Line-Shape Parameters Due to Confined Phonons in Silicon Nanowires*, Adv. Mater. Process. Technol. **6**, 669 (2020).

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Abbreviation

Silicon	Si
Nanostructures	NSs
Crystalline Si	c-Si
Porous silicon	Psi
Nanowires	NWs
Metal assisted chemical etching	MACE
Metal nanoparticles	MNPs
Silver nanoparticles	AgNPs
Phonon confinement model	PCM
Quantum Confinement Effect	QCE
Full width at half maximum	FWHM
Diffuse reflectance absorption	DRA
Photoluminescence	PL
Field emission scanning electron microscope	FESEM
Transmission electron microscope	TEM
Fast Fourier transformation	FFT
Instrument response function	IRF
Face centered cubic	FCC
Transverse optical	ТО
Longitudinal optical	LO
Density of states	DOS
Zone center phonon	ZCP
Laser induced etching	LIE
Electron-phonon	e-ph
Asymmetry ratio	α_R

Chapter 1

Introduction

Nano-science has created revolution in the modern world, displaying its extraordinary and exceptional indulgence along with the promising growth in every field of science [1-6]. No wonder the state of the art technologies and everyday technological advancements include the role of daily revolutionary modifications in nano-technology. Arguably, the field of electronics [7,8] has had the most intangible impact of nano-technological advancements. Especially the past few decades have witnessed the dramatic decrease in feature size along with increased processing speed. Amongst these semiconductor electronics technology has seen revolutionary change including the transition from macroscopic to nanoscale transistors. The birth history of semiconductors traces back to the invention of the rectifier in 1874, followed by the invention of point contact transistor [9] in 1947 by Bardeen and Brattain at Bell Laboratories. A decade later in 1959, the invention of bipolar integrated circuits, IC's by Kilby of Texas instruments and Noyce of Fairchild Semiconductor in the US, further paved for small scale electronics.

Nanotechnology has had a long and fascinating history and has gained considerable momentum following the Feynmans's famous lecture [10] in 1959 on "There is plenty of room at the bottom". Nano scaled materials not only allow one to exploit the fundamental strangeness of quantum mechanics [11] but also drive the interest of broader scientific community raging from the disciplines of science [12,13] and engineering.

The perturbed novel properties of semiconductors is due to the effect of quantum confinement (QC), enabling one to tailor vibrational [14],

Chapter 1

optical [15,16], electronic properties [17] of material and thus increasing its use in a arrange of devices. This effect is observed when the size of particle is too small to be comparable to the wavelength of electron. The confinement of electron and holes in semiconductor nanomaterials, significantly depends on the Bohr exciton radius of the material [18]. The bulk crystalline structure is preserved in nanomaterials but they have molecule like discrete electronic states exhibiting strong size dependent properties [15,19,20].

The vivid interest in these QC systems relates to the special nanoscopic physics that governs their properties as well as the various associated possible electronic and optoelectronic applications. Of the many semiconductor nanostructure (NS) systems that have been investigated in the context of QC, group-IV elements are among the most widely studied. From a central viewpoint, interest in this class of materials arises mainly because the indirect band gaps of Si and Ge preclude a straightforward understanding of the observed relatively strong photoluminescence arising from associated NS [21,22]. From a more practical point of view, NCs made up of these elements are compatible with the robust microelectronics industry upon which much of modern technology is based while also being biologically and environmentally benign.

Amongst all the semiconductors, silicon has been exhaustively exploited due to its second most natural abundance after oxygen. In nature, however, silicon is found in the form of compound with oxygen, aluminium and magnesium and thus is extracted and purified using various processes. The use of silicon in modern electronic devices that includes resistor, diodes, transistors, IC's has made it the most used semiconductor, owing to its resistance to very high temperature and current. Pure monocrystalline Si is being used as a wafer and mechanical support for IC's. Pure Silicon conducts electricity poorly, so it is dope with different impurities to increase the level of conductivity.

Another way to perturb the chemical and physical properties of a material is by confining it along one of its three dimensions [23–25].

For example, silicon being an indirect semiconductor has a band gap [26] of 1.1 eV. does not show photoluminescence, but when its dimension is confined along one of the axes, it starts emitting visible light [27,28]. Porous silicon nanowire (PSiNW) is one such candidate, which emits PL and was serendipitously discovered by Arthur Uhlir Jr. and Ingeborg at Bell's Laboratories [29] in USA, while working on electrolytic shaping of the surface of silicon and germanium. They were trying to develop an electrochemical method to machine silicon wafers for use in microelectronic circuits. Under the appropriate electrochemical conditions, the silicon wafer, did not dissolve as expected, but instead fine holes appeared, propagating primarily in the <100> direction in the wafer. PS, typically a few micrometers-thick film was thus produced by electrochemical etching of silicon wafer in HF solution under an anodic bias. In 1970s and 1980s a again a considerable interest in PS arose because the high surface area of PS was found to be useful as a model of the spectroscopic analysis of crystalline silicon (c-Si), as well as a precursor to generate thick oxide layers on silicon, and as a dielectric layer in capacitance-based chemical sensors [30,31].

The increase in the study of porous silicon exploded in the early 1990s due to the identification of quantum confinement effects (QCEs) in the absorption spectrum of PS by Ulrich Gosele [32]. Simultaneously Leigh Canham [33,34] at the Defence Research Agency in England reported efficient, bright red-orange photoluminescence. QCEs arise when the pores become extensive enough to overlap with each other, generating nan-meter Si [35].

After this discovery of visible light emission from PS, scientist started focussing on creating silicon-based optoelectronic devices [36], including switches [37], displays [38]. Modifications in the fabrication techniques to control the pore size, thickness and surface to volume ratio, led to its fabrication using various techniques. Various methods have been developed to fabricate SiNSs through top-down [39] as well as bottom up approaches [40]. For example metal assisted chemical etching, popularly known as MACE [41,42], Vapour-liquid-solid

growth (VLS) [43,44]and laser induced etching (LIE) [45,46] are used to obtain various SiNSs as NWs, PSiNWs, Si nanopores and fractal SiNSs.

Amongst all the techniques, (MACE) is one of the most extensively used techniques due to its economical and feasible nature, to prepare Si quantum wires by using the solution of hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2) for the chemical dissolution of Si. The Si NSs fabricated by this process is present as porous Si network, consisting of pores separated by thin walls of Si having thickness in the range of a few to several nano-meters. Properties of such materials depend on various experimental parameters such as etching time, concentration of HF and deposition time of metal nanoparticles. In the present study the Si NSs have been prepared by MACE technique. This technique is a method of porosification where metal nanoparticles are deposited onto semiconductors followed by etching in an etchant. Cartoon in Figure 1.1 shows the SEM morphology of SiNSs prepared using MACE. The perturbed physical and chemical properties of porous silicon prepared using MACE is of considerable interest. Some of which include, room temperature visible light emission, band gap enhancement, and phonon confinement. To use any material for its device applications requires thorough analysis of the perturbed properties using various spectroscopic and microscopic tools.



Figure 1.1: Cartoon depicting morphologies of SiNSs, prepared using MACE.

In last few decades, the era of nanoscience and nanotechnology, lowdimensional materials, especially semiconductors, have attracted much attention because of their technologically important tunable electronic [47] and opto-electronic properties, delivering promising many fields such as energy storage [48,49], potentials in conversion [50] and sensors [51–53], in comparison with their bulk counterparts and have gained enormous attention from researchers. In addition to the technological importance, SiNSs also provide very good platform to understand various physical phenomena at nanoscales to understand physics in quantum materials. These SiNSs are promising because of mastery over synthesis methods, and reduced size effect leading to modifications in electronic bandgap [54], optical and thermal properties. In addition, the growth of ordered dots, columns, and porous structures have become an active area of research due to its possible technological applications such as template for growing nanowires and nanorods, photonic bandgap material, buffer layer for the growth of high crystal quality, strain relaxed hetero epitaxial films [55].

Despite extensive research on the fabrication of low-dimension semiconductors such as SiNSs, an accurate control of their surface topography remains a key issue for the development of future optoelectronic at nanoscale. One of the main challenges is to develop ordered nanostructured surface with high quality and large surface area. The main bottleneck in the application of quantum dots^[39] is the difficulty of creating ordered structure with high uniformity in the size and crystallinity.

In the quest for potential novel applications, though various kinds of nanostructures have been fabricated which directly invites the development of advanced tool for superior characterization appropriate technique to harvest subtler physics at nano scale to compete with ever evolving and demanding need, especially today when the requirement to develop new materials and devices is the call of the hour.

Chapter 1

Amongst all the spectroscopic tools available for material characterization, Raman spectroscopy still remains one of the non-destructive tool to asses phase, doping, strain/stress, and effect of various other perturbations in a varietal class of materials.

Raman effect [56,57], named after the discovery of "a new radiation" observed as a consequence of inelastic scattering of photons from any material. Raman scattering, being a weak (low probability) phenomenon, remained as a topic of scientific importance until lasers were invented which enabled it to be developed as a molecular spectroscopic tool known as "Raman spectroscopy". With the advent of advanced lasers, photon detectors and machine interfacings, it has become one of the most versatile non-destructive spectroscopic tools in materials characterizations. Even though it is a spectroscopic tool that largely probes vibrational properties, it has advantages over IR spectroscopy due to flexibility in choosing the excitation source making it more appropriate for investigating biological samples as well [58]. Due to its interdisciplinary nature, Raman spectroscopy, very often in combination with IR spectroscopy, finds applications in almost all areas of science and technology including materials science & technology. However, development in modern technologies and involvement of machines have led to increased output in terms of data, the analysis of results still remains to be done by individuals and must be done carefully so that actual conclusions can be drawn. Raman data analysis is done by looking at the basic spectral parameters like peak position, width (characterized using full width at half maximum or FWHM) [59] etc to identify molecular structure. It is equally important to analyse the whole Raman spectral line-shape to get deeper insight about different scientific phenomena taking place at microscopic level that may affect the way a Raman spectrum gets manifested. This is more important in the fast growing area of science and technology.

In nano systems, detection of small scale phenomena and perturbed physical and chemical properties has helped scientific community to evolve and set up new characterization paradigms. As mentioned

above, among all the characterization techniques, basic and advanced Raman spectroscopy and microscopy have proven to be a quintessential and non-invasive method to analyse and understand device physics as well as to decipher any complex phenomena in nanoregime wherein in microscopy only a small amount of sample can be detected in a very simple and fast manner with low laser power with no damage to the sample. Apart from merely looking at Raman spectral peak positions and widths, experimentally obtained Raman spectral line shape when analysed and fitted with appropriate theoretical models, can yield precise information about the perturbation that have taken place due to various microscopic interactions like (QCE [60-63]), electron-phonon interaction [64] etc. Raman line shape parameters like peak position, FWHM, asymmetry ratio (α_R) are a prominent set to differentiate one phenomena from other. Typically asymmetry ratio (α_R) is defined as the ratio of spectral half width towards lower " Γ_L " and higher " Γ_H " wavenumber side of the peak position i.e, $\alpha_R = \Gamma_L / \Gamma_H$. Similar to QCE, electron-phonon interaction in SiNSs has been widely envisaged using Raman spectroscopy. Other perturbations that affect the Raman line-shape in are temperature [65], pressure [32], stress [66], excitation wavelength [67], doping type [68] and doping concentration etc., as shown in Figure 1.2. Looking at how uniquely (or otherwise) these perturbations affect the Raman lineshape, one can investigate the true nature of physical process taking place at subtler levels [69] in the material.

Raman scattering in solids, especially semiconductors, occurs from the zone centre phonons [62] (the k=0 selection rule) resulting in a sharp symmetric Raman spectrum having peak position corresponding to zone centre phonon frequency. This k=0 rule gets relaxed in NSs [70,71] where phonons other than zone centre also participate in the Raman scattering resulting in a red shifted and asymmetrically broaden Raman spectra. This happens due to the confinement of phonons within the physical boundary of the NSs. To understand confinement effect in NSs using Raman spectroscopy, Richter *et*

al [62]. gave PCM which was improved later by Campbell *et al* [72] This improved model not only explains the experimental observation but also proves to be very useful in estimating the size and degree of confinement in NSs. Phonon confinement effect in terms of asymmetric Raman line shape in Si NSs



Figure 1.2: Schematic representing effect of various perturbations on Raman line-shape.

has been investigated very extensively due to its capability of being extremely useful method in investigating subtle physics at nanoscales. In addition to confinement effect, Fano resonance [73–77] (electronphonon interaction) caused by the matching of energies of one phonon with discrete continuum provided either by heavy doping [78] or photoexcitation [79], is another factor that can induce asymmetry in Raman spectral line shape. 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 pre-maximum side and post-maximum side for heavily doped n- type [80] and p-type [81] Si respectively meaning that it depends on the nature of the system. Therefore in n-type quantum confined system (broadening in the pre maximum side of Raman line shape), Fano effect produces extra broadening in n-type system. On the other hand, for Fano effect in p-type confined system the situation will be entirely different because confinement effect result in increased half width in pre maximum side (appears asymmetric broadening) and Fano effect results the increased half width in post maximum side. The interplay of both the effect causes perturbation in the line-shape as analysed using parametric Raman line- shape analysis. The observation of interplay between the two effects is an interesting study and worth analysing.

In nanoscale systems where change in physical properties might be as small to be investigated to few atomic clusters [82], a technique detecting subtle changes is quintessential to discern such delicate deviations from their bulk counterparts. Size dependent properties and phenomena of NSs such as band gap enhancement [83], phonon confinement and electron-phonon coupling are extensively investigated using Raman spectroscopy/microscopy due to its non-invasive nature and sensitivity to detect subtler changes even at atomic scales. Studying the perturbed optical and electronic properties and hence analyzing above phenomena in nanomaterials requires an imperative modification in the existing experimental techniques wherein a quantum confinement induced modification in such phenomena takes place. Raman spectroscopy proves to be an appropriate tool due to the sensitivity of the whole Raman line-shape, and not only the peak position, to subtle perturbations in the system that directly or indirectly affect phonon in any way [84,85]. Raman spectroscopy when indulged in analyses of heavily doped confined systems manifests itself in the form of an asymmetric Raman line shape comprising of an antiresonance minima, maxima and a dopant peak [86,87]. A size induced variation in electron-phonon coupling can be easily analyzed by carefully fitting theoretical Raman line shape by experimentally obtained data points.

The objective of this thesis is too analyze perturbed physical properties of SiNSs like band gap enhancement via using a dual approach of theoretical and experimental investigations by utilizing a simple and economic technique named diffused reflectance spectroscopy through spectral line-shape analysis. In the proposed model, a theoretical line-shape has been derived by taking into account a size distribution function which represents a variation in absorption coefficient [88] as a function of size which in turn depends on the band gap thus on the excitation photon energy. In nanomaterials, the interferons [89] are confined in quantum domain and show an increasing e-ph coupling strength with a decrease in NSs size. However, this trend in e-ph coupling strength is exclusive and validated only if the dopant density/concentration, which provides sufficient carriers to the quasi continuum, remains constant and only size of NSs varies and hence such co-relation can be directly analyzed in a system where quasi electronic continuum is known to remain constant if the dopant density in system remains otherwise unaltered. However, in NSs prepared using MACE not only longitudinal variation in size is observed but a phase-induced dopant migration, which has been analyzed in this thesis, is very likely to cause perturbation in the quasi continuum and thus affecting its interference with one phonon states. In this case, the generic size dependent e-ph coupling is likely to get perturbed due to variation in doping density of the system due to external parameter which is dopant migration from NSs due to coexistence of solidus-liquidous phase during MACE which directly affect the e-ph coupling and is not a unswerving consequence of size reduction(increment).Such an amalgam of reduced electronic continuum and longitudinal heterogeneity in size makes it a stimulating and intriguing system to understand using Raman line shape analysis. The modified quasi-continuum (due to dopants'
Introduction

alteration) may get flattened or sharper depending on the system and thus will tend to modify the overall behavior of confined interferons to be detected using Raman spectroscopy by analyzing the overall spectral line-shape. The objective of this thesis is to use diffused reflectance spectroscopy, Raman microscopy/mapping (RM) as a technique that can be used to "see" certain physical processes taking place at the microscopic level which otherwise can only be understood indirectly, thus containing an element of ambiguity. This has been done by using the Raman spectroscopy aim mapping mode across the length of the nanowire to investigate not only its size profile, using quantum confinement model (the structural information) but also physical interactions at the nanoscale. It is observed that RM of (Si) nanowires NWs provides insight about size inhomogeneity across their length which might be originating inherently as a consequence of the synthesis process. The Raman mapping demonstration is used here on a simple and already known SiNWs system to realize its potential capabilities beyond the existing ones. This study might open a new way for in-depth studies of a hidden subtle physical phenomenon in nanomaterials so that these can be used more efficiently.

All the results, discussion and conclusions have been presented in the thesis as per the following chapter-wise plan:

Chapter 1 (current chapter): It provides an introduction and discusses the current status of the problem dealt here and defines the objectives.

Chapter 2: The general background and overview of Si is summarized in chapter 2 along with its basic properties and how it is affected by various perturbations. Other relevant theoretical backgrounds, helpful in explaining the results, are also included here.

Chapter 3: This chapter summarizes the experimental methods used to fabricate and characterize Si NSs. Recipe for sample preparation using MACE. Model and make of all the characterization tools and their working principle is also provided here for a quick reference.

Chapter 4: This chapter consists of diffused reflectance spectroscopic analysis to estimate inhomogeneity in size & size distribution in

SiNSs.

Chapter 5: This chapter comprises of cross sectional Raman mapping in order to understand the formation of fractal porous SiNWs using MACE.

Chapter 6: This chapter comprises of analysis of location of Fermi level in heavily doped p- type SiNSs by validating the zonal migration of dopant atoms caused due to MACE.

Chapter 7: This chapter contains a consolidated study of size dependent electron-phonon interaction in heavily doped n- & p- type fractal porous SiNWs established via cross-sectional mapping.

Chapter 8: All the conclusions deduced from the results reported in above chapters are listed here. This chapter also discusses possible future scope of work that can be carried out for further development in this field.

Chapter 2

General Overview and Theoretical Background

2.1 Overview of Si

Silicon [90,91], the second most abundant element (after oxygen) in the Earth's crust, making up 25.7% of the crust by mass, is the backbone for electronics and IC technology. It is most commonly found in nature as Si dioxide (SiO₂). Pure Si is a rigid and dark grey solid with a metallic lustre. It holds a crystalline structure same as that of diamond form of carbon. It shows many chemical and physical similarities with carbon. Highly purified Si, doped with elements such as boron, phosphorus and arsenic, is the basic material used in computer chips, transistors, Si diodes and various other electronic circuits. Three stable isotopes of the Si are known: ²⁸Si (92.2 %), ²⁹Si (4.7 %) and ³⁰Si (3.1 %). Other properties of Si are discussed below. General properties of Si have been given in appendix 1.

2.1.1 Crystal Structure of Si

Si is a non-metallic element which belongs to the fourth group of element in the periodic table with four electrons in its outermost shell. Each Si atom shares one of its four valence electrons in a covalent bond with each of four adjacent Si atoms. Crystal structure of Si is shown in Figure 2.1. It has diamond like structures consisting of two inter penetrating face centred cubic (FCC) lattices [92], displaced along the body diagonal by one-fourth of the diagonal length. It is regarded as an FCC lattice with a basis containing two identical atoms. In c-Si, each Si atom is connected to four other atoms tetrahedral. The



lattice parameter of c-Si is 0.543 nm and tetrahedral angle is 109.2° .

Figure 2.1: Crystal structure of Si [90].

2.1.2 Phonons in Si

The phonon dispersion curve [26,93,94] of c-Si is shown in Figure 2.2. Different transverse, longitudinal, acoustic, optic modes are marked as LA, LO, TA and TO in the Figure. 2.2. As it is well known that the Si is a non-polar semiconductor material due to that the frequency of LO and TO modes are equal [95] at the zone centre (k=0). It is evident from Figure 2.2 that, near zone edge the frequency of TA mode shows relatively flat nature as compared to other modes. It is also worth mentioning here that the energy of TA mode is comparatively lower than the LA mode. Understanding the phonon dispersion in a solid is important to understand the Raman scattering from that material and vice-versa.



Figure 2.2: Phonon dispersion curve of Si [96].

2.1.3. Band Structure and Optical Properties of Si

It is well known that the Si is an indirect band gap solid (in bulk form). Figure 2.3 shows the energy band structure of Si reported by Cardona and Pollak [26]. It is evident from Figure 2.3 that in case of c-Si, the valence band maximum is located at the centre of the Brillouin zone and the minimum of conduction band is located at X point along the Δ direction which makes it indirect band gap material with band gap of 1.1eV. Due to the indirect nature of band gap, c-Si cannot emit light (emission of photon when sufficient amount of energy have been incident on it) efficiently since the radiative recombination of the electron-hole pairs needs the participation of a momentum-conserving phonon, thus making the process less favourable. Unlike the other semiconductors like GaAs [97] and InP [98], in which the maximum of valence band and minimum of conduction band are located at the same k point which makes it a direct band gap materials. In this case, the radiative recombination is more probable as no mediating phonon is required.



Figure 2.3: Energy band diagram of Si [26].

Figure 2.4 shows the schematic representation of direct and indirect band gap transition. It is clear from Figure 2.4 that an indirect transition involves photons and phonons both at a time. In quantum mechanics there are two different processes namely first order and second order process. The first order process involves direct transition with no role of phonons whereas second order process involves indirect transitions where a photon must be destroyed and a phonon must be either created or destroyed.



Figure 2.4: Interband transitions in (a) direct band gap and (b) indirect band gap solids. The vertical arrow represents the photon absorption while wiggly arrow represents the absorption or emission of a phonon [99].

The rate of transition of an indirect absorption is therefore much smaller than that of direct absorption. The smaller transition rate for indirect process can be clearly shown in the absorption spectrum of Si [100] in Figure 2.5. The increase in absorption is slow because of the indirect nature of band of Si which having band gap of 1.1 eV.



Figure 2.5: Absorption coefficient versus photon energy for Si at room temperature [100].

In addition to this, there are two distinct absorption peaks at 3.5eV and 4.3eV (Figure 2.6) are present in the absorption spectra of Si when scanned in the range of 0-10 eV. The absorption coefficients in the spectral region around these two values are very large as compared to its value near band edge (1.1 eV) (as shown in the Figure 2.5). This is a significance of following two factors. Firstly, the band edge absorption is weak because it is indirect band gap material, and secondly, the density of states at the band edge is comparatively small. The measured absorption spectrum is actually dominated by direct absorption at photon energies where the density of states is very high. The 3.5 eV transition energy corresponds to the minimum direct separation between the conduction and valence band near the 'L' points (i.e. $L_1 - L_3$ in the Figure 2.3). Apart from this, the separation of the conduction and valence bands adjacent to the X point is also significant. This energy corresponds to the absorption maximum at 4.3 eV. A small kink appreciated near 5.4 eV, which corresponds to the energy E_3 , near 'L' point in Figure 2.3.



Figure 2.6: Room temperature inter-band absorption spectrum of Si [99].

2.2 Low Dimensional Semiconductors and Effect of Reduced Dimensionality

When the size or dimension of a material is reduced form a large or macroscopic size to a very small size, dramatic changes in properties of these nanomaterials can be observed. In these low-dimensional systems, electronic, optical and vibrational properties are different compared to that of the bulk mainly due to the quantum size effects [35]. The most dramatic changes in properties take place in the structures when the carriers/phonons are confined in the region of a characteristic length which is of the order of its Bohr exciton radius [101,102].

When the confining dimension is large compared to the de Broglie wavelength of the particle, the particle behaves as free particle within confined area. As the confining dimension is decreased and reaches the order of the de Broglie wave length, the electronic and vibrational states of particle are modified due to the overlap of the wave functions reflected from the barriers. This is defined as the "*quantum confinement*" [103,104]. The effect of reduction in size of these

semiconductors, known as quantum size effect [8,25], leads to confinement of electrons and phonons in one or more directions. Due to this quantum effect, the electronic and optical properties of the semiconductors can be tailored for novel device applications. Depending upon the degree of confinement, a variety of quantum structures can be fabricated with modulated properties. Some of the major properties that change with size of the low-dimensional semiconductors are discussed in following sub-sections.

2.2.1 Energy Gap Enhancement

Leading effect of reduced dimensions of the semiconductor is reflected in modification of electronic energy gap. Effective energy gap, of the quantum structure is enhanced due to quantum size effect (as shown in schematic of Figure 2.7). This enhancement in energy gap can be calculated using the analogy to the problem of a particle within a suitable potential barrier. Modifications of energy gap with confinement dimensions are given below [83,105]:



Figure 2.7: Schematic showing band gap enhancement as a consequence of quantum confinement effect.

(i) Quantum dots

In case of confinement in all three spatial directions, quantum dot or quantum box structures are formed depending on their curvilinear or rectangular cross-sections, respectively. Quantum confinement effect is most pronounced in such structures. Translational motion of the carriers is constrained along all directions and the energy Eigen value is given by:

$$E_{g_{eff}}^{0D} = E_g + \frac{\pi^2 \hbar^2}{2m_r} \left(\frac{1}{d_1^2} + \frac{1}{d_2^2} + \frac{1}{d_3^2} \right), \qquad (2.1)$$

where d_1 , d_2 and d_3 are the confinement dimensions along x-, y- and zdirections respectively.

(ii) Quantum wires

In case of confinement along two spatial directions, the motion along the third dimension is not confined and the structure is called quantum wire. Two-dimensionally confined quantum wire structure acts as a potential well that narrowly confines electrons and holes in two directions. If the confinement dimensions are taken to be along x- and y-directions, the motion of the carriers in the z-direction remains unaffected by the potential barrier. The energy Eigen value for quantum wire is given by:

$$E_{g_{eff}}^{1D} = E_g + \frac{\pi^2 \hbar^2}{2m_r} \left(\frac{1}{d_1^2} + \frac{1}{d_2^2}\right), \qquad (2.2)$$

where d_1 and d_2 are the confinement dimensions along x- and ydirection, respectively ($d_3 >> d_1, d_2$).

(iii) Quantum well

In case of confinement along one spatial direction, the structure is named as quantum wells. The motion of electrons and holes is confined in one dimension (along x direction, say) but is free to move in the other two directions (y-z directions). In these structures, the semiconductor with smaller band gap is sandwiched between larger bandgap semiconductors. If thickness of the narrow gap semiconductor layer is small enough, the energy of electrons and holes in the direction perpendicular to the interfaces is quantized. With analogy to the problem of a particle in an infinite well, the energy Eigen value of the system is given by

$$E_{g_{eff}}^{2D} = E_g + \frac{\pi^2 \hbar^2}{2m_r} \left(\frac{1}{d_1^2}\right), \qquad (2.3)$$

In Eq. 2.1 – 2.3, E_g is energy gap of the bulk and E_g^{eff} is energy gap due to confinement and m_r is reduced mass of electron and hole. Energy level diagram of a quantum well structure is shown in Figure 2.8.



Figure 2.8: Energy level diagram of a quantum well structure.

2.2.2 Modification in the Electron Density of States

Quantum confinement of charge carriers modifies the density of states in low-dimensional semiconductors. The density of states of crystalline semiconductor is a continuous parabolic function of energy. While in the case of low-dimensional semiconductors, carriers are confined to move and the momentum vector k takes well discrete values for confined directions. This leads to density of states which are different from that of crystalline semiconductors. Density of states g(E) for crystalline and low-dimensional semiconductors are given by Alivisatos *et al.* [106] as follows:

1. Crystalline semiconductor

$$g(E)_{3D}dE = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2} dE,$$
 (2.4)

Where *E* and m^* is the energy and effective mass of electrons.

2. Quantum well structure

$$g(E)_{2D}dE = \frac{m^*}{2\hbar^2} \sum_{i} H(E - E_i) dE,$$
 (2.5)

Where '*i*' is a quantum number used to label the discrete levels in confined direction and $H(E-E_i)$ is the Heaviside function. The $H(E-E_i)$

- = 1 for $(E-E_i) > 0$ and $H(E-E_i) = 0$ for $(E-E_i) < 0$.
- 3. Quantum wire Structure

$$g(E)_{1D}dE = \frac{1}{\pi} \left(\frac{m^*}{2\hbar^2}\right)^{1/2} \sum_i \frac{n_i H(E - E_i)}{(E - E_i)^{1/2}} dE, \quad (2.6)$$

4. Quantum dot Structure

$$g(E)_{0D}dE = \sum_{i} 2\delta (E - E_i) dE,$$
 (2.7)

Where $(E-E_i)$ is the delta function. Figure 2.9 shows the variation of density of states with energy according to Eqs. 2.4 to 2.7. Quantum dot shows discrete spectrum of a pseudo-atom or a molecular system, ideally with vanishing width of the states and a separation similar to that found for atoms and molecules. Density of states is generally used to determine various electronic and optical properties. Since g(E) varies differently in all the three cases of quantum confinement, the properties of a material can be drastically different for different degrees of confinement.



Figure 2.9: Density of states in different confinement configurations (a) bulk, (b) quantum well, (c) quantum wire and (d) quantum dot [107].

2.2.3 Photoluminescence

Photoluminescence is the spontaneous emission of light from a material under optical excitation. PL spectroscopy is an extremely sensitive and non-destructive method of probing the electronic structure of materials. Intensity and spectral content of this PL is a direct measure of various important material properties. In PL spectroscopy, photons are absorbed from an excitation source such as laser or lamp, which injects electrons into the conduction band and holes into the valence band. The electrons are initially created in higher electronic states in the conduction band and loose energy by emitting photons. In the case of photo-excitation, these electrons return to valence band resulting luminescence of lower frequency. This luminescence is called PL.

2.2.4. Photoluminescence from Si Nanostructures

Visible PL has been observed from Si NSs [21,34,38,108–110] unlike bulk Si, which has indirect bandgap corresponding to infrared region. Visible PL from Si NSs can be explained using uncertainty principle and zone folding as discussed below. When the electron is localized, its momentum becomes uncertain according to the Heisenberg Uncertainty Principle. This phenomenon may offer a solution to indirect bandgap of Si. The uncertainty principle, $\Delta p \cdot \Delta x \approx \hbar$ or $\Delta k \cdot$ $\Delta x \approx 1$, where Δx and Δk are the uncertainties in the position and wave vector, respectively. In c-Si, Δx is infinity due to its translational symmetry. Thus only transitions of electrons with $\Delta k = 0$ is allowed by the uncertainty principle. In a NS of size 'L', the uncertainty in position is 'L' which brings an uncertainty of 1/L in the momentum (i.e. $\Delta k \sim 1/L$). All the transitions are allowed when Δk lies in the range of 1/L. Therefore, optical recombination is possible in appropriately low dimensional materials. As a consequence, it can be said that the bandgap is effectively a direct type in nature for optical transitions to take place. However, to find the exact up-shift and its dependence on the confinement dimensions, rigorous band structure calculations have been primarily done for idealized Si quantum wire and dot structures using semi-empirical [83] and first-principles calculations [111].

Using the effective mass theory, some authors [112,113] have explained that the fundamental indirect band gap in Si is expected to behave like a direct band gap at the Brillion-zone centre. A concept of zone folding has also been used to explain the coupling between the conduction band minima and the valence band maxima [114]. In bulk Si, the indirect conduction band has six minima positioned at \pm (0, 0, 0.85) $2\pi/a_0$, \pm (0, 0.85, 0) $2\pi/a_0$ and \pm (0.85, 0, 0) $2\pi/a_0$, where the zone boundary is at $2\pi/a_0$ and a_0 (~ 5.43 Å) is the lattice constant. These minima are anisotropic ellipsoids with two light transverse electronic masses, m_T = 0.19 and one heavy longitudinal electronic mass, m_L =0.92.

These minima are up-shifted in energy by a large amount in the confinement plane and less amount in other directions. The concept of zone folding rests with an increase in the coupling of conduction band minima near the zone boundary and the valence band maxima at the zone centre. This is done conceptually by repeated folding of the Brillouin-zone itself in submultiples. This defines the new reduced zone boundary about which the conduction band is folded to the zone centre and making the direct bandgap. Different theories, which explain the visible PL from Si NSs at room temperature, are available in the literature to calculate analytically the exact up-shift and its dependence on the confinement dimensions. Most of the reported work on visible PL correlates this phenomenon due to quantum confinement effect [21,115,116]. Other proposed models attribute this PL due to oxide related interfacial defect states [117] and surface states [118].

2.3 Raman Scattering

Raman scattering is an inelastic light scattering phenomenon [80] When a beam of monochromatic light illuminates a gas, liquid or solid, a very small fraction of light is scattered in all directions. Scattered light consists of almost same incident frequency, known as Rayleigh scattering. Additional frequencies, known as Raman lines, are also present above and below the incident frequency [57] (possessing higher and lower energies than the energy of incident). The lines on the low frequency side of the exciting line are called 'Stokes' line, whereas those on the high frequency side are called 'anti-Stokes' lines. Observation of low and high frequency components along with the incident frequency in the scattered radiation is known as the Raman effect [56] and this type of scattering is called Raman scattering.

2.3.1 Raman Scattering in Semiconductors

In the Raman scattering [119,120] process, a certain amount of energy is gained or lost by an incident photon having energy $\hbar\omega_i$ (incident) in order to create or annihilate elementary excitations of the solid, usually phonons, resulting in a scattered photon of a different energy $\hbar\omega_s$ (scattered). The amount of energy transferred corresponds to the Eigen energy $\hbar\omega_j$ of the elementary excitation involved. The energy conservation in first-order Raman scattering in which one phonon participates is given by

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\omega_i, \qquad (2.8)$$

Here the "minus" sign stands for a phonon excitation (Stokes process) while the "plus" sign implies a phonon annihilation (anti-Stokes process). The momentum $\hbar k_i$ of the vibrational excitation is related to the momentum of the incident photon $\hbar k_j$ and scattered photon $\hbar k_s$ according to momentum conservation is given by

$$\hbar k_i = \hbar k_s \pm \hbar k_i, \qquad (2.9)$$

In fact, Raman interaction between photon and phonon in the semiconductor takes place through the involvement of the electronic virtual states [121] as shown in Figure 2.10. It shows Hamiltonian for electron-radiation and electron-lattice interaction as H_{E-R} and H_{E-L} , respectively. For homo polar semiconductor (e.g. Si), the electron lattice interaction is due to the excitation of phonons which perturb the

periodic potential acting on the electrons by the displacement of atoms. The electronic dipole moment M produced by an electric vector of the incident light is written as [122,123]

$$M_{\rho} = \sum_{\sigma} \alpha_{\rho\sigma} E_{\sigma}, \qquad (2.10)$$

where $\alpha_{\rho\sigma}$ is the polarizability tensor associated with electrons in the crystal. The electronic polarizability can be expanded in a power series of *r*,

$$\alpha_{\rho\sigma} = \alpha_{\rho\sigma}^{(0)} + \sum_{\mu} \alpha_{\rho\sigma,\mu} \cdot r_{\mu} + \sum_{\mu\nu} \alpha_{\rho\sigma,\mu\nu} \cdot r_{\mu} \cdot r_{\nu} + \cdots,$$
(2.11)

$$\alpha_{\rho\sigma,\mu} = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial r_{\mu}}\right)_{r=0} \text{ and } \alpha_{\rho\sigma,\mu\nu} = \left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial r_{\mu}\partial r_{\mu}}\right)_{r=0}, \quad (2.12)$$

In Eq.2.12, the second term is linear in *r* and the third term is quadratic in *r* which gives rise to first-order and second-order Raman scattering, respectively. Figure 2.10(a) shows the first-order Raman scattering process. For Si, the electron-lattice interaction is due to the excitation of phonons, which perturbs the periodic potential acting on the electrons by displacement of atoms. Since k_i and k_s (~105 cm⁻¹) are negligible in comparison to the width of the Brillouin zone (~3x10⁸ cm⁻¹), momentum conservation allows the first-order Raman scattering for the phonon frequency at $k \approx 0$ (i.e. wavelength of the phonon is very large compared to the lattice). This is known as selection rule of the first-order Raman scattering for phonons. Chapter 2



Figure 2.10: Raman scattering processes in terms of elementary interactions H_{E-L} (Electron-Lattice interaction Hamiltonian), H_{E-R} (Electron-Radiation interaction Hamiltonian), ω_i (frequency of incident photon), ω_j (frequency of vibrational excitation) and ω_s (frequency of scattered photon).(a) first-order Raman scattering process and (b),(c) shows second-order Raman scattering.

Second-order Raman scattering, in which two phonons participate, is either a line spectrum or a continuous spectrum [120]. Second-order line Raman spectrum is due to two successive first-orders Raman scattering as shown in Figure 2.10(b) and the frequency shift is the sum or difference of Raman shifts occurring in the first-order Raman spectrum. The line nature of the second-order scattering is the result of wave-vector conservation in two successive first-order Raman scattering.

The second order continuous Raman spectrum is due to a scattering process in which a pair of phonons participates in a single event as shown in Figure 2.10(c). Since wave-vectors of two phonons should be equal and opposite according to the conservation of wave-vectors. Therefore, the second order continuous Raman spectrum reflects a combined density of pairs of phonons with equal and opposite wave-

vectors as well as the frequency dependence of the electron-lattice and electron-radiation interaction.

2.3.2 Raman Scattering in Crystalline Si

Phonon frequencies present in the c-Si can be obtained from the phonon dispersion curve shown in the Figure 2.2. Figure 2.11 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⁻¹ with natural line width of 4 cm⁻¹ at room temperature. Second-order Raman scattering [124] is shown in Figure 2.11 in the frequency range 200–500 cm⁻¹ and 550 –1000 cm⁻¹. A kink at 230 cm⁻¹ and the peaks at 300 cm⁻¹ and 435 cm⁻¹ are associated with the second order transverse acoustic (2TA) phonons (see Figure 2.2) from the critical points at L, X and near Σ directions, respectively.



Figure 2.11: Raman spectrum of c-Si.

Weak scattering at 460cm^{-1} is associated with Raman scattering involving phonons along and near Σ direction. The features at 610 cm^{-1} and 820 cm^{-1} in the two phonon Raman spectra are contributed by two acoustic and optic phonons in the Σ direction, respectively. Scattering in the range 900-1050 cm⁻¹ is identified with second-order transverse optic (2TO) phonon overtones from the critical point at X, while shoulders at 940cm⁻¹ and 975 cm⁻¹ are associated with 2TO phonon overtones at Wand L point respectively [125-127].

2.3.3 Raman Scattering from Nano- Crystalline

Semiconductor

Raman scattering measurement is a powerful and sensitive atomic scale probe and can provide in-depth information on the structural modification caused by formation of nano crystallites and disorder on the semiconductor surface. It is an extremely useful tool for obtaining information about structural quality of a material at the atomic scale as it depends on lattice excitations. The technique is also sensitive to perturbation to electronic state of the solid. Study of Raman scattering from nanomaterials and disordered semiconductors is based on phenomenological PCM proposed by Richter *et al.* [62], in which the correlation length shortening leads to softening and asymmetric broadening of first-order optical phonon modes.

In a crystalline material, the region over which the spatial correlation function extends is infinite, which leads to $k \approx 0$ momentum selection rule of first-order Raman scattering. However, in nano-crystalline and disordered semiconductors, the phonons are confined to the small particle volume, resulting in relaxation of the momentum selection rule $k \approx 0$, and cause the softening and asymmetric broadening of the phonon modes in the Raman spectra. When the size of the particle is reduced to the order of nano-meter, the wave function of optical phonons will no longer be a plane wave and the localization of wave function leads to a relaxation of $k \approx 0$ selection rule for first-order Raman active optical mode [62]. Therefore, not only the zone-centre phonons with wave vector $k \approx 0$ but also those away from the zone centre [128,129] with k > 0 also take part in the Raman scattering process. Since the optical phonon dispersion relations in most semiconductors have negative dispersion, the Raman spectra exhibit downward shift in peak position and broadening of the peak width i.e. phonon softening of Raman active optical mode.

2.4 Origin of electron-Phonon Coupling in Heavily Doped n- and p-type Si

In heavily doped c-Si, Raman line-shape exhibits asymmetry and peak shift [78,89]. Such changes in the Raman line-shape can be explained with the Fano-type [74] interaction model based on adiscrete continuum interaction. It was Ugo Fano [77], 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.



Figure 2.12: Conduction bands of heavily doped n-type c-Si [64].

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 (e-ph) 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^{19} cm⁻³, the semiconductor behaves like a degenerate semiconductor.

Position of the Fermi level goes deep inside the conduction band [130] (for n-type semiconductor) as shown in Figure 2.12. This gives rise to continuous electronic Raman scattering due to inter-band transitions between the Δ_1 and Δ_2 bands along (100) directions [64,131,132]. A continuum of transitions exists from a minimum energy $\hbar\omega_{min}$ to a maximum energy $\hbar\omega_{max}$ determined by the Fermi level E_F as shown in Figure 2.12.



Figure 2.13:Conduction bands of heavily doped p-type c-Si [67]

Similary, for p-type Si, incident light ω excites from the light-hole band (light) to the conduction band (cond) an electron, which, by emitting a scattered photon ω' , deexcites to the heavy-hole band (heavy), leaving a net transition light—heavy. These intervalence-band transitions give a Raman spectrum with cu offs at ω_m and ω_M , as depicted in the energy band diagram as shown in Figure 2.13, depicting the isotropic parabolic energy bands with the Fermi energy E_F in the valence bands.

If, energy $\hbar\omega_0$ of a discrete optical phonon state, which has the same symmetry as the inter-band transitions, falls within the continuum, interference between a discrete state and the continuum, takes place [64,131], i.e.

$$\hbar\omega_{min} < \hbar\omega_0 < \hbar\omega_{max} , \qquad (2.13)$$

when this condition is satisfied, the zone-centre phonon mode in the Raman spectrum of heavily doped c-Si leads to asymmetric line shapes. Raman line-shape in the presence of Fano interference is expressed by

$$I_F(\omega) = \frac{(q+\varepsilon)^2}{1+\varepsilon^2},$$
(2.14)

Where $\varepsilon = \frac{\omega - \omega_0}{\gamma/2}$; γ and ω_0 being FWHM, and observed wavenumber of Fano transition respectively (reflected as peak position in Raman-Fano line-shape). Here the quantity 'q' is known as Fano asymmetry parameter which measures the extent of Fano interference. Smaller value of 'q' means strong e-ph interaction. The presence of Fano effect will result in increased half width in the pre-maximum side and postmaximum side for heavily doped n- type and p-type Si respectively. Figure 2.14 shows the calculated Raman line shape for n- and p-type semiconductor and bottom panel shows the asymmetry ratio for positive and negative q value for p- and n-type Si.



Figure 2.14: Raman line shape for different value of q (n-type) for negative q values (p-type) for positive q values and bottom panel shows asymmetry ratio for positive and negative q value [133].

2.5 Theoretical study of Raman line shapes due to various perturbations

2.5.1 Raman Scattering from Low Dimensional Si: Theoretical background

Raman scattering replicates the nature of zone-centered optical phonons in crystalline solids. Raman spectrum obtained from Si NSs shows different nature as compared to that from c-Si because the optical phonon's frequency in the Si NSs is likely to change from its bulk counterpart due to the finite size (confinement effect) of the material. Thus, the Raman spectral line-shape function from the Si NSs must be modified, from a typical Lorentzian function for c-Si, in accordance with the change in optical phonons frequency. At of symmetry nanoscales. the breakdown translational of (nano)crystalline materials at its grain boundaries, results in the deviation of vibrational contributions in the Raman spectra of that material [80]. As the size of materials is reduced to the order of its Bohr exciton radius, the effect of confinement of optical phonon vibration is more pronounced [14,62,134] which is reflected in Raman scattering.

With no exaggeration, Raman spectroscopy is said to be one of the most important tools which categorize the phase (crystalline, amorphous or nanocrystalline) [135–137]. Different models exist to illustrate the Raman line-shape resulting from the Si NSs [128,136,138]. The first-order Raman spectrum provides a fast and convenient method to analyse both the vibrational properties of crystalline as well as amorphous semiconductors. Since NSs of semiconducting material are quasi-crystalline, their Raman spectra are expected to be present in the intermediate range between the spectra of the corresponding crystalline and amorphous nature of the material.

Lot of research have been done in order to understand the vibrational properties in Si NSs [66,139,139], confined in one or more dimensions, using Raman spectroscopy. All the results usually show a (red-) shift in

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the peak position of the first-order Raman line of crystalline semiconductors along with a spectral broadening [140–142] which results in asymmetric Raman spectrum from Si NSs. Figure 2.15 shows the typical phonon dispersion and corresponding Raman line-shape of Si, where left hand side and right hand side display Raman active optical mode for c-Si and Si NSs, respectively. Raman scattering is used to estimate the Si NSs size using PCM proposed by Richter *et al.* [62], which was further modified by Campbell *et al* [136].



Figure 2.15: Schematic diagram showing the phonon dispersion and Raman line-shape of Si, where left hand side and right hand side display Raman active optical mode for c-Si and Si NSs, respectively.

2.5.2 Phonon Confinement Model

In a single crystal, only zone centered optical phonons contribute to Raman spectrum (near the Brillouin-zone center i.e, k = 0) due to the momentum conservation rule. The PCM [102,202] accounts well for the observed Raman line-shape from the Si NSs. Richter *et al.* [62] proposed a very harmonious PCM for confined phonons in the Si NSs of spherical shape with diameter L. The plane wave function of the phonon is restricted within the finite sized NSs. The wave function of a

phonon with wave vector k_0 , in a crystal is defined in polar coordinates as [136]:

$$\Phi(k_0, r) = u(k_0, r)e^{-i\vec{k}_0 \cdot r}, \qquad (2.15)$$

where $u(k_0, r)$ is the periodicity of the lattice. In case of a finite crystal of dimension L, the phonons are restricted to its volume. Phonons inside the Si NSs can be described by the following weighting functions $W(\vec{r}, \vec{L})$ [136].

$$\Psi\left(\vec{k}_{0},\vec{r}\right) = W\left(\vec{r},\vec{L}\right)\varphi\left(\vec{k}_{0},\vec{r}\right), \qquad (2.16)$$

Using Eq. (2.15) in the Eq. (2.16)

$$\Psi\left(\vec{k}_{0},\vec{r}\right) = \Psi'\left(\vec{k}_{0},\vec{r}\right)u\left(\vec{k}_{0},\vec{r}\right), \qquad (2.17)$$

where,

$$\Psi'(\vec{k}_0, \vec{r}) = W(\vec{r}, \vec{L})e^{-i\vec{k}_0.\vec{r}}, \qquad (2.18)$$

Richter *et al.*[102] chose the $W(\vec{r}, \vec{L})$ to be a Gaussian of the form $exp(-2r^2/L^2)$, with a phonon amplitude of 1/e at the boundary of the finite crystal. For line-shape of the Raman spectrum, $\Psi'(\vec{k}_0, \vec{r})$ might be expanded in a Fourier series as:

$$\Psi'(\vec{k}_0, \vec{r}) = \int C(\vec{k}_0, k) e^{i \vec{k}_0, \vec{r}} d^3 k.1 , \qquad (2.19)$$

where the corresponding Fourier coefficient $C(k_0, k)$ is given by [102]

$$C(\vec{k}_0, k) = \frac{1}{(2\pi)^3} \int \Psi'(\vec{k}_0, r) e^{-i\vec{k}\cdot r} d^3 r, \qquad (2.20)$$

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 $|C(\vec{k}_0, k)|^2 \sim exp$ (- $k^2L^2/4$), where k_0 is assumed to be 0. Thus intensity of the first-order Raman scattering, I (ω), can be written as [62].

$$I(\omega) = \int \frac{|C(\vec{k}_0, k)|^2}{\left[\{\omega - \omega(k)\}^2 + \left(\frac{\gamma_0}{2}\right)^2\right]} d^3k, \qquad (2.21)$$

where $\omega(k)$ is the phonon dispersion function for the optical branch of c-Si and γ_0 is natural line width of Raman spectrum of c-Si. This assumption is justified owing to the fact that only a small portion of the

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Brillouin-zone centered at the γ point contributes to the scattering. Different weighting functions, namely *sinc* [Eq. (2.22)], *exponential* [Eq. (2.23)] and *Gaussian* [Eq. (2.24)] respectively have been proposed for the Fourier coefficients [204] as given below.

$$|C(0,k)|^2 \approx \frac{Sin\left(\frac{KL}{2}\right)}{(4\pi^2 - q^2L^2)^2}, \qquad W(r,L) = \frac{Sin\left(\frac{2\pi r}{L}\right)}{\left(\frac{2\pi r}{L}\right)}, \qquad (2.22)$$

$$|C(0,k)|^2 \approx \frac{1}{(16\pi^2 - k^2 L^2)^4}, \quad W(r,L) = e^{-4\pi^2 r}/L , \qquad (2.23)$$

$$|C(0,k)|^2 \approx \frac{e^{-k^2 L^2}}{16} \pi^2$$
, $W(r,L) = e^{-8\pi^2 r}/L^2$, (2.24)

Figure 2.16 shows the confined NSs in three, two or one dimension (sphere, column and thin film, respectively). Effect of the size on the position and shape of the Raman band is strongest for a sphere whereas marginal for ultra-thin films. Many research groups [134,143–145] have established theoretical formalisms for calculating first-order Raman scattering from NSs. Shape and size distribution in an ensemble of small NSs have also been incorporated in their calculations along with the effect of the reduced size[102,214].





It is found that the Raman line-shape from Si NSs are explained very well using the relation $|C(0,k)|^2 = exp[-(k^2L^2/4a^2)]$ [136]. For two dimensional confined systems the volume integration (d^3k) in Eq. 2.21

needs to be replaced by the area integration (d^2k) . Therefore the Raman line shape for a given size L for one dimensional confinement is:

$$I(\omega,L) = \int_0^1 \frac{e^{\frac{-k^2 L^2}{4a^2}}}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma}{2}\right)^2} d^2k, \qquad (2.25)$$

It is possible that all the NSs may not have the same size. To incorporate the effect of this distribution, a log normal size distribution

function of the form $\phi(D) = \frac{1}{\sigma D \sqrt{2\pi}} exp\left\{-\frac{\log\left(\frac{D}{D_0}\right)^2}{2\sigma^2}\right\}$ with σ as the

width of distribution and a fitting parameter, D_0 is the mean SiNWs size and D_1 , D_2 corresponds to minimum and maximum sizes respectively. can be included in Eq. 2.25. It causes an additional broadening in the Raman line-shape described by Eq. 2.25. Incorporating these two modifications, Eq. 2.25 is modified to Eq. 2.26:

$$I(\omega, D) = \int_{D_1}^{D} \phi(D) \left[\int_0^1 \frac{exp^{\frac{-k^2 D^2}{4a^2}}}{[\omega - \omega(k)]^2 + \left(\frac{\Gamma}{2}\right)^2} d^n k \right] dD, \qquad (2.26)$$

Here, '*n*' shows the degree of confinement and may take value 1, 2 or 3 for 1D, 2D or 3D confinement respectively.

2.5.3 Evolution of Asymmetric Raman Line-Shape from NSs

As discussed in the above section, due to momentum conservation law, only zone cantered (k=0) phonons participate in Raman scattering for crystalline materials. As a result, symmetric, sharp peak is observed in the case of crystalline material cantered at frequency corresponding to the zone cantered phonon frequency. The formulism of Raman line shape has been started from phonon dispersion relation of respective material. In the present study phonon dispersion relation of Si, given by Eq. 2.27, is used while analysing Raman spectral line-shape using Eq. 2.25 & 2.26. It is evident from Figure 2.17 that Raman line shape shows a typical symmetric Raman line-shape for bulk Si represented

by a Lorentzian line-shape and can be written as Eq. 2.28.Inset of Figure 2.17 shows the longitudinal optic (LO) branch of phonon dispersion relation for Si (Eq. 2.27). The discrete points shown in inset of Figure 2.17 shows the data reported in literature for the same [94].

$$\omega(k) = \sqrt{171400 + 100000 \cos \frac{\pi k}{2}}, \qquad (2.27)$$

The equation of Raman line shape for a crystalline bulk material is written as:

$$I(\omega) = \frac{1}{[\omega - \omega_0]^2 + (\gamma/2)^2} , \qquad (2.28)$$



Figure 2.17: Symmetric Raman line shape for c-Si calculated using Eq. 2.28 and inset shows the dispersion curve for Si evaluated using Eq. 2.27.

where, ω_0 is $\omega(0)$ (Eq. 2.28) which is equal to 521 cm⁻¹ for c-Si, γ is the full width at half maximum (FWHM) of the spectrum. As an example, symmetric Raman peak in the case of bulk Si is observed at ~521cm⁻¹ with FWHM of 4 cm⁻¹. But in the case of its nanostructured form, this selection rule gets relaxed and phonons other than the zone centred ones also contribute in a crystallite of finite dimension [14,146]. This results in a change in the first order Raman spectrum which is typically Lorentzian for crystalline materials. Line-shapes of Raman spectra from nanostructures are expected to be intermediate between those of the corresponding crystalline and amorphous materials. For example, a broad band around 480cm⁻¹ can be observed in the Raman spectra from amorphous Si [147,148] whereas at the other extreme of c-Si, a sharp symmetric Lorentzian peak is observed at 521cm⁻¹ corresponding to the zone-cantered phonon (Figure 2.17) [137]. The change in the Raman line-shape parameters (peak position and FWHM) is useful in determining the size, shape and size distribution of NSs, since phonon softening and broadening of Raman lines are related to the size of nanostructures.

2.5.4 Effect of Size on Raman Line Shape

As discussed above, an asymmetrically broadened and red-shifted Raman line-shapes, represented by Eq. 2.25, are observed from Si NSs [63,149]. It is important here to mention that, there are three key observations, which are used to identify presence of confinement effect in Si, first, red-shifted Raman line-shape with respect to the c-Si, second, the non-unity asymmetry ratio (the ratio of half width towards lower energy side to the half width towards higher energy side) and third the broadened Raman line shape as compared to its c-Si counterpart. Asymmetry ratio is the measure of asymmetric broadening of Raman line shape and will be discussed later. It is clear from Eq. 2.25 that Raman line shape depends on the size of NSs (L).

Figure 2.18(a) shows the calculated Raman line shapes using Eq.2.25 by putting different crystallite sizes for a nano-system which is confined in one dimension only. The exponential term in Eq. 2.25 also takes care of the size dependence of the Raman line-shape by taking weighted average of contribution from each phonon present on the phonon dispersion curve [137]. Equation 2.25 can be understood as the basic Raman line-shape function for semiconductors nanostructured in particular and nanostructured materials in general. It is evident from Figure 2.18(a) that as the size of Si NSs decreases from 10 nm to 2 nm

the broadening and asymmetry of Raman line shape increases along with spectral red-shift with respect to the c-Si. It is also evident from the Raman line shape generated using Eq.2.25 that the peak position is more redshifted for 2 nm size as compared to the same for 10nm size.

To discuss quantitatively about the nature of these Raman line shapes, it is important to define the parameter called asymmetry ratio which is the ratio of the half widths towards lower energy side (γ_L) and higher energy side (γ_H) at I/2 *i.e.* at 50% of the total intensity respectively of the Raman peak (*i.e.* $\alpha_R = \frac{\gamma_L}{\gamma_H}$) as shown in Figure 2.18 (b) which also defines the pre-maximum and post-maximum regions in a Raman spectrum.



Figure 2.18: (a) Raman line-shapes theoretically generated using PCM Eq. 2.21 for different Si NSs sizes. Inset shows the asymmetry ratio (left Y-axis) and peak position (right Y-axis) with respect to size of Si NSs.(b) depicted pre-maximum & post maximum sides in Raman line shape and the half widths in lower energy side (γ_L) and

higher energy side ($\gamma_{\rm H}$) at I/2 *i.e.* at 50% of the total intensity I. To further confirm the asymmetric line shape and shift in peak position the asymmetry ratio and peak position have been calculated using Figure 2.18(a) and plotted as a function of size of Si NSs which is displayed in inset of Figure 2.18(a). It is evident from inset of Figure 2.18(a) that as the size of Si NSs decreases from 10nm to 2nm then the value of α_R increases or the Raman line shape become more asymmetrically broadened with respect to its bulk counterpart. It is also appreciated from the same inset of Figure 2.18(a) (blue data points) that the peak position get more red shifted for smaller Si NSs. The peak is shifted gradually from 520 cm^{-1} to 515cm⁻¹ for 10 to 2nm Si NSs respectively [80,150]. However most widely used, the PCM, discussed above, is not the only model used for Raman analysis. A modified phonon confinement model [128] is also used in this context though with limited acceptability due to its demerits as discussed below.

2.6 Electron-Optical Phonon Interaction: Fano Resonance

Generally, a resonance is thought to be an improvement of the response of a system to an external excitation at a specific frequency. It is referred to as the resonant frequency or natural frequency of the system. In many classical textbooks a resonance is introduced by the means of a harmonic oscillator with periodic forcing. When the frequency of the driving force is close to the natural frequency of the oscillator, the amplitude of the latter is growing toward its maximal value. Often many physical systems may also exhibit the opposite phenomenon when their response is suppressed if some resonance condition is met (this has led to a term *antiresonance*). The Lorentzian formula has been used as fundamental resonance line shape for many years, which is given by symmetric line profile and known as Breit-Wigner resonance [151]. The second resonance is characterized as asymmetric line profile and is of interest in the present chapter. In 1961, in a quantum mechanical study of the autoionizing states of atoms, Ugo Fano discovered a new type of resonance which now bears his name i.e. Fano resonance [75,152] (second resonance). In contrast to a Lorentzian resonance, the Fano resonance exhibits a distinctly asymmetric shape [73,153].

Fano resonance is the universal properties of a physical system[236] which takes place in a system where a discrete energy state lies within a continuum of energy states [69,76,154]. Fano resonance is generally the interference of the waves associated with transitions of discrete states (lying in the continuum) and the continuum of states. As a result of Fano resonance, a characteristics asymmetric line shape is observed. As it is well known that the Fano effect is caused by interference of waves, and interference may be constructive as well as destructive, therefore resonance (due to constructive interference) and antiresonance [152] (due to destructive interference) both are simultaneously observed in the Fano spectrum. The schematic diagram in Figure 2.19 makes it easy to qualitatively visualize the Fano resonance.

This type of phenomenon may be observed in variety of systems including atoms [155], solid materials [78], molecules [156,157] as well as in nanostructure [73]etc. Semiconductors can be a typical example to see this Fano resonance because in semiconductors phonons, having discrete energies, can interact with continuum of states, which may be provided by the electronic states under special conditions like heavy doping on quantum confinement effect. Fano used a perturbation method to explain the appearance of asymmetric resonances. Fano obtained the general formula for the shape of the resonance profile [74] of a scattering cross section, which is given by Eq 2.29.

$$I_F(\omega) = \frac{(q+\epsilon)^2}{(1+\epsilon^2)},$$
(2.29)

where q is the phenomenological shape or Fano parameter and ϵ 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. 2.29. The amplitude of 'q' provides the measure of electron phonon interaction with a smaller

value of '|q|' meaning strong electron-phonon interaction.

$$\in = \frac{\omega - \omega_0}{\gamma/2} \,, \tag{2.30}$$

Raman as well as IR spectroscopies are amongst various techniques [158–160] to study the possible Fano interaction in a system. In the present study Raman spectroscopy has been used to study the Fano resonance in c-Si and Si NSs.



Figure 2.19: Schematic diagram representing Fano resonance.

2.6.1 Fano Resonance in Crystalline Si

In well-tailored c-Si, the electron-phonon coupling in terms of interference between electronic continuum and optic phonons results in an asymmetric Raman line-shape. Manifestation of the Fano interference is one of the well-studied properties in the heavily doped ($>1\times10^{19}$ cm⁻³) Si wafer [161]. The origin of Fano resonance in semiconductors is the phonons interference with continuum of states created due to heavy doping [162,163] or photoexcitation [164]. The asymmetry of Raman line-shape depends on the doping type if induced by Fano resonance. In heavily doped p-type semiconductor, electronic continuum is created in valence band due to transition of light hole to heavy hole [131] while created in conduction band in case of heavily doped n-type [64]. Fano resonance resulting from interference

between discreet phonon and valence band electronic continuum (in ntype system) produces asymmetric broadening in a way that lower half width (γ_L) is more than the higher half width (γ_H) in the Raman spectrum while in p-type (interference between phonon and valance band continuum) it is other way round.

As a result, any of the spectral half widths, towards lower- or higherfrequency side, of the Raman peak may dominate over the other. Figure 2.20 shows the Fano Raman line shapes expected from heavily doped (Figure 2.20a & 2.20b) and undoped c-Si (Figure 2.20c). The Raman line-shape asymmetry, often characterized by asymmetry ratio $\alpha_{\rm R} = \frac{\gamma_{\rm L}}{\gamma_{\rm H}}$ (Figure 2.20c), can be observed for doped Si whereas a unit value of α_R results when the line is symmetric as in the case of c-Si. A Fano Raman line-shape from heavily doped p- and n- type c-Si gives an α_R value of less than one (<1) and more than one (>1) respectively as the lower half width is less than the higher half width for a p-type semiconductor whereas it is other way round for an n-type system. It is also important to mention here that Fano resonance is an interference which must possess constructive as well as destructive interference. In Fano Raman line-shape it is manifested as an antiresonance dip (destructive interference, minimum spectral intensity) which is not observed in Raman line-shapes where Fano resonance is absent or very weak (Figure 2.20). This is an important signature of presence of Fano resonance in a system. As a characteristic of Fano effect, the antiresonance dip and the wider half-width are observed in the opposite sides of the Raman peaks position [133].


Figure 2.20: Theoretical Raman line shapes obtained using Eq. 2.29 for (a) heavily doped n-type c-Si (c-Si-N) (b) heavily doped p-type c-Si (c-Si-P) (d) Fano parameter dependent α_R for heavily doped n and p-type Si.

The theoretical Raman line-shapes, shown in Figure 2.20, have been generated using well established general Fano-Raman line shapes equation (Eq. 2.29) which takes care of Fano resonance for both n- and p-type semiconductor by appropriately choosing the sign of Fano parameter (q). Figure 2.20 (a) & (b) show the Raman line-shapes, obtained using Eq. 6.1, for different negative and positive values of Fano asymmetry parameter, q, representing a heavily doped n- and p-type c-Si system whereas Figure 2.20 (c) shows the theoretical Raman line shapes from c-Si. The variation of Fano-Raman line-shape α_R as a function of absolute values of q has been shown in Figure 2.20(d). 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) and α_R approaches asymptotically towards unit α_R value for infinitely large values of |q| (Figure 2.20 d). It can clearly be observed that the value of α_R increases with 1/|q| for n-type Si and decreases for p-type Si because of the different nature of electronic continuum in n- & p-type Si [87,163]. An accompanied anti-resonance dip can also be seen very clearly in Figure 2.20(a) & (b) by slanted arrow sign. To validate abovementioned theoretical predictions, Raman line-shape analyses have been done from heavily doped n- & p-type Si wafers and compared with their intrinsic counterparts. Both the Si wafers have been chosen, in terms of doping levels, so that it qualifies the condition (having sufficient doping level) to exhibit Fano effect. Figure 2.20 shows the Raman scattering from heavily doped n- and p-type c-Si along with the low doped c-Si of both the types. The black dotted curve in Figure 2.20 (c) shows the Raman scattering from intrinsic Si wafer (c-Si) showing the typical Lorentzian Raman line shape with peak position at ~ 520.5 cm⁻¹ & FWHM of ~ 4 cm⁻¹.

2.6.2 Fano Resonance in Quantum Confined Si

As discussed above, asymmetric Raman spectral line-shapes are observed from discrete optical phonons due to quantum confinement effect. It would be interesting to see how this asymmetry is affected by the introduction of Fano resonance in the same system where quantum confinement effect is already present. Fano resonance has been observed due to inter-sub-bands transitions in semiconductor quantum wells [165]. In such systems, the phonons and the electronic excitations, participating in the Raman scattering, have discrete quantized levels due to spatial confinement. In appropriately designed semiconductor super lattices, Fano resonance of intra sub-band electronic transitions with optical phonons has also been studied. In super lattices, the conduction sub-band can be easily tailored to make it wide enough so that the contribution from the optical phonons overlap. There are several reports on laser-induced Fano resonance in the SiNWs of diameter 5-15 nm [164]. Gupta et al. [165] fitted their experimental Raman scattering data using the asymmetric Fano lineshape of the c-Si (Eq. 2.29) without considering any quantum confinement effect. This is not possible for low dimensional materials where quantum confinement is inherent in the system. The interplay between Fano and quantum confinement effects is debatable unless it is investigated clearly. All the reports on Fano interaction in the Si NSs lack a clear theory as well as experiment on the mechanism of electron-phonon interaction. There are attempts to investigate the presence of Fano interaction in low dimensional systems. Still an indepth study is required regarding the issues related to Fano interaction in the Si NSs, 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 interplay between Fano and nano combine effect. A suitably designed low dimensional semiconductor to observe nano-effect with appropriate doping to observe Fano resonance can be investigated by Raman spectroscopy. First a comprehensive theoretical Raman line shape function has been generated with appropriate modification in the general Fano line-shape to incorporate the size effect and weighting function, which have been extensively used to study this type of effect.

To see the combination of Fano and nano effects (quantum confined system) (F-C) on Raman line shape the following equation has been used, which is a well-accepted approach for this purpose [70,220,258].

$$I_{FL}(\omega) = \int_0^1 \exp(-k^2 L^2 / 4a^2) \frac{(q+\varepsilon')^2}{1+\varepsilon'^2} d^n k , \quad (2.31)$$

where $\varepsilon' = [\omega - \omega(k)]^2 / (\gamma/2)^2$ the $\omega(k)$ is the phonon dispersion relation representing optic phonons in Si and is given by $\omega(k) = [A + B \cos(\pi k/2)]^{0.5}$ with A = 171400 cm⁻² and B = 100000 cm⁻². 'q' is the Fano asymmetry parameter. The γ , 'L' and 'a' are the spectral width, particle size and lattice constant respectively. The theoretical Raman line-shapes represented by Eq.2.31 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) for a fixed vale of L (size of NSs), displayed in Figure 2.21.



Figure 2.21: Theoretical Raman line shapes obtained using Eq. 2.31 for (a) heavily doped n-type low dimensional Si (b) heavily doped p-type low dimensional Si (c) Fano parameter dependent α_R for heavily doped low dimensional for n and p-type Si.

To study these effects, first Raman line shapes have been obtained only for nano effect in Si NSs of size 3 nm followed by inclusion of Fano resonance contribution by using three different |q| values of 5, 4 and 3. Negative values of q in Figure 2.21(a) represent how Fano resonance affects the quantum confinement effect for n-type Si NSs. When finite negative value of q is introduced, the α_R increase with 1/|q| (i.e, deviating away from symmetric nature) because in n-type semiconductors Fano resonance and nano-effect increases premaximum half width (Γ_L) without changing the post-maximum half width (Γ_H) (see Figure 2.21(c)). This results in increase of α_R more rapidly with 1/|q| in n-type confined system (Figure 2.21(c)).

It means that the Fano resonance adds to the already existing asymmetry for a low dimensional n-type semiconductor system. On the other hand, Fano effect in p-type confined system induces an increase in the post-maximum half width ($\gamma_{\rm H}$) without changing the premaximum half width ($\gamma_{\rm L}$) as decided by the nanocrystallite size.

Chapter 3

Experimental Methodology and Sample Preparation

Experimental details, including various characterization techniques used, and methodology adopted for the research work is discussed in the current chapter. The details of sample preparation technique has also been provided in the current chapter.

3.1 Sample Preparation

Most of the samples containing Si NSs used in the present study have been fabricated using metal induced etching (MIE). For some studies, Si NSs have been prepared using laser induced chemical etching (LIE) techniques also. Details of the methods and recipe used are as follows.

3.1.1 Metal Induced Etching Method

Amongst various techniques of nanomaterial fabrication, including CVD, PVD, MBE, MIE [48,166,167] is one of the simplest and economic methods. MIE is a twostep method in which, first metal nanoparticles (MNPs), mainly silver (Ag) or gold (Au), are deposited on a clean semiconductor surface usually 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 deposition step (or pre-porosification step), wafers (containing metal NPs) are transferred into etching solution for porosification. A typical etching solution for this purpose consists of hydrofluoric acid (HF) and hydrogen peroxide (H₂O₂). After a particular time of etching, porous Si/Si NSs get fabricated on the semiconductor surface. In this method, the materials and chemicals used are Si wafer, HF, AgNO₃,KAuCl₄, H₂O₂, distilled water (DI) and HNO₃.The steps involved in sample preparation are discussed below.

Si wafer cutting and superficial cleaning: The n- and p-type Si wafers of required dimensions were cut using a diamond tip glasscutter. Since the surficial cleaning of Si substrates is critical for sample fabrication, these were cleaned to remove inorganic impurities present on the surface using the ultrasonic bath. Substrates were subsequently cleaned in acetone and iso-propanol (IPA) for 10 minutes each followed by washing with DI water.

Surface treatment: The Si wafer were further washed with 5% HF solution to remove the thin oxide layer formed on the surface of Si wafer due to exposure to air and then with DI water to remove unnecessary fluoride ions attached on the surface of the Si wafer.

Metal Deposition: These wafers were then dipped in solution containing 4.8M HF and 5mM AgNO₃and KAuCl₄ for required deposition time to deposit Ag nanoparticles (AgNPs) and Au nanoparticles (AuNPs) respectively 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: The MNPs (AgNPs/AuNPs) deposited Si wafer is then kept for etching in an etching solution containing 4.6M HF and $0.5M H_2O_2$. Etching time decides the length of the SiNWs with a direct proportionality between the two.



Figure 3.1: Schematic diagram of step by step formation of SiNWs.(1) cleaned Si wafer, (2) MNPs deposited Si wafer, (3) etched Si wafer,(4) increase etching time and (5) SiNWs after removal of MNPs.

Removal of Ag- & Au-NPs: The etched Si wafer (SiNWs) is dipped in the HNO₃ acid for two min to remove the MNPs present inside the pores. The strong oxide layer is formed on the surface of SiNWs after the treatment of HNO₃ acid. In order to remove the oxide layer from the surface of SiNWs, samples were transferred to the HF solution and then washed with DI water. Figure 3.1 displayed the schematic diagram of steps involved in the MIE technique.

3.2 Instruments' Details

3.2.1 Scanning Electron Microscope

Scanning electron microscopy (SEM) is a noncontact, non-destructive technique for imaging surfaces to understand the morphology. Figure 3.2 displays the schematic diagram of SEM. The SEM employs a focused beam of high-energy(which typically has an energy ranging from 0.2 keV to 50 keV). These electrons, with significant amounts of kinetic energy, generate a range of signals on interaction with the surface of specimens. The signals that are obtained from the electron-sample interactions reveal information about the sample's surface.

3.2.1.1 Signals Generated

Electron-matter interaction leads to emission of secondary electrons (SEs), backscattered electrons (BSEs), Auger electrons, X-rays, etc. In case of SEM, the interaction products most frequently used for the generation of images are (i) SEs and (ii) BSEs.

Secondary electrons (SE)

When the incident electron beam hits the specimen, secondary electrons are produced from the emission of the valence electrons of the constituent atoms in the specimen. Since the energy of secondary electrons is very small generally less than 50keVSEs are extremely abundant and the SE yield (the number emitted per primary electron), is dependent on the accelerating voltage.

Backscattered electrons (BSE):

All electrons having energies higher than 50keV are BSE and are generated by elastic scattering and BSE yield depends on atomic number Z, so information from a relatively deep region is contained in the backscattered electrons. The BSE are sensitive to the composition of the specimen.

<u>X-Rays</u>: When electrons in the inner shells are excited, X-rays are generated whose energies correspond to the energy difference between the shells involved in this transition. The generated X-rays are

basically used for elemental analysis in SEM.



Figure 3.2: Schematic diagram of SEM.

3.2.1.2 Imaging in SEM: The interaction of e-beam with sample does not occur at a point but throughout the volume, these sizes of volume depend on beam energy and shape of interaction volume and atomic number.

Components of the instrument: The SEM requires an electron probe, a specimen stage to place the specimen, a secondary-electron detector to collect secondary electrons, an image display unit, and an operation system to perform various operations.

i) <u>Electron source</u>: The illumination system of SEM consists of an electron source, which is maintained at a negative potential. The

emitted electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is passed through a magnetic lens system.

<u>ii) Condenser Lens and Objective Lens:</u> Placing a lens below the electron gun enables to adjust the diameter of the electron beam. Two-stage lenses are located below the electron gun. The objective is a very important lens that determines the final diameter of the electron probe upto 5 to 10 nm.

<u>iii) Detector:</u> A scintillator is coated on the tip of the detector and a high voltage of about 10 kV is applied to it. The secondary electrons hit the scintillator and generate the light signal. This light is directed to a photo-multiplier tube PMT and amplified, then transferred to the display unit. Since the scanning on the display unit is synchronized with the electron-probe scan, brightness variation, which depends on the number of the secondary electrons thus forming an SEM image. A cathode-ray tube (CRT) or liquid-crystal display (LCD) is used as a display unit. In this work SEM images were recorded using Supra55 Zeiss, oxford instruments.

3.2.2 Transmission Electron Microscope

Transmission electron microscopy (TEM) is used to study the local structures, morphology, dispersion of multicomponent polymers, cross sections and crystallization of metallic alloys, semiconductor's micro, nano and angstrom-structure of composite materials etc. Figure 3.3 shows the schematic diagram of TEM. In this technique, a beam of high energy electrons (typically 100–400 keV) is collimated by magnetic lenses and allowed to pass through a specimen in very high vacuum. The transmitted beam and a number of diffracted beams can form a resultant diffraction pattern, which is imaged on a fluorescent screen kept below the specimen. The diffraction pattern gives the information regarding lattice spacing and symmetry of the structure under consideration. Alternatively, either the transmitted beam or the diffracted beams forms a magnified image of the sample on the screen as bright-and dark field imaging manners respectively. This gives information about the size and shape of the micro, nano and angstrom-

structural constituents of the samples. High resolution image contains information about the atomic structure of the material. This can be obtained by recombining the transmitted beam and diffracted beams together [168,169].



Figure 3.3: Schematic diagram of TEM [169].

3.3 Raman Spectroscopy

Raman scattering [56,170], after its discovery, has now been established as one of the versatile spectroscopic tools widely used, not only to study crystal structure, chemical composition, crystal defects but also to investigate different physical phenomena taking place at microscopic levels like confinement, chemical compositions, defect states etc.Whether the objective is qualitative or quantitative, Raman spectroscopy can provide key information, easily and quickly, specifying the chemical composition and the structure of the probed material. The Raman spectroscopy is used to observe vibrational, rotational and other low frequency modes in the samples under investigation. It relies on inelastic scattering or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared or near ultraviolet range. The schematic of experimental set-up of a Raman spectrometer is shown in Figure 3.4.



Figure 3.4: Schematic diagram of Raman Spectrometer

The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted towards lower values of energy. The shift in energy gives information about the vibrational modes in the system [2,125,171]. In the Raman scattering, a sample is illuminated with a laser beam. 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 laser line (Rayleigh scattering) is filtered out, while the rest of the collected light is dispersed onto a detector. The scattered light is analysed 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 as shown in the experimental setup in Figure 3.5

Figure 3.5: Horiba Jobin Yvon micro-Raman spectrometer used in this study.

3.4 Diffuse Reflectance Spectroscopy

When electromagnetic radiation (light), in the UV-Visible region, interacts with matter, various effects can be observed such as reflection, scattering, absorption, transmission and fluorescence/phosphorescence. Total potential energy of a molecule can be represented as the sum of its electronic, rotational and vibrational energies. When energy of incident light is equal to the energy required to excite an electron from a lower energy level to higher level, the light is absorbed. UV-Vis spectroscopy deals with how the electromagnetic radiation is, absorbed, transmitted and reflected by/through a material. The block diagram of a typical UV-Vis spectrophotometer is shown in Figure 3.6.



Figure 3.6: Experimental set-up for UV-Vis diffuse reflectance spectroscopy.

Working principle

The amount of light absorbed is decided by the ratio of incident radiation (I_o) and the reflected or transmitted radiation (I). Quantitatively absorbance is described by following equation:

$$A = -\log\left(\frac{I_0}{I}\right),\tag{3.1}$$

where, A is absorbance, I_o and I are the intensities of incident and transmitted light respectively at a given wavelength. A UV-Vis spectrophotometer uses a tungsten-halogen or deuterium lamp as a source. A dispersion device like a monochromator is used to select the incident wavelength. A detector, which converts UV- visible light into electrical signal is the final component of the spectrophotometer. It is easy to estimate bandgap (Eg) from absorption spectra, in case of solid films of known low thickness, due to low scattering properties. However, in colloidal samples, due to large surface area exposure scattering is enhanced. As dispersed light does not reach up to the detector it is counted as absorbed light. Figure 3.7(a) shows the photograph of UV-Vis setup used in the current study. UV-Vis spectra from opaque materials like porous Si/ Si NSs are recorded by directly putting the sample below the target plate shown in Figure 3.7(b).



Figure 3.7: Experimental set up for diffuse reflectance measurement (a) Carry 60 UV-Vis spectrometer, (b) an integrating sphere attachment to detect diffuse reflectance.

Diffuse reflectance spectroscopy (DRS) enables one to obtain E_g of opaque samples [172,173]. The estimation of E_g using DRS utilizesKubelka&Munk model [174], in which diffuse reflectance R is related to Kubelka–Munk function F(R) by following equation:

$$F(R) = \frac{(1-R)^2}{2R},$$
(3.2)

where, R denotes the percentage reflectance from the sample. If hv is the energy of photon, a graph between $[F(R).hv]^2$ versus hv (in eV) can provide the E_g values of a sample with direct bandgap. An indirect bandgap can be obtained from a plot of $[F(R).hv]^{1/2}$ versus hv [175,176].A UV-Vis spectrometer model Carry 60 of Agilent make has been used in the current work.

3.5 Photoluminescence Spectroscopy

To investigate the emission characteristic of Si NSs, PL measurements were performed using a Dongwoo Optron PL system with an He-Cd laser, having excitation wavelength of 325 nm. The PL setup has been developed on the optical table using the combination of lens and mirror assembly. Figure 3.8 shows the schematic picture of setup developed for PL measurement using 325 nm diode laser. The laser beam coming from laser source has been directed with the help of mirrors and

focused on the sample using the lens (L). The emission of light from sample is collected using lens assembly and focus on the optical fiber based Spectrograph. The final signal has been recorded using spectrograph which is connected with the computer. All measurements have been done at room temperature as well as down to 11 K. The schematic of the PL measurement setup is shown in Figure 3.8. The output of a laser light source (325 nm) is passed through the excitation slit and sample is placed in the path of the monochromatic light with an angle close to 45° .



Figure 3.8: Schematic diagram of PL setup

Chapter 3

Chapter 4 Diffused Reflectance Spectroscopy to Study Size distribution in SiNWs

This chapter deals with the analysis of perturbed optical properties like enhanced band gap and visible light emission from heavily doped p- & n- type fractal porous SiNSs. Enhanced band gap has been analysed by developing a theoretical model which incorporates the size dependent modulation in band gap. The average sizes and size distribution have been analysed with this framework and have been validated using dual approach of theoretical and experimental methodology using Raman spectroscopy¹. Fresh samples of heavily doped n- & p- type SiNSSs have been prepared, named as sample-n & sample-p respectively.

¹ Manushree *et al.*, J. Phys. Chem. A , 123, 16, 3607–3614, (2019)

4.1 Surface Morphology of p- & n- type fractal porous SiNWs

Heavily doped p- & n-type Si NSs have been fabricated using MACE technique. Figure 4.1 shows the SEM image of a clean surface of bulk Si wafer before any etching procedure takes place.



Figure 4.1: SEM image of a clean surface of Si wafer.

Figure 4.2 (a) and (b) shows the top surface SEM images for sample –n and sample-p. The surface morphologies confirm the porosification process that has taken place due to MACE of Si wafer by the process described earlier in section 3.



Figure 4.2: Top surface SEM images of (a) sample-n and (b) sample-p

Figure 4.3 shows the cross-sectional SEM view of heavily doped wafer, confirming the presence of micro-wires. The cross-sectional SEM however predicts the presence of well aligned vertical micro-

wires but the presence of fractal porous SiNWs however could still not be appreciated using SEM morphology. To visualize the presence of nano-meter sized Si, TEM has been carried out as shown in Figure 4.4. However these wires are thick as compared to the bohr's excitonic radius of Silicon (~ 5nm) but a finer silicon nanostructures (a few nano-meters) are present inside these nanowires which are small enough to show quantum confinement effect. It is also important here to mention that all the silicon nanostructures are not of the same size and possess some distribution. Considering the fact that these microscopic techniques only reveal information about a smaller area (~ 0.01μ m²) of the sample, one need to be very careful while quantifying the size and SD of these nanostructures using transmission electron microscopy. The distribution of nanostructures estimated will depend on the technique by which it has been quantified thus a detailed discussion on validation of the same is required.



Fig 4.3: X-sectional SEM images of (a) sample-n and (b) sample-p.

The fractal nanometre sized Si can be easily visualised through TEM images shown for both sample-p & sample -n. A closer look at the TEM images in Figure 4.4 reveal the presence of ~6 nm & ~ 3 nm sized fractal NWs from sample-n and sample-p respectively. It is also important here to mention that all the silicon nanostructures are not of the same size and possess some distribution. To further analyse the size and size distribution present in SiNWs, diffused reflectance spectroscopy and Raman spectroscopy along with their theoretical

modelling has been presented in the discussion later.



Figure 4.4: TEM morphologies of (a) sample-n & (b) sample-p.

The presence of fractal like porous SiNWs as confirmed using SEM and TEM gives only morphological analysis. The etching mechanism during the formation of SiNSs is such that, different portions of wafer stay in etching solution for a different period of time. This causes an inhomogeneous variation of size across the length of NWs, as explained in the etching mechanism below.

4.2 Etching mechanism during the formation of SiNWs

As discussed above, the MIE method involves mainly two steps, the deposition of MNPs and the porosification step. When the clean Si wafer is dipped into the solution of AgNO₃ and HF, the Ag⁺ ions, available in the solution of AgNO₃ & HF sit on the surface of Si. Here Ag⁺ takes one electron from the Si and gets neutralized for getting deposited as AgNPs after many such ions' neutralization on the surface. The exchange of electron from Si to Ag⁺ is favourable because the redox energy for the pair Ag⁺/Ag (0.79 V) is higher than the valence band energy of Si (0.62 V) [41] as depicted in Figure 4.5 which shows the redox pair energies and valence band energies.



Figure 4.5: The schematic diagram showing redox pair energies with respect to hydrogen electrode potential.

The exchange of electron from Si to Ag^+ induces injection of holes (creation of positive site in Si) in the Si which eventually initiates the porosification [177–179]. After taking the electron from Si wafer [180], AgNPs gets deposited on the surface of Si wafer. Further in the next step, theses AgNPs deposited samples are put into the etching solution which contains proper ratio of HF and H₂O₂. The fluoride ions (F^-) present in the etching solution attack the positive sites of Si (where hole is present). This attack is known to be resulting in H₂SiF₆ before getting dissolved in HF solution and creates a physical pit on the surface of Si [181].

The steps involved in dissolution of Si in the HF solution is depicted in the Figure 4.6 [181]. Further transfer of another electron from Ag to H_2O_2 takes place which results reduction of H_2O_2 and creation of Ag⁺ to start the next cycle of etching by providing continuous supply of Ag⁺ and thus of the holes (h⁺). The exchange of electron process and transfer of electron is favourable because the redox energy for the pair



Figure 4.6: Dissolution mechanism of Si in the HF proposed by Lehmann and Foll [181].

 H_2O_2 / H_2O (1.78 V) is higher (Figure 4.5) than the redox energy for the pair Ag⁺/Ag (0.79 V) [41]. The continuation of cycle is governed by etching time which decides the depth of pits inside the Si wafer.

The schematic displayed in Figure 4.7 shows the overall step-by-step formation mechanism involved in MIE. It is worth mentioning here that the dissolution starts from the sites where metal nanoparticles are present (Fig 4.7). Figure 4.7 indicates that, if more metal nanoparticles cover the surface of Si wafer than it will result in higher porosification leading to highly porous Si surface. As the top surface of the wafer remains in the solution for longer etching period as compared to the

bottom one, this causes an inhomogeneity in the size of SiNSs. Moreover etching periods of longer than one hour causes the formation of an amorphous like phase of Si, whose morphological details has been presented in Appendix 2. Details of this are beyond the scope of this thesis.



Figure 4.7: The schematic diagram depicting the porosification during MACE.

The chemical reactions involved during the fabrication of SiNWs in MIE are as follows [182]:

Creation of hole (1)	$Ag^+ + e^- \rightarrow Ag,$
Si dissolution (2)	$Si + 4h^+ + 6HF \rightarrow H_2SiF_6 + 4H^+,$
to start etching cycle (3)	$H_2O_2 + 2Ag \rightarrow 2H_2O + 2Ag^+ + 2e^-,$

4.3 Photoluminescence from SiNWs

Room temperature visible photoluminescence from porous Si is a noted phenomenon and has been discussed many times. Bulk Si being and indirect band gap semiconductor does not have luminescent properties. When one of the dimensions of Si is confined, it starts showing visible PL indicating its transformation from indirect to direct band gap, with the width of PL spectrum and is a consequence of band gap broadening due to the effect of quantum confinement.

The PL obtained from heavily doped p- & n-type SiNSs has been shown in Figure 4.8. The PL spectrum centred at 1.9 eV, well above the indirect band gap of bulk Si, established the band gap broadening, whereas the broadened PL whereas the broadened PL spectrum hints at the presence of size distribution in SiNSs.



Figure 4.8: The schematic diagram showing redox pair energies with respect to hydrogen electrode potential.

4.4 Diffused reflectance spectroscopy of SiNWs

To estimate the size of SiNSs prepared using MACE, DRS has been employed. The optical technique widely used to calculate the band gap of material is employed here by doing theoretical modelling to incorporate the modulated size dependent band gap. The mean size and size distribution obtained has been validated using Raman spectroscopy.

The light-matter interaction and quantum confinement effect brings the two techniques, Raman and diffused reflectance spectroscopy, on a common platform and thus can be correlated for the purpose of size analysis. In other words, interaction of light with matter therefore remains an insightful and intuitive probe in order to deal with the materials' properties at the nanoscale. The confinement of electrons in the nanostructures leads to interesting perturbations in the optical properties like band gap [113], absorption etc. Due to the size effect the reformed band gap of SiNWs changes significantly as given by Eq. 4.1 and hence absorption coefficient being directly related to the band gap of the material is altered for individual size.

$$E(D) = E_g + \frac{\gamma}{D^m}, \qquad (4.1)$$

where, E(D) in eV is the band gap of materials of size D in nm, E_g is the bulk band gap, γ and m are the confinement parameters defined using effective mass theory approximation. If, the SiNWs fabricated using metal induced etching are to be analysed by absorption spectroscopy, the resultant experimental spectra when fitted well with the theoretical equation will convey relevant information about the SD present in the system, because of the size effect which eventually forces the absorption to change for each size. With the in principle capability to be used for size analysis established, a way to do so needs to be understood so that scientists can use it efficiently.

The main aim of this study is to establish absorption spectroscopy as an easier and efficient technique for estimation of mean size and SD in nanostructures. This has been done by analysing a diffuse reflectance spectral line-shape by means of the proposed line-shape function developed by incorporating the size dependence of band gap. The model has been used for consolidate size analysis of two SiNWs samples prepared by metal induced etching technique. The estimated size and SD has been compared with the results obtained using Raman spectroscopy, a well-established technique for this purpose. A discussion is also presented regarding the consistency between the results obtained by line-shape analysis of Raman and diffused reflectance spectroscopy's results. The sizes estimated using the two techniques were consistent, which means that the SiNWs samples are homogeneous from the point of view of the distribution of sizes is concerned. The proposed model establishes how the diffused reflectance spectroscopy can be used for size analysis in a nanostructured sample. Furthermore, way to interpret the consistency or inconsistency, as may be the case, of diffused reflectance spectroscopy's results with Raman results has also been presented. Convergence of modifications in phonon spectrum and electronic structure has been shown as the key factor in developing the model for yielding information about SD which is connected through the confinement effect in nanostructured samples.

Manifestation of the presence of SD is by means of modification of electronic structure leading to a change in band gap that consequently gets reflected in the absorption spectra from nanostructures. Thus, the size-dependent band gap, as shown in Eq 4.1, plays a major role in the analysis of the absorption spectrum generated by the material. Due to the presence of uniform and large crystallite size in the bulk Si, the absorption spectrum is sharp with a band gap of 1.17 eV. On the contrary, when the crystallite size is reduced to the nano regime, the effective band gap increases in accordance with Eq 4.1. Also, the absorption spectra pertaining to each size are different from each other due to the fact that absorption is directly related to the band gap of a material.

This in all signifies that if there is size distribution present in the sample, it should be manifested in the form of a monotonous continuous spectrum for SiNWs, unlike the sharp step-like spectrum, as shown in the schematic. The experimentally obtained spectrum can then be fitted with the appropriate theoretical line shape consisting of a size distribution function, as done in the present study. In order to find out the values of the minimum, mean, and maximum sized wires present in the samples, theoretical fitting of the absorption coefficient, obtained from the diffuse reflectance spectroscopy has been carried out. Raman spectroscopy, as mentioned earlier, being a primordial tool to deal with the vivid class of materials, phenomena, and interactions,

has been used in the present study to confirm the result obtained from diffuse reflectance spectroscopy.

The absorption spectra from the two samples, obtained using diffused reflectance spectroscopy, are shown in Figure 4.9. The as obtained spectra have been suitably processed using Kubelka Munk (KM) model. As the KM function F(R) is directly proportional to absorption coefficient ((α)) that can be expressed as follows

$$\alpha = \frac{A(h\nu - E_g)^{1/n}}{h\nu} \quad , \tag{4.2}$$

where, A is a constant, n = 0.5 (or 2) for direct (or indirect) band gap semiconductor and hv is the incident photon energy. The size dependence of band gap given by Eq. 4.1 and the fact the absorption spectra of both samples originates from different band gaps, so to acquire a smooth fit, E_g has been replaced by the size-dependent band gap (Eq. 4.1). To evaluated the size distribution present in the samples, a log-normal size distribution function ($\phi(D)$) has been incorporated for deducing the nanostructure SD present in the sample. After above incorporation, Eq. 4.2 modifies to following Eq. 4.3.

$$\alpha(h\nu) = \frac{1}{h\nu} \int_{D_1}^{D_2} [h\nu - E(D)]^{\frac{1}{2}} \phi(D) \, dD \tag{4.3}$$

where, $\phi(D) = \frac{1}{\sigma D \sqrt{2\pi}} exp\left\{-\frac{\log\left(\frac{D}{D_0}\right)^2}{2\sigma^2}\right\}$ with σ as the width of

distribution and a fitting parameter, D_0 is the mean SiNWs size and D_{I_1} , D_2 corresponds to minimum and maximum sizes respectively.

The experimental data, represented by discrete points in Figure 4.9, have been fitted with Eq. 4.3 (the solid lines in Figure 4.9) to obtain the sizes as listed in Table-4.1 corresponding to the best fit. Values obtained clearly predict that sample-n contains thicker SiNWs with mean size of 5.8 nm whereas sample-p contains relatively thinner SiNWs of sizes in the range of ~ 3 nm. It is important here to mention that the sizes predicted by diffused reflectance spectroscopy is

consistent with the ones estimated roughly from the transmission electron microscopy image (Figure 4.4) which predicts average size of 6 nm and 3.5 nm from sample-n and sample –p respectively. Another interesting observation from the SD estimation using diffused reflectance spectroscopy is the prediction of different distribution widths in the two samples. The distribution is rather sharp in sample-n with a distribution of 2.2 nm as compared to sample-p which shows a broader distribution of 7 nm.

Figure 4.9 shows the diffused reflectance spectra of heavily doped sample-n & -p, the diffused reflectance spectra obtained for both the samples have been theoretically modelled to extract the mean size and size distribution present in the silicon wafer.



Figure 4.9: Absorption spectra of sample-n and sample-p. Discrete data points show the experimentally obtained spectra whereas the solid lines correspond to the theoretical line-shape (Eq.4.3) along with schematic of enhanced band gap of both the samples as a result of quantum confinement (insets).

4.5 Raman spectroscopy of SiNSs

Raman spectroscopy which is a widely used versatile tool to explain various physical phenomena and interactions taking place in the material is used here for a specific purpose of estimation of size distribution present in the two samples so that the results obtained using diffused reflectance spectra can be validated. As mentioned earlier, the Raman spectra from SiNWs are red-shifted and asymmetrically broadened as compared to that from crystalline silicon. The Raman spectra from sample-p, sample-n and crystalline silicon is shown in Figure 4.10 where the black dotted sharp and symmetric Raman line shape peaked at 520.5 cm⁻¹ shows the latter. The asymmetric Raman line-shape, originating due to phonon confinement effect (as explained above) can be represented using Eq. 4.4, as proposed by Richter et al. and later modified by Campbell et al., which is used to estimate the mean size and SD.



Figure 4.10: Raman spectra for sample-n and sample-p along with c-Si. Red and blue solid lines represent the theoretical Raman line shapes (Eq. 4.5) whereas the discrete data points represent the experimentally acquired data points.

It is important here to mention for completeness that, Eq. 4.4 includes Fano resonance arising in heavily doped silicon due to the interaction between discrete phonons and electronic continuum available in the system due to heavy doping. Though the study has been carried out on highly doped samples, which along with quantum effect shows the Fano effect, but the interpretation of size distribution is the area of interest in the present analysis. The consolidate general theoretical Fano-Raman line shape equation takes the following form:

$$I(\omega, D) = \int_0^1 exp\left\{-\frac{k^2 D^2}{4a^2}\right\} \frac{(\varepsilon+q)^2}{1+\varepsilon^2} d^n k , \qquad (4.4)$$

where, $\varepsilon = \left\{\frac{\omega - \omega(k)}{0.5\Gamma}\right\}$, *D*, *a*, Γ denote the nanocrystallite size, lattice constant and line width (4 cm⁻¹) of c-Si respectively. Here '*n*' is the degree of quantum confinement which has been chosen to be 2 for the case of SiNWs. The $\omega(k) = \sqrt{171400 + 100000 \cos \frac{\pi k}{2}}$ is the phonon dispersion relation for Si and *q* is the Fano parameter which is the measure of extent of electron-phonon interaction present in the system. The same size distribution function which is used to fit the absorption spectra for the two samples has been used in the theoretical Raman line-shape equation as well to yield the following final Raman line-shape (Eq. 4.7):

$$I_{2}(\omega, D) = \int_{D_{1}}^{D_{2}} \phi(D) I(\omega, D) dD , \qquad (4.5)$$

The experimentally obtained Raman scattering data , represented by discrete points, (Figure 4.10) have been fitted with Eq.4.5 and the values of D_0 , D_1 and D_2 corresponding to best fit are listed in Table 4.1 (in brackets). It is interesting here to see not only that the mean size and SD estimated from Raman and diffused reflectance spectra are same but are consistent with the one obtained from transmission electron microscopy image (Figure 4.4). Raman spectra also predict a smaller mean size & broader distribution for sample-p as compared to a relatively larger SiNWs size & smaller SD for sample-n. The consistency, with respect to the values of size and SD estimated, between the Raman and diffused reflectance spectroscopy is not trivial but contains following important aspects. Firstly, it means that a careful analysis of optical spectra using the proposed spectral line-shape can be used for estimation of nanocrystallite size as an alternative to the Raman spectroscopy.

Overall, the above mentioned results could be well summarised by looking at the schematic in Figure 4.11, which correlates the SD to a given Raman or optical spectra from silicon nanostructures along with crystalline form shown for comparison. The Raman spectrum of bulk silicon is sharp and has a symmetric Lorentzian line-shape with the peak positioned at ~520.5 cm⁻¹, (Figure 4.11a) corresponding to the zone centred phonons in the whole crystal. It is important here to mention that in the crystalline silicon, all the phonons have the same frequency (corresponding to zone-centered phonons) as depicted in Figure 4.11a. On the other hand, when the material size is reduced to "nano" dimension, the Raman spectrum becomes asymmetric and red shifted, as compared to its bulk counterpart due to phonons' modulation under confinement induced perturbation. In silicon nanostructures, the participation of phonons is governed by the broken momentum conservation rule as discussed above, due to which, several phonons with different frequencies start taking part in the Raman scattering. If the material has different nanocrystallite size, the light scattering from each nanowire will generate a spectrum which will have information about the sizes of the wires that participated in the scattering process. The Raman scattering from SiNWs present inside the area illuminated for collecting Raman spectrum will result in the asymmetric line-shape (Figure 4.11b) which will contain this information. This method is rather well-established and will be used in the current context for validation later on.

Another manifestation of the presence of SD is by means of modification of electronic structure leading to change in band gap which consequently gets reflected in the absorption spectra from nanostructures. Thus the size dependent band gap, as shown in Eq. 4.1, plays a major role in the analysis of the absorption spectrum generated by the material. Due to the presence of uniform and large crystallite size in the bulk Si, the absorption spectrum is sharp with a band gap of 1.17 eV (Figure 4.11c). On contrary, when the crystallite size is reduced to the nano regime, the effective band gap increases in accordance with Eq. 4.1 which is apparent from schematic shown in Figure 4.11d. Also, the absorption spectrum pertaining to each size is different from each other due to the fact that absorption is directly related to the band gap of a material. This in all signifies that if there is size distribution present in the sample, it should be manifested in the

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form of a monotonous continuous spectrum for SiNWs, unlike the sharp step-like spectrum, as shown in the schematic. The experimentally obtained spectrum can then be fitted with appropriate theoretical line-shape consisting of a size distribution function, as done in the present study. In order to find out the values of the minimum, mean and maximum sized wires present in the samples, theoretical fitting of the absorption coefficient, obtained from the diffused reflectance spectroscopy has been carried out. Raman spectroscopy, as mentioned earlier, being a primordial tool to deal with the vivid class of materials, phenomena and interactions, has been used in the present study to confirm the result obtained from diffused reflectance spectroscopy



Figure 4.11: Schematic showing (a) unique phonons leading to sharp Raman spectrum from crystalline silicon, (b) dispersed phonons leading to asymmetric Raman spectrum from nano-silicon, (c) typical absorption spectrum from bulk silicon and (d) deviation from ideal step-like absorption spectrum from nano materials.

This is important as optical absorption technique is very economic as compared to Raman scattering however the latter has other advantages. Another importance comes from the comparison of the estimated values obtained by the two techniques. If the two techniques yield the same values, it means that the sample is homogeneous upto the extent of mm size on the sample which is the area that gets exposed while carrying out the absorption spectra. In contrary, if the two results are not consistent that does not mean that the model is incorrect, rather it means that the homogeneity of the sample is limited. The rationale behind this conclusion is that Raman and optical spectra examines different extent on the same sample due to different probe size which is a few microns for Raman and upto a few mm for absorption spectroscopy. Irrespective of the consistency between the two techniques, diffused reflectance spectroscopy still proves to be an alternate technique for estimation of size and SD for nanomaterials.

 Table 4.1: Values of minimum, mean and maximum sizes of SiNWs

 obtained from optical and Raman spectroscopy.

	Size estimated f	rom optical spectrosc	copy (Size estimated	
Sample	from RS) (nm)			
	<i>D</i> ₁	D ₀	D ₂	
Sample-p	2.8 (3)	3 (3.5)	9.8 (10)	
Sample-n	4.5 (4.3)	5.8 (6)	6.7 (7)	

4.6 Summary

Nanowires of silicon, prepared by metal induced etching, show a distribution of size rather than a uniform size as revealed by broad photoluminescence spectra from the two samples fabricated from nand p-type silicon wafers. The diffuse reflectance spectra from these two samples, analysed using a newly proposed theoretical model, reveal that diffuse reflectance spectroscopy can be used to estimate the mean size and size distribution of nanostructures. The mean size and size distribution from optical spectra show consistent results with the predicted values using transmission electron microscopy. The general theoretical model has been developed for estimating the size of nanostructures by proposing a theoretical line-shape function corresponding to an absorption spectrum from the sample. The proposed equation has been devised on the basis of the concept of quantum confinement induced spectrum of band gaps from individual nanowires, thus leading to different absorption/ reflectance from each nanoparticle having different sizes. The resultant spectrum is thus the sum value of all these spectral values represented by the spectrum and the line-shape function. This has been incorporated using an appropriate size distribution function in theoretical formulation for absorption coefficient as a function of excited photon energy. These estimated values of size and size distribution are in consonance with the values estimated using well-established Raman spectroscopic framework. The consistency between Raman and diffuse reflectance spectroscopy's results not only validates the proposed model for this purpose but also means that the size distribution is homogeneously distributed in the samples reported here. Thus, the proposed methodology here not only successfully estimates the size and size distribution but also can be utilized to understand the homogeneity of nanomaterial.
Chapter 5 Cross-sectional Raman Mapping in Fractal Porous SiNWs

Current chapter deal with the analysis of time dependent etching behaviours in heavily doped p- & n- type SiNSs, suing cross-sectional Raman mapping. The presence of smaller sized SiNSs present near the tip of the etched wafer is found to be originating from the fact that the top portion of the wafer stays in the etching solution for the longest time duration as compared to the bottom portion, which is probed to be crystalline. The interplay of electron-phonon interaction with quantum confinement has been validated by validating the presence of inhomogeneity in NSs' size. This study has been performed on samples namely p⁺-SiNWs, p⁺-cSi and n⁺-SiNWs corresponding to heavily doped p-type SiNSs , heavily doped p-type c-Si and heavily doped ptype SiNSs. The results presented in this chapter are published².

² Manushree *et al.*, J. Phys. Chem. C, 124, 11, 6467–6471, (2020)

Manushree et al., J Raman Spectrosc, 52, 12, 2100, (2021)

5.1 Top surface Raman Scattering from SiNWs

As explained earlier, Raman scattering which is a non-destructive technique to assess nano-crystallite size has been employed here to assess size of the top surface of the etched wafer. The sizes obtained at the top surface of the wafer do not agree well with that obtained from the bottom portion. The time dependent etching that takes place, causes a variation in nanostructures' size across the length of the nanowire and hence is manifested in terms of an asymmetric Raman line map comprising of spatial information in terms of a point, line, area map.

Consequent to porosification, the Si wafer, appears to be containing vertically aligned SiNWs (sample p+ -SiNWs) as evident from the SEM images (Figure 5.1a). The top view SEM image (Figure 5.1a) very clearly shows pore formation on the surface of Si wafer. The most



Figure 5.1: (a) Surface morphology of porosified p-type Si wafer in top view and cross-sectional view (top inset) along with zoomed portion of the wire-type structures, (b) Raman spectra from the starting Si wafer (p^+ -cSi) and silicon nanowires (p^+ -SiNWs) obtained after porosification.

probable mechanisms involved in the porosification of Si wafer using chemical etching along with the chemical reaction involved during MACE which have been summarized in the section 4.2. The cross sectional image in Figure 5.1a (top inset) shows well-aligned wire-like structures and hint at the possible presence of SiNWs in the sample as will be substantiated and quantified later on. However, the low resolution SEM image indicates a smooth wire-like structures, only a magnified look reveals that the wires themselves are porous in nature and consists of finer nanostructures (bottom inset Figure 5.1a). Whether these nanostructures have been miniaturized enough, i.e, smaller than 5 nm (the Bohr exciton radius), to have attained the quantum nature can be investigated using Raman scattering which also helps in estimating the size of these nanostructures. Additionally, the Raman spectroscopy will also be helpful in understanding other microscopic phenomenon, if any, taking place at the nanoscale as discussed below.

As mentioned above, manifestation of quantum confinement effect can be in various forms which, in SiNWs, can be seen best using Raman spectroscopy and may be identified by an asymmetrically broadened (asymmetry ratio value of more than unity) and red shifted spectral line-shape corresponding to optic phonons. The asymmetry as defined in section 2 as the ratio γ_r (asymmetry ratio) = γ_l / γ_h where, γ_l and γ_h are the half widths towards the lower and higher energy side respectively of the spectral maximum. To investigate and quantify the quantum confinement effect, Raman spectrum from sample p⁺SiNWs (Figure 5.1b) has been recorded which shows a spectral line-shape with peak at 518 cm⁻¹ and width (full width at half maximum or FWHM) of 13 cm⁻¹ and an asymmetry ratio of 0.8. Observation of an α_r value less than one appears anomalous to the usual observation of α_r of more than one from a quantum confined system where γ_l is more than γ_h due to relaxation of zone canter (zero wave-vector) phonon Raman selection rule and participation of finite (non-zero) wave-vector phonons in the Raman scattering from nanostructures. The said anomaly is observed in p-type confined system due to interplay between above-mentioned phonon confinement effect and Fano (electron-phonon) interaction. In p-type material (i.e, the present case) apart from the confinement effect, which increases the value of γ_l , the Fano effect induces increase in γ_h as well which compensates for the confinement induced γ_l thus is visible as sub-unity asymmetry ratio. In comparison, in the crystalline

system (sample p^+ -cSi, Figure 5.1b) where quantum confinement effect is absent and asymmetry of the Raman line-shape is caused by Fano effect alone the Raman spectrum is characterized with an asymmetry ratio of $\alpha_r = 0.4$. In other words, the asymmetry of the Raman spectrum from the crystalline counterpart is uncompensated and remains more asymmetric as dictated by the Fano effect solely. It is important here to mention that the overall FRaman line-shape in general and asymmetry in particular will dependent on the interplay between the two effects, Fano and quantum confinement as discussed in section 2. This is reflected in the value of α_r which can less than, more than or even equal to unity if the Fano effect is more than, less than or equal to the quantum confinement effect respectively. The individual contributions from Fano and confinement is governed by the extent of electron-phonon interaction and the nano crystallite size respectively and thus can be quantified using the values of q (Fano asymmetry parameter) and D (size) as discussed below.

The Raman line-shape, originating due to combined effect of quantum confinement and Fano is represented using Eq. 5.1 generating using phonon confinement effect which has been used here to estimate the mean crystallite size and Fano parameter. More detail about the origin of Eq. 5.1 and a qualitative description explaining the significance of various terms in Eq. 5.1 has been provided in the section 2:

$$I(\omega) = \int_0^1 \left[e^{-\frac{k^2 D^2}{4\alpha^2}} \left\{ \frac{(\varepsilon+q)^2}{1+\varepsilon^2} \right\} \right] d^n k , \qquad (5.1)$$

where, $\varepsilon = \left[\frac{\omega - \omega(k)}{\Gamma/2}\right]$, *D*, *a*, Γ denote the nanocrystallite size, lattice constant and line width (~ 4 cm⁻¹) of c-Si respectively. Here 'n=2' is the degree of quantum confinement for the case of SiNWs. The $\omega(k) = \sqrt{171400 + 100000 \cos \frac{\pi k}{2}}$ is the phonon dispersion relation for Si and 'q' is the Fano asymmetry parameter which is the measure of extent of electron-phonon interaction present in the system. The experimentally obtained Raman scattering data, represented by discrete points, (Figure 5.1b) have been fitted with Eq. 5.1 and the

value corresponding to the best fit curve (solid line, Figure 5.1b) comes out to be 6 nm for sample p^+ -SiNWs as listed in Table 5.1 (in bracket) along with the obtained Fano parameter q(= 10). Since confinement effect is absent in crystalline sample (sample p^+ -cSi), the value of q, the only fitting parameter, is obtained to be 4 meaning a strong Fano interaction as also evident from the anti-resonance dip (shown by arrow) in the curve (Figure 5.1b). Putting simplistically, the Raman spectral analysis can not only identify but also quantifies the electron-phonon interaction and/or Fano effect in a sample by measuring the asymmetry (ratio) of the Raman spectrum.

Table 5.1: Raman Parameters Calculated from Fitting of RamanSpectra by Theoretical Fano–Raman Line Shape (Eq.5.1).

Sample (size)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Asymmetry Ratio ($\alpha_r = \gamma_l / \gamma_h$)	q
p ⁺ -cSi	521.0	5	0.4	4
p ⁺ - SiNWs (6 nm)	518.0	13	0.8	10

5.2 Raman Mapping/micro-spectroscopy

Raman microscopy, as mentioned above, is a technique that integrates microscopy and spectroscopy by pairing optical microscope with Raman spectroscopy. It provides an extensive methodology for qualitative as well as quantitative detection of samples requiring little sample preparation. Raman mapping done in confocal geometry is capable to probe the materials at the laser spot size of submicron sizes when equipped with an optical microscopy and can be improved to a few nanometers when integrated with AFM probe. Spectroscopy and microscopy when done separately probe different domain sizes for e.g. Microscopic techniques like TEM, AFM probe a few nanometers of the sample, whereas techniques like SEM, UV-Vis and PL probe macroscopic domains. Raman microscopy integrated with spatial information, creates an image by integrating the spectroscopic properties at the domain size of that for the case of microscopy.

Recent works on Raman mapping shows its unique capabilities to explore it in different domains of science and technology to noninvasively extract information as opposed to the classical Raman spectroscopy which acquires a single spectrum and hence limits the spatial information to be added for the advantage of holistic analysis. In recent years, Raman microscopy has evolved as a tool to identify new systems with evolved capabilities and better design for faster data acquisitions. Instrumentation of Raman mapping is very simple which includes an automated motorized XY stage, with the help of which the sample is scanned using a particular wavelength laser beam focussed in confocal geometry to acquire spectra from each position in a synchronized way. Each spectrum acquired at every point is then assigned as a pixel, on the Raman image, comprising of spectral elements with the third axis being represented in terms of false colored axis. The spatial information can be acquired in terms of line, point or area map, as per the demand of detection & monitoring of the system under investigation. Abundant knowledge regarding detection and quantification of physical phenomena at small scale has been leveraged using Raman microscopy, being a sensitive tool to study perturbations induced due to temperature, pressure, doping, phase change, defects, concentration etc. The possibility of modern advancement in Raman measurement technique to solve dynamic problems as per the need has an edge over other spectroscopic tool vis-à-vis the analysis of a given system. Despite simplicity and immense potential in the multidisciplinary areas, hesitancy is seen in the use of Raman microscopy probably due to less awareness about the capabilities of the technique which needs to be highlighted so that better science can be done.

5.3 Cross-sectional Raman mapping in p-type SiNWs

However, the above-mentioned top surface Raman analysis of SiNSs appears simple but comes with a word of caution which is as follows. The laser, used for Raman scattering, has a finite penetration depth and thus a given Raman spectrum contains information from the interaction volume depending on the spot size and the penetration depth. This is likely to add an extent of ambiguity in the interpretation if the sample is inhomogeneous along the depth. The nature of mechanism involved in the MACE technique (used here) is such that as the etching progress during personification, different portion of the wire remains in the etching solution for different durations and thus the progress of etching (removal of Si atoms) is different in different direction which is time dependent as well (as discussed in section 4). This enforces nonuniform etching of the wafer along the depth. Thus, the portion where wires have been formed in the initial stages (top wafer surface) prolonged micro-etching will take place as compared to the one closest to the surface at the end of the final etching process. This will yield smallest sizes near the top surface as compared to the relatively smaller nanostructures at microscopic level near the wafer-wire junction. As a consequence, the wire is likely to have inhomogeneous micro-level nanostructures along the depth due to fractal nature of the (porous-) nanowires.

This "possibility" of the inhomogeneity needs to be either confirmed or discounted. Raman microscopy has been employed here for this purpose where a set of Raman spectra are recorded and stitched together in the form of an image by scanning the excitation laser along the cross-section of the sample starting from the unetched portion (of wafer) up to the visible SiNWs tip. The set up and the schematic in which the Raman image has been recorded have been shown in Figure 5.2a along with the Raman map (Figure 5.2b). The point zero corresponds to the portion closest to the wafer likely that has remained unetched thus the corresponding point shows a closest spectral



resemblance to sample p^+ -cSi (Figure 5.1b). To further clarify that the

Figure 5.2: Schematic showing the set up for recording Crosssectional Raman image from the p-type porosified silicon wafer consisting of nanostructures containing wire along with the (b) crosssectional Raman Image

different position, optical images have been captured during Raman microscopic measurement (shown in Appendix A3)At this point on the cross-section map, the sample is showing mainly Fano effect as there is minimum quantum confinement effect taking place as reflected in no widening of the lower half width of Raman signal. Just to mention that the points on the Raman image with same color correspond to the same intensity given by the color bar shown on the left hand side of the Raman image. While moving towards the tip of the SiNWs, the lower half width (γ_1) can be seen increasing and thus compensating the Fano induced higher half width (γ_h). Since the value of γ_l is a measure of size of the nanostructure, responsible for quantum confinement, an increasing γ_1 means decreasing size (which is responsible for quantum confinement effect) while moving towards the tip of the wire. Keeping the monotonous trend of increasing, γ_l equals γ_h at ~2.5 μm representing a near symmetric Raman spectrum similar to the one in Figure 5.1b (sample p+-SiNWs).

On further moving towards the tip, due to further decrease in the occult nanostructures' size, the quantum confinement effect appears to

start dominating and the value of γ_1 surpasses that of γ_h resulting in a Raman spectral feature with αr more than unity which continues till the tip visible to the Raman microscope. This size dependent interplay between γ_1 and γ_h can be seen from the individual Raman spectra presented in Figure 5.3. A position dependent variation of the Raman spectral feature along the wire length very clearly establishes that there is an inhomogeneity in the nanostructures' size present inside the SiNWs prepared using MIE technique thus clearing any ambiguity related to this. Alternatively, Raman spectral analysis will yield the information about phenomena taking place at microscopic level (confinement as well as Fano) from all the nanostructures present in the sample up to the penetration volume on the sample.

On the other hand, transmission electron microscopy can investigate inhomogeneity only in the microstructures, of course on a limited size on the sample. Thus, Raman microscopy proves to be a technique using which one can actually "see" the microstructures as well as micro-level physical phenomena simultaneously.



Figure 5.3: Individual position dependent Raman spectra of the Raman Image.





Figure 5.4: (a) Schematic showing the set up for recording Crosssectional Raman image from the n-type porosified silicon wafer consisting of nanostructures containing wire along with the (b) crosssectional Raman Image.

To further validate this technique and conclusions therein, crosssectional Raman microscopic image from an n-type SiNWs has also been recorded (Figure 5.4) revealing a continuously increasing asymmetry (maintaining the value of α_r more than unity all along) while scanning from the unetched portion (4 µm) towards the tip of the wire (zero µm). This observation is in contrary to the observation for p-type SiNWs (Figure 5.2) because in n-type quantum confined systems the Fano and quantum confinement effects always adds up rather than compensating each other. Elucidative interplay of Fano and quantum confinement has been already presented in section 2. Nevertheless, a monotonous increase in the asymmetry of the Raman line-shape while moving from the bottom of the wire to the tip establishes the presence of nanostructures' inhomogeneity along the depth of the wire (pores) which is not possible to establish by any other technique.

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5.5 Summary

In conclusion, Raman microscopy proves to be an effective technique to establish the presence of inhomogeneity in the nanostructures' size along the wire's length as demonstrated on silicon nanowires of p-type and further validated on n-type samples. The Raman map thus recorded reveals that smaller nanocrystallite are present near the tip of the wire as compared to the bottom of the wire as seen and quantified using the position (depth) dependent Raman spectral features. Moreover, the Raman image additionally enables one to "see" microscopic quantum phenomena like confinement and Fano effects (and their interplay) rather than only providing information about the microstructures unlike other traditional microscopic techniques. This makes Raman imaging appropriate of an blend microscopy and spectroscopy.

Chapter 6 Fermi Level Repositioning in p-type SiNSs

Current work deals with a system where Si nanostructures (NSs) are fabricated from heavily doped p-type (boron doped) wafer where Fermi level in the Si NSs has been observed to have got modified by not only size (due to quantum confinement) but also due to unprecedented observation of spatial dopant concentration change (due to proposed zonal depletion effect). The above-mentioned Fermi level modification has been observed as a consequence of the fabrication process which is MACE. Raman scattering, being very sensitive to subtle changes in a system [183–186], has been employed to investigate dopant/impurity migration from nanowires to consequently establish the mechanism that leads to such a spatial distribution of dopants. Simple physics' principles suggest how chemical etching induces selective deviations in Fermi levels which on investigation was found correct experimentally. A fundamental science driven hypothesis, duly validated using Raman spectroscopy, has been used to explain how migration of dopants result in uneven dopants' concentration to force effective deviation of Fermi level with respect to modified band edge. This study³ has potential to open a new insight on some of the unexplored physical phenomenon in nano materials to build next generation technologies.

³ Manushree et al., J. Phys. Chem. C , 124, 30, 16675–16679, (2020)

6.1 Top Surface SEM and Raman Characterization of c-Si and p-SiNSs

As mentioned in section 3, the sample, containing nanostructures of Si, has been prepared using MACE [42,187] of a single crystal Si (c-Si) wafer. Post MACE, the Si wafer is known to become porous consisting of nanometer sized Si NSs present in a wire like structures in fractal geometry. This can be confirmed from the SEM micrograph (Figure 6.1a) and corresponding cross-sectional image (inset, Figure 6.1a). A low magnification cross-sectional SEM image of the post-etching wafer (Figure 6.1b) shows that the porosification takes place on both the surfaces (top and bottom sides of wafer) to yield fractal Si NSs [188–191]. As mentioned above, Raman spectroscopy has been employed here to investigate the above-mentioned SiNSs in the sample and subsequent size quantification. An asymmetrically broadened and red-shifted Raman spectrum (black curve, Figure 6.1c), as a manifestation of combined effect of confined phonons [72,192] and electron-phonon interaction [185,193,194], have been observed from the porosified sample with peak at 518 cm⁻¹, width (full width at half maximum or FWHM) of 13 cm⁻¹ and an asymmetry ratio ($\alpha_r = \gamma_1 / \gamma_h$) of 0.8 where γ_l and γ_h are the half widths towards the lower and higher energy sides respectively of the spectral maximum. On the other hand, Raman spectrum (red curve, Figure 6.1c) from c-Si, used for etching, with $\alpha_r = 0.4$ has been observed. All the Raman results have been analysed here within the framework of FANTUM model (as explained in section 2) to quantify the Si NSs size and Fano parameters from the c-Si and Si NSs as summarized in Table 6.1 A careful analysis of Raman results (Figure 6.1c & Table 6.1) outlines two very important findings which are as follows. First, Si NSs of small enough sizes have been fabricated which are expected to exhibit quantum confinement effect and thus will have effect on band structure modification as will be discussed below. Second, the value of Fano parameter for c-Si is

less than that for the Si NSs meaning a weak Fano interaction in the latter. Both of this will be discussed below in detail to reveal interesting and unexplored aspect of nanomaterials that has major consequences from science as well as technology point of view.



Figure 6.1: (a) SEM images of porosified p-type Si wafer in top view and cross-sectional view (inset), (b) low magnification SEM image showing cross section of whole wafer that underwent porosification, (c) Raman spectra from the crystalline Si and Si NSs with discrete points showing the experimental data and solid lines represent the theoretical fit using Eq 2.31.

Table 6.1: Raman Parameters Calculated from Fitting of RamanSpectra by Theoretical Fano–Raman Line Shape (Eq.2.31).

Sample (size)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Asymmetry Ratio $\left(\alpha_r = \frac{\gamma \mathbf{l}}{\gamma \mathbf{h}}\right)$	q
crystalline Si wafer	521	6	0.4	4
Si NSs (6 nm)	518	13	0.8	10

6.2 Fermi level repositioning in p-SiNSs

Band gap enhancement is one of the main consequences of quantum confinement effect [33,195] as discussed in section 2. As a result of carriers' confinement, the conduction (valance) band minimum (maximum) gets pulled (pushed) due to modification in the electronic structure. Thus the present sample, post-porosofication, will result in higher band gaps (E_{Si NSs}) near the two surfaces where Si NSs are present (0 < x < a & b < x < c; shown in green) with unchanged band gap of ~1.1 eV (E_{c-Si}) in the unetched region (a $\leq x \leq b$; shown in orange) of the wafer as shown schematically in Figure 6.2a. Under this modified band situation, the positions of Fermi level in the three regions will be worth analyzing and can be deduced as followed. In the middle region, the Fermi level (red transparent rectangle, Figure 6.2a) will lie close to the valance band as the Si wafer used was of ptype. Since the whole sample, consisting of c-Si and Si NSs parts, is single with no external bias applied, a common Fermi level for the whole region is expected.



Figure 6.2: (a) Schematic representation of energy band structure of the etched Si wafer showing relative position of Fermi level and (b) Raman spectra from c-Si and Si NSs with zoomed portion (inset) showing Boron peaks (* and # marked) and antiresonance dip in c-Si sample.

Keeping this as the constraint of the system means that the Fermi level will maintain the proximity to the valance band in the c-Si region whereas it effectively deviates away from the valance band maxima in the Si NSs region (0 < x < a & b < x < c) due to actually confinement induced band edge shift as depicted in Figure 6.2a. In other words, the separation between the Fermi level and the valance band maxima (E_{F} - E_{V}) is bigger in the region containing Si NSs as compared to the unetched portion which is heavily doped with boron.

Relative position of E_F with respect to E_V , known to be a consequence of doping concentration, means that the doping concentration in the Si NSs region is lower as compared to the unetched region [196] indicating a possible zonal depletion of dopants. Before discussing the possible origin and technological aspect of such a spatial variation of the dopants, it is important to confirm the above mentioned aspect. Raman spectroscopy has been employed for the purpose by comparing the Raman spectra obtained from the Si NSs and c-Si (Figure 6.2b) which shows two peaks, one near 520 cm-1, the usual optical phonon mode, and the other near 620 cm^{-1} , corresponding to the Boron present in the sample [67,85,197–199]. Observation of the low intense Boron peak (marked # right inset, Figure 6.2b) as compared to that in the c-Si wafer (marked * right inset, Figure 6.2b) is a direct indication that relatively lower dopant concentration is present in the Si NSs. Alternatively the Raman line-shape analysis can also be employed as an indirect method to re-ascertain the abovementioned statement as follows. Firstly, presence of a prominent antiresonance in the Raman spectrum from c-Si (arrow in left inset, Figure 6.2b) is a signature of higher electron-phonon coupling as compared to that in Si NSs where the anti-resonance dip is missing thus suggesting a poor coupling. Since the electron-phonon coupling is a direct consequence of doping concentration it means that the dopant concentration is actually lower in the Si NSs region. Secondly, this observation can be quantified using the Fano asymmetry parameter (Table-6.1) which also shows weak Fano coupling, or higher 'q' value (=10), thus low dopant concentration in Si NSs in comparison with the c-Si region (q=4) of the same sample. The above observations from the Raman spectra establish the fact that after porosification, the dopants get depleted in

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the region where Si NSs are present consequent upon etching. However such a direct observation of zonal dopants' concentration is unprecedented, modification in conductivity in Si nanowires have been reported but remains unexplained which can be explained using the present observation.

6.3 Reduced doping in SiNSs & hypothesis of zonal migration

The abovementioned observation is very important from application as well as materials' properties point of view as it gives an opportunity to understand carrier dynamics and to exploit it in a device. This will be discussed later on after discussing the possible origin of the induced spatial variation in doping distribution. Since the wafer used for etching had uniform distribution of dopants, the dopants' redistribution must have taken place during porosification process. Thus the migration of dopants from the c-Si has taken place during the course of etching. A strong driving force is required for such a mass drift which can be understood as follows by considering the etching process with the help of the schematic (Figure 6.3a). Figures 6.3a(I) to 6.3a(III) shows the usual steps of clean wafer, followed by silver nanoparticle deposition and subsequent wire formation respectively [189,200]. The wire like structures are formed as a result of chemical reactions between Si wafer and the etching solution $(HF+H_2O_2)$ which etch out the Si atoms (in amorphous state) from the wafer with time (as discussed in section 4). After a finite time, with continuous etching process, the wafer being etched can be represented schematically like the one shown in Figure 6.3a(IV) which shows pores (the etched out portion) separated by wire-like crystalline structures containing Si NSs in fractal form as mentioned above. In the Figure 6.3a(IV), the etched out Si-atoms have been shown as red dots whereas the ones still bound inside the wafer have been shown with grey dots with yellow dots representing the boron atoms. The etched out Si atoms is known to leave the wafer in amorphous state (as SiF₆) which remains in contact with the region on the wafer, which is yet to be etched [201–204]. Considering the amorphous phase to be analogous to a liquidous state, at a given time during etching a liquidous/solidus junction is maintained. This, in a way, mimics the situation that a solid goes through during zone melting refinement. Under this situation, the free energy dynamics of the interfaces involved pushes the impurities (here the dopants) from the solidus (here the partial pore walls) to the liquidous (here the pores with amorphous Si) as depicted more clearly in Figure 6.2b which shows reduced doping case of SiNSs as compared to c-Si.



Figure 6.3: (a) Schematic representation of the usual steps showing (I) clean wafer, (II) silver nanoparticle deposition, (III) subsequent wire formation and (IV) typical pore-pore-wall type arrangement achieved after a finite time with zoomed portion of two pores (b), and (c) Raman spectrum from the pore region and intrinsic c-Si

This can be understood through a very simple experiment (more details in Appendix 4) at home by freezing a solution containing water and ink (water soluble). This is shown in the Figure 6.4 that how the ink pigments get segregated to the region that freezes at the end when the solution undergoes solid-liquid phase transition. Overall it means that the boron atoms, doped as impurities, will migrate to the pores from the pore walls thus resulting in low boron density in the wire region. Since these wire-like portion contains the Si NSs therefore has lower dopant density as conclude above. On the other hand, the doping density in the middle region of wafer, which did not undergo etching at all, remains unchanged. However, the above process explains the dopants' drift; the main underlying hypothesis that pores are analogous to liquidous (amorphous) phase is yet to be proved. This has been done using Raman spectroscopy carried out from the pore region as shown in Figure 6.3c which shows a broad peak around 490 cm⁻¹, confirming the presence of amorphous Si [184]. In Figure 6.3c, Raman spectrum from an intrinsic c-Si is also shown for comparison. The other peak ~ 518 cm⁻¹ is present due to the usual red shifted phonon mode from Si NSs similar to other reports available in literature [17].



Figure 6.4: The suspension of water and blue ink (a) just prepared, (b) after 4 hours of freezing and (c) after complete freezing

Raman experiment confirms the presence of amorphous Si, analogous to liquid phase, inside the pore thus validating the explanation of dopants' zonal depletion in the etched wafer which leaves the Si NSs with low dopant concentration. As mentioned above, such a band structure may be useful in designing an integrated rectifier with only one type wafer by appropriately tuning the etching. Of course more study will be required before it can be used for technologically important applications by designing devices by exploiting the available unequally spaced Fermi energy. One such possible application could be an integrated diode that does not need different type of doping.

6.4 Summary

In conclusion, a zonal depletion of dopants and consequent position dependent shift in Fermi level in fractal SiNSs, a technologically important phenomenon, have been observed as a result of metal assisted etching process. A spatial variation in the dopants has been established directly using Raman spectroscopy experiments which show different dopant concentration in Si NSs region as compared to its bulk counterpart. On validation, using theoretical line-shape analysis of experimental Raman data, a poor Fano coupling in Si NSs was observed as compared to crystalline Si to ascertain the abovementioned low dopant's concentration in the nanostructures. An etching induced mass migration of boron (the process similar to the one that take place during zone refining) from crystalline Si to the pores containing amorphous Si residue from etching, has been found as the origin of zonal dopants' depletion which is also validated using Raman spectroscopy.

Chapter 7 Size Dependent Electron-phonon Interaction in Fractal Porous SiNWs

This chapter deals with the quantum size effects on interferons (electron-phonon bound states), confined in fractal SiNSs studied using Raman spectro-microscopy. A paradoxical size dependence of Fano parameters, estimated from Raman spectra, has been observed as a consequence of longitudinal variation of nanocrystallite size along the Si wires leading to local variations in the dopants' density which actually starts governing the Fano coupling thus liberating the interferons to exhibit the typical quantum size effect. These interferons are more dominated by the effective reduction in dopants' density rather than the quantum confinement effect. Detailed experimental and theoretical Raman line-shape analysis have been carried out to solve the paradox by establishing that the increasing size effect actually is accompanied by receding Fano coupling due to weakened electronic continuum. The latter has been validated⁴ by observing a consequent variation in the Raman signal from dopants which was found consistent with the above conclusion.

⁴ Manushree et al., J. Phys. Chem. C, 125, 23, 12767–12773, (2021)

Manushree et al., J. Phys. Chem. Lett., 12, 8, 2044–2051, (2021)

7.1 Top-surface characterization of p-SiNWs

The Si wafer etched using MIE becomes porous and show fractal nature [189,190,205] as can be seen using electron microscopy (Figure 7.1a). A low-resolution top surface SEM confirms (Figure 7.1a) the formation of porous silicon likely in wire-like structure formed as a consequence of reaction between the Si wafer and the etching. To noticeably "see" the nano-porous fractal structures, TEM has been performed and sizes from a wire like portion (from square box) has been qualitatively estimated, which clearly shows the presence of wire like structures along with the formation of embedded nanostructures of size (~5 nm), as apparent from the magnified TEM image on the top right side (lateral-right inset, Figure 7.1a).



Figure 7.1: (a) Surface morphology of porosified p-type Si wafer along with corresponding TEM images showing nanowires (left inset) and magnified view showing fractal structures (top right inset), (b) Raman spectra from the crystalline Si (c-Si) and Si NSs with discrete points showing the experimental data and solid lines represent the theoretical fit using confinement model (Eq.7.1)

It is important to mention here that not much variation in the diameter of the Si wire can be noticed at the macroscopic level. To quantify the nanometer size, Raman spectroscopy has been performed on the sample which shows a red-shifted and asymmetrically broadened

Raman spectrum (green curve, Figure 7.1b). In the confined systems, behavior of restricted phonons is governed by and asymmetric Raman line shape deviating from its bulk counterpart due to relaxation in momentum conservation. An appropriate Raman line-shape accounting for phonon confinement was developed by Richter et al. [206] and later modified by Campbell and Fauchet [207]. Various line shapes according to the regimes of suitability have later been developed accounting for concerned effect from very small sized nanoclusters [208,209], amorphous materials [184,210] and nanocrystals [211]. For the confined interferons [212,213] participating in electron-phonon interaction [183,214,215] in the porosified sample which is manifested in Raman spectrum with a 13 cm⁻¹ broad peak centered at 518 cm⁻¹ and shows an asymmetry ratio ($\alpha_r = \gamma_1/\gamma_h$) of 0.8, where γ_l and γ_h are the half widths toward the lower- and higher-energy sides, respectively, of the spectral maximum. In comparison, the c-Si wafer (used for etching), shows an asymmetric Raman line-shape with $\alpha_r = 0.4$ (brown curve, Figure 7.1b) meaning a more asymmetric lineshape as compared to the Si NSs. The laser related effects are absent and being a non-polar semiconductor, the role of surface phonons is also ruled out [216–219] Thus the relaxation in asymmetry, consequent to reduction in size, take place due to confined interferons in the Si NSs and accordingly the Raman line-shape are analyzed using the line-shape function predicted by Fantum model [220] (more details in SI) given by Eq. 1 to quantify the size and Fano parameter, q:

$$I(\omega, L) = \int_0^1 exp \left\{ -\frac{k^2 L^2}{4a^2} \right\}_{1+\epsilon^2}^{(\epsilon+q)^2} d^n k , \qquad (7.1)$$

where, $\varepsilon = \left\{\frac{\omega - \omega(k)}{\Gamma/2}\right\}$, L, a, Γ denote the nanocrystallite size, lattice constant and line width (4 cm⁻¹) of c-Si respectively. Here '*n*=2' is the degree of quantum confinement for the case of SiNWs. The $\omega(k) =$

 $[\]sqrt{171400 + 100000 \cos{\frac{\pi k}{2}}}$ is the phonon dispersion relation for Si and q is the Fano asymmetry parameter which is the measure of extent of electron-phonon interaction present in the system. As mentioned in section 2, overlapping of electronic energy with discrete phonon gives

rise to an asymmetric line shape due to interference [191,221,222]. Such Raman line-shapes have two distinct features, first the doping dependent asymmetry in which the Fano-Raman line-shape should be broader in lower energy side of the peak for n-type semiconductor (α_r >1) whereas it should be broader in the higher energy side of the peak for p-type semiconductor ($\alpha_r < 1$) [191]. Second signature of the presence of Fano effect in a system is the observation of antiresonance. The antiresonance and broadening of half widths are observed in the opposite sides of the peak in the spectrum showing Fano interaction. This model predicts an asymmetric Raman line-shape equation which can be fitted with the experimental Raman data to estimate the Si NSs size and 'q' for further analysis and deconvolute the individual effects namely e-phonon interaction and quantum confinement. The corresponding fitting of Raman data in Figure 7.1b with Eq. 7.1 yield the q values of 4 and 10 from c-Si and a 6 nm sized Si NSs respectively which is consistent with the experimentally observed asymmetry and width (full width at half maxima or FWHM) mentioned above. It is important here to mention that a larger value of q (= 10) is obtained from Si NSs as compared to that (q=4) for c-Si indicating a stronger Fano interaction in the latter which is not consistent with the well-known size dependent Fano effect [222-224] which predicts a strong Fano coupling in smaller Si NSs. To discount, or confirm, a possible anomaly in the size dependence of interferons' behavior further investigations are required and accordingly understood. Raman spectroscopy, an established tool having advantages over several other techniques [185,186] has been used here to investigate the above-mentioned anomaly in the size dependent interferon behaviors as discussed below.

7.2 Size dependent electron-phonon interaction in p-SiNWs

The fractal like geometry of nanostructures and the fabrication techniques invites preferentially advanced investigation using Raman

spectroscopy to draw forth anomalies that are concealed in the explicit manifestation of quantum confinement. Top surface Raman spectra are expected to have information about the size only from (and near) the tip of the nanowire henceforth not delivering complete information about whole sample and thus various phenomena that require an overall assessment of system remain untouched. To understand the true nature of various subtle processes, cross sectional Raman spectromicroscopy of a porosified sample has been done by obtaining Raman spectra along the length of the wire starting from substrate (c-Si) to the tip of nano wire, as shown in SEM image in Figure7.2a. Raman spectra obtained from five different positions along the wire have been shown in figure 7.2b (the legends have been marked to guide the location from where spectra have been recorded.



Figure 7.2: (a) Cross-sectional SEM image of Si wire sample, (b) position dependent Raman spectra at five different positions along the wire cross-section and (c) the consolidated cross-sectional spatial Raman image generated using all the Raman spectra acquired during mapping. The position on Y-axis has been marked with respect to the Si substrate.

The experimental Raman data (discrete points) have been theoretically fitted using FANTUM [188,222,224] line-shape function which gives information about the confined interferons rather than only phonons. The Si NSs' size and Fano parameter, obtained corresponding to best fitting (solid line, Figure 7.2b) have been listed in table 7.1. The five Raman spectra used for size dependent study are only representative

data out of several Raman spectra recorded to study the longitudinal variation in Raman spectral feature as can be seen in the form of the Raman image (Figure 7.2c). The Raman image in Figure 7.2c clearly shows how the Raman spectra varies along the length of the wire and changes the line-shape from a value of $\alpha_r < 1$ to $\alpha_r > 1$ while scanning from the substrate to the tip of the wire. Such variation along the length of the Si wire is attributed due to the longitudinal variation in Si NSs size consequent to the fractal nature of the sample [183] introduced due to the etching process.

Table 7.1: Estimated Fano parameters (q) and Si NSs size (L) obtained from theoretical fitting (using Eq. 7.1) of different Raman spectra in Figure 7.2b.

Longitudinal position	S 1	S2	S 3	S4	S5
(Figure 2)					
q	4	6.4	7.3	8.5	10
L (nm)	∞ (bulk)	8.2	6.5	4.3	3.2

The estimated Si NSs size and Fano parameters analysis (table 7.1) shows clearly that the Si NSs size decreases along the wire from substrate (point S1, bulk) to the tip of the nanowire (point S5, 3.2 nm). Along with the variation of size across the wire, it is also important to note the variation of q which depicts the strength of electron phonon interaction in these sizes. As reported by Sagar et al. [223] and Kumar et al. [214] increased quantum confinement (smaller NSs size) leads to stronger electron phonon interaction, which on contrary in this case is increasing, as evident from theoretical fitting using FANTUM model and table 7.1. The apparent anomaly in Figure 7.1 appears evident (Figure 7.2b & table 7.1) from the ambiguous set of obtained parameters indicating the anomalous interaction of quantum confined interferons. Also, before attempting to explain this anomaly, it is important to mention here that the reported quantum 'q-L' variation is valid for a given doping (carrier) concentrations in the

sample [214,225]. In other words, the above-mentioned behavior can be said to be anomalous only if the dopant concentration (an important parameter in Fano interaction) remains constant along the Si wire. In contrary, a possibility of reduction in carrier concentration due to dopants' migration has been predicted [226] which means that a continuous variation of carrier concentration along the whole length is possible. In other words, the doping in sample reduces as one move from substrate to the tip of wire due to migration of dopant atoms along with reduction in nanostructure sizes.

7.3 Band gap enhancement & zonal depletion of dopant atom

The above-mentioned hypothesis, to be validated later on, has been explained by considering the Si NSs size variation along the wire's length to be graded rather than continuous for easier modeling. Figure 7.3 shows a schematic diagram depicting the combined effect of Band gap enhancement and dopant mass migration as the size of the microscopic nanostructures gets reduced (Bulk to L4), where the latter is supposed to be a consequence of fabrication technique involved for the porosification of the sample. As apparent from q values estimated for different sizes, anomalous decrease of electron-phonon interaction with decreasing size is discernable in wholesome picture (table 7.1). But a microscopic assessment leads to two different phenomena namely, quantum confinement and mass migration of dopant atoms, decoding this anomaly to prove it to be a pseudo paradox.

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Figure 7.3: Schematic representation of combined effect dopants' mass migration and quantum confinement on the band structure of fractal Si wire where the relative position of intrinsic and heavily doped p-type wafer has been marked with dotted and solid lines respectively along with inset showing the typical band gap vs size variation.

Interplay between these two is known to cause such anomaly and thus deceiving the actual picture at the macroscopic level which can be validated as follows. The band gap enhancement due to quantum confinement is a noted phenomenon [33] leading to increase in band gap, visible on the same sample in the present case as one moves from substrate (c-Si) to SiNWs tip. An unmoved Fermi level, being the representative of the whole sample, predicts that different regions along the wire length consists of different carrier concentration as can be appreciated from its position relative to the band edge [226]. It is clear from Figure 7.3 that the dopant's concentration is minimum in the region on the wire where smallest Si NSs are present. Since the Fano

coupling is directly proportional to the carrier concentration [225], a poor Fano coupling between thus generated continuum and confined phonon, will become inevitable near the tip of the wire. At the same time, the quantum size effect will be maximum at the tip thus enforcing a stronger coupling. On the whole, the dominating of the two effects will dictate the overall Raman line-shape. In the current scenario it appears that the Fano component is eventually little near the tip where Si NSs are the smallest. Before making the final conclusions about the most dominant cause, a better clarity about the available size dependent dopants' concentration, at last some quantification is necessary.

Above-mentioned depletion of dopants (boron in this case) can be semi-quantified directly using the analysis of boron peak in the Raman spectra recorded from different positions along the wire's length (Figure 7.4a). Plenty of boron ions are present in the substrate as evident from a clear peak near 620 cm⁻¹ (pink curve) originating due to borons [197] present in the Si lattice. The intensity of this peak continuously decreases while moving towards the surface of the sample. The intensity of this peak completely vanishes in the Raman spectrum collected from the tip (surface) region meaning that little boron are present near the surface. The concentration of the boron atoms is actually inadequate to create sufficient continuum for Fano interaction to take place. This has been experimentally proved by analyzing the zooming the position dependent Raman spectra (near the base of the spectra) as shown in Figure 7.4b. The Raman spectra obtained from the substrate region (pink curve) shows a clear antiresonance dip meaning a stronger Fano coupling. The anti-resonance dip gradually decreases and vanishes completely in the Raman spectrum collected from the surface region (blue curve) where the Raman spectra is fully dominated by the confinement effect. In other words, even though the available quantum confinement effect is the maximum near the surface region (where smallest NSs are present) but



little Fano interaction to experience this quantum effect thus remains completely dominated by the phonon confinement alone.

Figure 7.4: (a) Position dependent Raman spectra corresponding to localized Boron peak (at 620 cm⁻¹) and (b) Zoomed Raman spectra showing decreasing antiresonance while moving from the substrate towards the surface region.

While moving on the Si wire from bulk towards the surface, the decreasing boron concentration recedes to the increasing quantum size effect more rapidly to get overwhelmed by the confinement effect. As mentioned above, a wholesome analysis to understand the observed Fano paradox (the anomalous size dependent variation of Fano parameter and its interplay with Si NSs size), duly validated by experimental and theoretical approaches, has been presented. A careful analysis of the Raman spectral line-shape must be carried out without which it may lead to wrong conclusions.

In conclusion, a spatial Raman spectromicroscopic study reveals that confined interferons in silicon (Si) nanostructures (NSs) show a paradoxical variation of Fano asymmetry parameter (q) with respect to NSs size as compared to the typical quantum confined effect. A detailed theoretical and experimental Raman line-shape analyses resolves the anomaly in the reported size vs q dependence. The above mentioned pseudo anomalous behavior of interferons, or the "quantum Fano paradox", was found to be a consequence of fractal nature of the Si wires present in the sample which consists of SiNSs of different sizes along the Si wire prepared by metal assisted etching as clearly seen using cross-sectional Raman microscopy. The longitudinal variation in Si microcrystallite size (in nanometer range) actually evokes a gradual depletion of dopants resulting in their etching induced migration, stronger for smaller nano-crystallites, which recedes to the size dependent Fano parameter variation. In other words, little Fano coupling in smaller Si NSs is a consequence of lower dopants concentration rather than the quantum size effect. Besides theoretical Raman line-shape deconvolution, the gradual zonal dopants' variation has been experimentally validated using the analysis of Boron's Raman signal variation and associate anti-resonance along the Si wire.

7.4 Top-surface characterization of n-SiNWs

The porous nature of the etched Si wafer can be confirmed from the top surface electron micrograph (Figure 7.5). Inset shows the magnified view of sample, indicating presence of interconnected pores with wire like structures. Typically these samples contain wires like structures in nano-fractal geometry which is unappreciable at this resolution. To comprehend these nano-fractals⁵³, TEM has been carried out which shows that wires of ~ 100 nm diameter are present in sample with a few nanometers sized NSs present in the wire at microscopic level. Such a vague and inaccurate size depiction from electron micrographs leads to inscrutable size dependent analysis of various properties thus are treated here as qualitative in nature to proceed.



Figure 7.5: (a) Top surface morphology and magnified view (left inset) of porosified n-type Si wafer along with the TEM image showing fractal nature of nanowires (right inset) and, (b) Top surface Raman spectra recorded from the crystalline Si (c-Si) and Si NSs with the inset showing theoretical fitting of data point using FANTUM model (Eq.7.1).

To quantify possible nanometer sizes overt in TEM micrographs, Raman spectroscopy has been performed on the porosified sample which shows a perturbed red shifted and asymmetrically broadened Raman line shape (pink curve, Figure 7.5b) as compared to its bulk counterpart (cyan curves, Figure 7.5b), wherein the experimentally obtained spectra have been fitted using theoretical Raman line shape accounting for both quantum confinement and Fano interference in heavily doped nano-fractal porous Si. Analysis of such an asymmetric Raman line shape has been done under the framework of FANTUM model, which represents the obtained line-shape by Eq. 7.1, in which 'n' (taken as fitting parameter), is related to the degree of confinement and takes values of 0, 1 or 2 for systems with one- two- and three degrees of confinement. Alternatively 'n' can take non integer values (taken as 0.3 in the present case for better fitting) for systems where distinct confinement order cannot be defined.

The obtained Raman spectrum (blue curve, Figure 7.5b) is 5 cm⁻¹ broad and asymmetric and centred near ~519.5 cm⁻¹ as compared to c-Si wafer wherein the peak is positioned at ~520 cm⁻¹ and is less asymmetric as compared to porous sample (inset Figure 7.5b). The

asymmetric nature of Raman line-shape is known to originate due to the e-ph (Fano) coupling from heavily doped c-Si (the present case). The variation of asymmetry in the two samples results due to the introduced quantum confinement effect on interferons in the porous silicon which is absent in the c-Si. To understand the exact behaviour of interferons with size Eq. 7.1 has been used to fit the experimental data set (discrete points, Figure 7.5b) and two substantial set of parameters obtained from theoretical fitting of above mentioned experimental data are 'q' and 'L' which denote strength of electronphonon coupling and size of the NSs respectively. It is important to consider the combined effect, especially in a system where perturbed positions of Fermi level, conduction and valence band might be perceived as an effect of confinement⁴⁷. The obtained set of parameters for above theoretical fittings are($L=\infty,q=-10$; for c-Si) and (L=7.5 nm, q=-15; for n^+ -SiNWs). These values indicates following two things, first, the system is in weak confinement regime and second, the Si NSs are in mixed states showing confinement in more than one but less than two dimensions. This is typical of systems where the shape of the structures are not distinct like the present case where pores are connected in a way that they neither behave as nanowires nor as films. This is also visible from SEM image in the inset of Figure 7.5a. A closer analysis at these parameters dictates the size dependence of electron -phonon coupling and an increased q value for SiNWs as compared to c-Si indicating a weaker Fano coupling likely due to compromised electronic concentration in NWs and hence a consequent reduction in electron-phonon coupling obverse to the size dependent interferon behaviour in NSs. It is important to note that any variation in size especially around Bohr exciton radius of Si (~5nm for Si), leads to a significant alteration in the strength of electron phonon coupling. To closely analyse such an ambiguous (apparently) size dependent behaviour of interferons, an etched wafer which is a suitable system for studying the size dependent variation of interferons has been taken into account owing to the inhomogeneity in lateral size due to

porosification of Si wafer using MACE as reported elsewhere. While in the Figure 7.5b, both the Raman spectra have been recorded from top surface, this beneficent situation of longitudinal variation in size inherent in the etched Si wafer can reveal the true nature of electronphonon coupling in such systems. Cross sectional Raman microscopy has been employed here to understand vertical size dependent electronphonon interaction combined with the effect of gradually perturbed doping as discussed below.

7.5 Size dependent electron-phonon interaction in n-SiNWs

Figure 7.6a, shows the consolidated scanned Raman map of porous wafer with appropriate step size taken using a line scan. The variation in Raman line-shape recorded along the length of the porous wire can be appreciated from the Raman image very clearly showing an increase in spectral asymmetry while moving from the c-Si base to the tip of the wire. To quantify the heterogeneous sizes across the etched Si porous wire, estimation of size (L) and electron-phonon coupling parameter (q) has been done. Figure 7.6b shows Raman spectra (constituting the Raman image in Figure 7.6a) from four different positions as indicated by the legends (say sample points N1 to N4) locating the positions where the Raman spectra have been recorded. Theoretical fitting (using Eq.7.1) of experimental dataset (discrete points) has been performed and shown as continuous line. Table 7.2 shows q and L values obtained after fitting of experimental data points using theoretical FANTUM model (Eq.7.1). As mentioned above a longitudinal size variation has already been established due to the metal assisted etching accounting for the larger sizes near the substrate and smaller one across the tip of the NWs. A closer look at the Raman map reveals a more asymmetric Raman line shape (>1) near the tip of the nanowires and it becomes symmetric as one moves to c-Si. Here $\alpha_r = \gamma_l/\gamma_h$ is defined as asymmetry ratio with γ_l and γ_h as spectral half widths towards the lowand high energy side of the peak position respectively. The sizes



obtained from theoretical fitting and the Raman map clearly indicates the presence of relatively smaller sizes near the tip of the NWs.

Figure 7.6: (a) Cross-sectional Raman map acquired from substrate to tip of the porous Si wire and (b) Raman spectra acquired from four different positions (marked as legends) along with theoretical data fit (solid line).

Fano parameter (q) estimated from the four spectra found to increase with decreasing size is an indicative of reduced Fano coupling which is atypical behavior as per the usual quantum confinement effect. Since, the line-shapes, and asymmetry therein, has contributions from Fano coupling and confinement it means that e-ph coupling is decreasing while moving towards the tip likely due to corresponding decrease in doping density. Also this behavior of reduced e-ph coupling with decreasing NSs size is an incongruity to the one reported by Sagar et al [223]. and Kumar et al [214]. where an increase Fano coupling is reported in smaller NSs. Before attempting to explain the anomalous trend of q vs L in this system it is important to note that the size dependent interferon behavior is noted in a system where doping density remains constant throughout the sample. On the contrary in this case a reduction in dopant atom is apparent from the obtained set of q value from Raman spectra of top surface of nanowire in Figure 7.5b. Also a mass migration of dopant atoms from SiNWs and consequent reduction in doping density has been reported for the ones prepared
using MACE which makes it a case to understand the electronic concentration in such a system. When the concentration is decreased, on decreasing the size, the electronic continuum becomes flatter thus will have poorer Fano coupling and that is exactly what is visible above. The variation in electronic concentration is observed in the above system because the dopants are known to selectively migrate from nanowire region to pore. Such a selective migration of dopant atoms (phosphorus in this case) leads to reduction in electron-phonon coupling. The variation in electronic concentration along the length of the wire has been analyzed below.

Table 7.2: Estimated Fano parameters (q) and mean Si NSs size (L) obtained from theoretical fitting (using Eq. 7.1) of different Raman spectra in Figure 7.6b.

Longitudinal position	N1	N2	N3	N4
(Figure 7.6b)				
q	-16	-14	-12	-10
L (nm)	7.2	7.8	82	13
	1.2	7.0	0.2	(bulk)

Band gap enhancement due to quantum confinement is a noted phenomenon in nanostructures .Figure 7.7 depicts the corresponding band diagram which shows an increased band gap in the region of porous wire with the Fermi level shown close to the conduction band (being n-type) in the c-Si region (left side, Figure 7.7). Since the porous wires are on the c-Si wafer constitute a single system with no bias applied, the value of Fermi energy remains the same throughout the sample along the depth (x-axis, Figure 7.7). As a consequence, in case of NSs, the relative position Fermi level with respect to



conduction band is farther than that in bulk Si confirming the reduction in dopants' density.

Figure 7.7: Schematic showing representative band diagram of consolidated c-Si/porous Si wire structure showing band gap enhancement in the latter and associated relative Fermi level position.

A constant Fermi level established via thermal equilibrium in the whole system is a typical characteristic of a system which in this case establishes the migration of carriers from NWs to the pores that are formed during the etching process. As shown in Figure 7.7, a farther edge of Fermi level for the case of NWs depicts a depleted carrier concentration in the confined region along with the band gap enhancement due to quantum confinement. Such a vertical depletion of dopant atom causes gradual concentration gradient which will directly flatten the electronic continuum and thus is expected to affect the electron-phonon coupling in NSs in this case. Thus on moving towards the tip of the porous wire, strength of the Fano coupling is decreasing due to non-availability of sufficient carriers. This allows the confinement effects to dominate over the Fano effect for smaller sizes.

To further confirm whether electronic concentration decreases in smaller NSs locally, Raman spectra for samples N1 and N4 (the two extreme positions) have been plotted in Figure 7.8a with a zoomed portion to look for antiresonance dip, one of the most important consequences of Fano interference. A steeper antiresonance dip can be seen in spectrum N4 (wafer side of the porous wire) which is not that prominent for spectrum N1 (the tip region). Figure 7.8 (b) shows the variation in Fano parameter (q) with size (L) for the four samples as one moves from substrate to the tip of the nanowires.



Figure 7.8: (a) Zoomed Raman spectra from N1 and N4 showing absent antiresonance dip in latter and (b) variation of NSs size &Fano parameter (y-axes) along the length L of porous wire (x-axis).

Overall, the porous Si wires prepared directly on c-Si wafer shows decrease in the size of the microscopic Si NSs and corresponding Fano parameter values (Figure 7.8b). The latter is a consequence of availability of relatively less dopant concentration due to zonal depletion of dopant atoms near the tip of the NWs. While moving along the porous wire from substrate towards tip, the doping depletion weakens the Fano coupling while phonon confinement strengthens. The combined effect of band gap modulation via longitudinal variation in size leading to Fermi level deviation from band edge along with variation in dopant density envelopes the size dependent variation of eph interaction. A detailed analysis reveals insufficient electronic concentration available for quantum sized wires to form strongly bound interferons as compared to that in c-Si.

7.6 Summary

Current work reports discovery of an atypical size dependence of Raman-Fano parameters from boron doped (p-type) and phosphorous doped n-type SiNSs up to an extent to get deceived of observing an (pseudo-)anomalous behavior. An increasing Fano coupling parameter (with decreasing size), obtained using Fano line-shape fitting of Raman spectra, is noticed which actually was found to be consistent with the known size dependent Fano effect as established by careful deconvolution of the Raman line-shape by incorporating the effect of gradual nanosize variation along the Si micro-wires. The wire like structures, prepared using metal assisted etching, exhibit depletion of dopants as a consequence of fabrication process due to fractal nature of the Si NSs. The quantum effect was found to exhibit a dual role of a typical band gap enhancement and atypical zonal dopant depletion with the latter being dominating. These two effects force the interferons to behave in a pseudo-anomalous manner only to get revealed after careful Raman line-shape analysis followed by experimental validation using quantitative Raman spectro-microscopy. The gradual size variation in the prepared fractal Si NSs leads to a graded energy band system where doping concentration also decreases inherently with decreasing size due to Fermi surface migration of dopants thus responsible for the above-said quantum Fano effect.

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Chapter 8

Conclusions and Future Scope

New scientific findings along with all the conclusions deduced from the results reported in above chapters are listed here. This chapter also discusses future scope of work that can be carried out for further development in this field.

8.1 New scientific Findings in the present Thesis work

- Anomalous Fano paradox and its size dependent interplay between extent of quantum confinement and Fano resonance in heavily doped, being validated using Raman mapping.
- Analyzing the interplay of phonon confinement effect and electron-phonon interaction by using duly validated approach of theoretical Raman line shape fitting of experimentally observed Raman line shape from heavily doped nanostructures.
- To understand and validate time dependent etching mechanism in using cross sectional Raman mapping.
- To understand the dopant behavior in SiNSs using Raman microscopy in heavily doped p-& n-type SiNSs.
- To identify and analyze the (in) homogeneity in nanostructures size prepared using MACE by utilizing Raman microscopy as a non-destructive tool.
- Develop an understanding of fermi level reposition in heavily doped silicon SiNSs by establishing Raman microscopy as a technique to assess electronic properties.

- Understanding Size dependent electron-phonon interaction in heavily doped p- & n- type SiNSs by understanding the interplay between phonon confinement and Fano resonance.
- Analyzing size distribution in heavily doped SiNSs using diffused reflectance spectroscopy (DRS), by developing a theoretical model to incorporate the effect of quantum confinement and correlating the results with the ones obtained from Raman microscopy.

8.2 Conclusions

- ✤ Porous SiNSs have been prepared using MACE.
- Longitudinal inhomogeneity in NSs size, due to fabrication process is observed in heavily doped p- & n- type SiNSs.
- Cross-sectional Raman mapping has been performed on porosified Si wafer to understand the role of etching mechanism during MACE of Si wafer and prolonged etching exposure of the top portion of Si wafer immersed in etching solution is known to cause reduction in NSs size as compared to the bottom portion of the Si wafer. The following has been validated using Raman microscopy.
- Interplay between quantum confinement and Fano interaction, across the length of the NW, has been validated using theoretical & parametrical Raman line-shape analysis.
- The modulation in the band gap due to the effect of quantum confinement and hence in the diffused reflectance spectrum obtained from SiNSs have been studied by developing a theoretical line shape which represents a variation in absorption coefficient as a function of size.
- The theoretical model developed to fit the experimentally obtained absorption coefficients quantifies the size distribution and mean size present in the samples.

- The mean size and size distribution, estimated from optical spectra show consistent results with the predicted values using transmission electron microscopy and Raman spectroscopy.
- A zonal depletion of dopants and consequent position dependent shift in the Fermi level in fractal SiNSs, a technologically important phenomenon, have been observed as a result of the metal-assisted etching process.
- A spatial variation in the dopants has been established directly using Raman spectroscopy experiments, which show different dopant concentrations in the Si NSs region as compared to its bulk counterpart.
- On validation, using theoretical line-shape analysis of experimental Raman data, a poor Fano coupling in Si NSs was observed as compared to crystalline Si to ascertain the above-mentioned low dopant's concentration in the nanostructures.
- Size dependent Fano paradox in fractal SiNSs has been analyzed using Raman spectroscopy.
- Cross-sectional Raman microscopic measurement combined with theoretical Raman line shape analysis establishes an anomalous decreasing electron-phonon interaction with an increase in NSSs size as opposed to generic size dependent electron-phonon interaction established in previous studies.
- The said size dependent anomaly is found to be originating due to the combined effect of zonal depletion of dopants atoms near the tip of the nanowire, as compared to the ones near substrate.

8.3 Future Scope

This work is mainly focused on the spectroscopic analysis including cross-sectional Raman mapping of low dimension Si fabricated using MACE technique. There is much scope to extend this work further in future. Some possible studies are described below:

- Wavelength dependent electron-phonon interactions in fractal SiNSs can provide a wholesome insight into the dependence of Fano coupling in heavily doped NSs, especially when there are several key parameters as actual players perturbing the system.
- Probing penetration depth of SiNSs cross-sectional Raman microscopy can be done to understand and empirically formulise a relationship between SiNSs' size and penetration depth.
- Study of electronic continuum using theoretical and experimental Raman line-shape analysis and hence analysis of electronic continuum provided by heavy doping as well as by different laser excitation.
- Modelling the equation for electronic Raman scattering and merging it with existing Fano Raman line shape can help in clearly identifying the extent of participation of electronic continuum.
- After successful understanding of physics of fabricated NSs, they can be explored in for various device applications like charge storage, energy storage etc.

Appendices

Appendix 1

Silicon elemental facts

Classification:	Si is a metalloid		
Atomic weight	28 0855 g/mo	1	
Density @ 20° C·	233 g/cm^3	1	
Atomic volume:	$12.55 \text{ g/cm}^3/\text{mol}$		
Atomic volume.			
		St	tate
State:	solid		
Melting point:		$1687 \text{ K} (1414 ^{\circ}\text{C})$	
Boiling point:	35381	$X (3265 ^{\circ}C)$	
Doming point.	55561	x (3203°C)	
		Ener	rgie
Specific heat capacity:	0.71 J	$g^{-1} K^{-1}$	
Heat of fusion:		kJ mol ⁻¹	
1 st ionization energy.		kJ mol ⁻¹	
3 rd ionization energy:		4 kI mol^{-1}	
Heat of atomization:	456 k	mol^{-1}	
Heat of vaporization:	350 k	mol ⁻¹	
2^{nd} ionization anargy:	1577 I	^r I mol ⁻¹	
Electron affinity:	13771	kJ mol ⁻¹	
 		dation & Float	ror
	UXI		101
Shells	:	2,8,4	
Min. oxidation number	:	-4	
Min. common oxidatio	on no. :	-4	
Electronegativity (Paul	ling Scale):	1.9	
Electron configuration		$1s^2 2s^2 2p^6 3s^2$	3n
Max oxidation numbe	r ·	10 1 0 1 0 1 0 1 0	۰p
Max. common oxidatio	n n n	1	
Polorizobility volume	лі по	4 5 1 Å ³	
Polarizability volume	:	5.4 A	
	Appearance	e & Characteri	stic
 Structure :		diamond struct	ture
Hardness ·		11 9 GPa	

Color :

Reactions & Compounds

silvery

Reaction with air:noneReaction with 15 M HNO3:noneOxide(s):SiO2Hydride(s):SiH4 (silane), Si2H6 + moreReaction with 6 M HC1:noneReaction with 6 M NaOH: mild, \Rightarrow silicatesChloride(s): SiCl4, Si2Cl6 + more

Conductivity

Thermal conductivity:	$149 \text{ W m}^{-1} \text{ K}^{-1}$
Electrical conductivity:	$1.2 \text{ x } 10^{-5} \text{ S cm}^{-1}$

Abundance & Isotopes

Abundance earth's crust: 28 % by weight, 21 % ppm by moles Abundance solar system: 900 ppm by weight, 40 ppm

Isotopes

Silicon has 14 isotopes whose half-lives are known, with mass numbers 22 to 36. Of these, three are stable: ²⁸Si, ²⁹Si and ³⁰Si.

Harmful effects

Si is not known to be toxic, but if breathed in as a fine silica/silicate dust it may cause chronic respiratory problems. Silicates such as asbestos are carcinogenic.

Characteristics

Si is a hard, relatively inert metalloid and it's crystalline form is very brittle with a marked metallic lustre. Si occurs mainly in nature as the oxide and as silicates. The solid form of Si does not react with oxygen, water and most acids. Si reacts with halogens or dilute alkalis. Si also has the unusual property that it expands as it freezes (like water).

Appendix 2



Figure A2.1: (a) Top view and cross-sectional (inset) SEM micrograph and (b) TEM image with SAED pattern (inset) of fractal Si sample (heavily doped) etched for a period of 90 minutes. The above morphological analysis shows the presence of amorphous like phase formation due to prolonged etching periods.

Figure A2. 1b shows the TEM image of sample showing thin wire like fractal structures encapsulated inside an amorphous matrix. Different contrast in TEM image around the wire depicts different electron density.



Figure A2.2: XRD pattern of etched Si wafer comprising of broad humps and sharp peaks depicting the presence of both disordered domain and nanocrystalline silicon.

Figure A2.2 shows X ray diffraction characterization of etched Si wafer, with a broad hump at ~28.4 $^{\circ}$ and ~ 43.5 $^{\circ}$ confirming the presence of amorphous Silicon sheath around nano-crystalline Si. Specifically the sharp peaks located at 47.3, and 56.1 $^{\circ}$ can be completely indexed as the (220), and (311) planes of crystal silicon (JCPDS No. 27- 1402), which is consistent with the literature and hence depicting the presence of nanocrystalline silicon along with amorphous silicon.



Figure A2.3: Stokes and antistokes spectra measured for crystalline Si (p-type).

Appendix 3



Figure A3.1: Optical image of p⁺-SiNWs sample, used for Raman mapping study.



Figure A3.2: Optical image of n^+ -SiNWs sample, used for Raman mapping study.

Appendix 4

Experiment to show impurity migration at solidus-liquidus interface

For understanding how impurities migrate from solid phase to liquid phase, a simple experiment has been done as follows:

Step 1: A few drops of blue water soluble fountain pen ink (impurity) have been mixed in half a cup of water (Figure 6.4a).

Step 2: The above suspension was kept in a freezer for four hours to initiate the freezing of water. After four hours of freezing, the above suspension is shown in Figure 6.4b which shows uneven distribution of ink (unlike in the starting as shown in Figure 6.4a) due to partial freezing of water which pushes the ink from the frozen part to the liquid part as the whole cup does not freeze at the same time.

Step 3: After complete freezing of the suspension, the ink gets pushed to a limited part in the cup which is frozen at last (Figure 6.4c).

It clearly shows that when a phase change take place, the impurity (the component in less concentration) gets pushed to the liquid state from the solid state as driven by principles of thermodynamic.

This makes the basis of silicon wafers refinement using float zone technique.

References

- S. B. Anantharaman, C. E. Stevens, J. Lynch, B. Song, J. Hou, H. Zhang, K. Jo, P. Kumar, J.-C. Blancon, A. D. Mohite, J. R. Hendrickson, and D. Jariwala, *Self-Hybridized Polaritonic Emission from Layered Perovskites*, Nano Lett. **21**, 6245 (2021).
- [2] J. W. Jeong, S. R. Yang, Y. H. Hur, S. W. Kim, K. M. Baek, S. Yim, H.-I. Jang, J. H. Park, S. Y. Lee, C.-O. Park, and Y. S. Jung, *High-Resolution Nanotransfer Printing Applicable to Diverse Surfaces via Interface-Targeted Adhesion Switching*, Nat. Commun. 5, 5387 (2014).
- [3] M. Björnmalm, K. J. Thurecht, M. Michael, A. M. Scott, and F. Caruso, *Bridging Bio–Nano Science and Cancer Nanomedicine*, ACS Nano 11, 9594 (2017).
- [4] X. Cai, J. Dong, J. Liu, H. Zheng, C. Kaweeteerawat, F. Wang, Z. Ji, and R. Li, *Multi-Hierarchical Profiling the Structure-Activity Relationships of Engineered Nanomaterials at Nano-Bio Interfaces*, Nat. Commun. 9, 1 (2018).
- [5] R. Lebrun, S. Tsunegi, P. Bortolotti, H. Kubota, A. S. Jenkins, M. Romera, K. Yakushiji, A. Fukushima, J. Grollier, S. Yuasa, and V. Cros, *Mutual Synchronization of Spin Torque Nano-Oscillators through a Long-Range and Tunable Electrical Coupling Scheme*, Nat. Commun. 8, 1 (2017).
- [6] N. J. Halas, Plasmonics Sheds Light on the Nanotechnology of Daguerreotypes, Proc. Natl. Acad. Sci. 116, 13724 (2019).
- [7] Y. Li, F. Qian, J. Xiang, and C. M. Lieber, *Nanowire Electronic and Optoelectronic Devices*, Mater. Today **9**, 18 (2006).
- [8] X. Zhao, C. M. Wei, L. Yang, and M. Y. Chou, *Quantum Confinement and Electronic Properties of Silicon Nanowires*, Phys. Rev. Lett. 92, 236805 (2004).
- [9] A. Gutierrez-Aitken, 5.04 High-Speed InP-Based Heterojunction Bipolar Transistors, in Comprehensive Semiconductor Science and Technology, edited by P. Bhattacharya, R. Fornari, and H. Kamimura (Elsevier, Amsterdam, 2011), pp. 114–175.
- [10] R. P. Feynman, *There's Plenty of Room at the Bottom [Data Storage]*, J. Microelectromechanical Syst. **1**, 60 (1992).
- [11] A. D. Yoffe, Low-Dimensional Systems: Quantum Size Effects and Electronic Properties of Semiconductor Microcrystallites (Zero-Dimensional Systems) and Some Quasi-Two-Dimensional Systems, Adv. Phys. (2006).
- [12] A. Castellanos-Gomez, G. Rubio-Bollinger, S. Barja, M. Garnica, A. L. Vázquez de Parga, R. Miranda, and N. Agraït, *Periodic Spatial Variation of the Electron-Phonon Interaction in Epitaxial Graphene on Ru(0001)*, Appl. Phys. Lett. **102**, 063114 (2013).
- [13] L. Gu, D. J. Hall, Z. Qin, E. Anglin, J. Joo, D. J. Mooney, S. B. Howell, and M. J. Sailor, *In Vivo Time-Gated Fluorescence Imaging with Biodegradable Luminescent Porous Silicon Nanoparticles*, Nat. Commun. 4, 1 (2013).
- [14] K. W. Adu, H. R. Gutiérrez, U. J. Kim, G. U. Sumanasekera,

and P. C. Eklund, *Confined Phonons in Si Nanowires*, Nano Lett. 5, 409 (2005).

- [15] D. L. Ferreira, J. C. L. Sousa, R. N. Maronesi, J. Bettini, M. A. Schiavon, A. V. N. C. Teixeira, and A. G. Silva, *Size-Dependent Bandgap and Particle Size Distribution of Colloidal Semiconductor Nanocrystals*, J. Chem. Phys. **147**, 154102 (2017).
- [16] A. Mittelstädt, A. Schliwa, and P. Klenovský, Modeling Electronic and Optical Properties of III–V Quantum Dots— Selected Recent Developments, Light Sci. Appl. 11, 1 (2022).
- [17] R. Kumar, H. Yan, R. L. McCreery, and A. J. Bergren, *Electron-Beam Evaporated Silicon as a Top Contact for Molecular Electronic Device Fabrication*, Phys Chem Chem Phys **13**, 14318 (2011).
- [18] C. Lin, K. Gong, D. F. Kelley, and A. M. Kelley, *Size-Dependent Exciton–Phonon Coupling in CdSe Nanocrystals through Resonance Raman Excitation Profile Analysis*, J. Phys. Chem. C **119**, 7491 (2015).
- [19] M. Aghajamali, H. Xie, M. Javadi, W. P. Kalisvaart, J. M. Buriak, and J. G. C. Veinot, *Size and Surface Effects of Silicon Nanocrystals in Graphene Aerogel Composite Anodes for Lithium Ion Batteries*, Chem. Mater. **30**, 7782 (2018).
- [20] R. Espiau de Lamaëstre and H. Bernas, Significance of Lognormal Nanocrystal Size Distributions, Phys. Rev. B 73, 125317 (2006).
- [21] G. Ledoux, O. Guillois, D. Porterat, C. Reynaud, F. Huisken, B. Kohn, and V. Paillard, *Photoluminescence Properties of Silicon Nanocrystals as a Function of Their Size*, Phys. Rev. B 62, 15942 (2000).
- [22] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, *Emerging Photoluminescence in Monolayer MoS2*, Nano Lett. **10**, 1271 (2010).
- [23] L. Craco, S. S. Carara, T. A. da Silva Pereira, and M. V. Milošević, *Electronic States in an Atomistic Carbon Quantum Dot Patterned in Graphene*, Phys. Rev. B 93, 155417 (2016).
- [24] S. Pradhan, D. Bhujel, B. Gurung, D. Sharma, S. Basel, S. Rasaily, S. Thapa, S. Borthakur, W. L. Ling, L. Saikia, P. Reiss, A. Pariyar, and S. Tamang, *Stable Lead-Halide Perovskite Quantum Dots as Efficient Visible Light Photocatalysts for Organic Transformations*, Nanoscale Adv. 3, 1464 (2021).
- [25] W. L. Wilson, P. F. Szajowski, and L. E. Brus, *Quantum Confinement in Size-Selected, Surface-Oxidized Silicon Nanocrystals*, Science (1993).
- [26] M. Cardona and F. H. Pollak, *Energy-Band Structure of Germanium and Silicon: The K-p Method*, Phys. Rev. 142, 530 (1966).
- [27] L. T. Canham, Luminescence Bands and Their Proposed Origins In Highly Porous Silicon, Phys. Status Solidi B 190, 9 (1995).
- [28] L. Canham, *Porous Silicon Formation by Porous Silica Reduction*, in *Handbook of Porous Silicon*, edited by L. Canham

(Springer International Publishing, 2014), pp. 1–8.

- [29] A. Uhlir Jr., *Electrolytic Shaping of Germanium and Silicon*, Bell Syst. Tech. J. **35**, 333 (1956).
- [30] P. Borowicz, A. Taube, W. Rzodkiewicz, M. Latek, and S. Gierałtowska, *Raman Spectra of High-κ Dielectric Layers Investigated with Micro-Raman Spectroscopy Comparison with Silicon Dioxide*, Sci. World J. **2013**, e208081 (2013).
- [31] Wiley-VCH Porous Silicon in Practice, https://www.wileyvch.de/en?option=com_eshop&view=product&isbn=97835273137 85&title=Porous%20Silicon%20in%20Practice.
- [32] C. Ulrich, A. Debernardi, E. Anastassakis, K. Syassen, and M. Cardona, *Raman Linewidths of Phonons in Si, Ge, and SiC under Pressure*, Phys. Status Solidi B **211**, 293 (1999).
- [33] R. T. Collins, P. M. Fauchet, and M. A. Tischler, *Porous Silicon: From Luminescence to LEDs*, Phys. Today **50**, 24 (1997).
- [34] L. T. Canham, Silicon Quantum Wire Array Fabrication by Electrochemical and Chemical Dissolution of Wafers, Appl. Phys. Lett. 57, 1046 (1990).
- [35] O. Millo, I. Balberg, D. Azulay, T. K. Purkait, A. K. Swarnakar, E. Rivard, and J. G. C. Veinot, *Direct Evaluation of the Quantum Confinement Effect in Single Isolated Ge Nanocrystals*, J. Phys. Chem. Lett. 6, 3396 (2015).
- [36] R. A. Soref, *Silicon-Based Optoelectronics*, Proc. IEEE **81**, 1687 (1993).
- [37] L. Baraban, B. Ibarlucea, E. Baek, and G. Cuniberti, *Hybrid Silicon Nanowire Devices and Their Functional Diversity*, Adv. Sci. 6, 1900522 (2019).
- [38] G. Brönstrup, N. Jahr, C. Leiterer, A. Csáki, W. Fritzsche, and S. Christiansen, *Optical Properties of Individual Silicon Nanowires for Photonic Devices*, ACS Nano 4, 7113 (2010).
- [39] D. Xia, D. Li, Z. Ku, Y. Luo, and S. R. J. Brueck, *Top-Down Approaches to the Formation of Silica Nanoparticle Patterns*, Langmuir **23**, 5377 (2007).
- [40] F. Dai, J. Zai, R. Yi, M. L. Gordin, H. Sohn, S. Chen, and D. Wang, Bottom-up Synthesis of High Surface Area Mesoporous Crystalline Silicon and Evaluation of Its Hydrogen Evolution Performance, Nat. Commun. 5, 1 (2014).
- [41] Y. Qi, Z. Wang, M. Zhang, F. Yang, and X. Wang, A Processing Window for Fabricating Heavily Doped Silicon Nanowires by Metal-Assisted Chemical Etching, J. Phys. Chem. C 117, 25090 (2013).
- [42] Z. Huang, N. Geyer, P. Werner, J. de Boor, and U. Gösele, Metal-Assisted Chemical Etching of Silicon: A Review, Adv. Mater. 23, 285 (2011).
- [43] S. Acharya and A. Kottantharayil, VLS Growth of Silicon Nanowires in Cold Wall Cat-CVD Chamber, in 2014 IEEE 2nd International Conference on Emerging Electronics (ICEE) (2014), pp. 1–4.
- [44] C. Celle, C. Mouchet, E. Rouvière, J.-P. Simonato, D. Mariolle, N. Chevalier, and A. Brioude, *Controlled in Situ N-Doping of*

Silicon Nanowires during VLS Growth and Their Characterization by Scanning Spreading Resistance Microscopy, J. Phys. Chem. C 114, 760 (2010).

- [45] H. S. Mavi, A. K. Shukla, R. Kumar, S. Rath, B. Joshi, and S. S. Islam, *Quantum Confinement Effects in Silicon Nanocrystals Produced by Laser-Induced Etching and Cw Laser Annealing*, Semicond. Sci. Technol. 21, 1627 (2006).
- [46] N. Fukata, T. Oshima, N. Okada, S. Matsushita, T. Tsurui, J. Chen, T. Sekiguchi, and K. Murakami, *Phonon Confinement and Impurity Doping in Silicon Nanowires Synthesized by Laser Ablation*, https://doi.org/10.4028/www.scientific.net/SSP.131-133.553.
- [47] W. H. Butler and R. K. Williams, *Electron-Phonon Interaction and Lattice Thermal Conductivity*, Phys. Rev. B **18**, 6483 (1978).
- [48] B. M. Bang, H. Kim, H.-K. Song, J. Cho, and S. Park, *Scalable Approach to Multi-Dimensional Bulk Si Anodes via Metal-Assisted Chemical Etching*, Energy Environ. Sci. **4**, 5013 (2011).
- [49] P. H. Morel, G. Haberfehlner, D. Lafond, G. Audoit, V. Jousseaume, C. Leroux, M. Fayolle-Lecocq, T. Baron, and T. Ernst, *Ultra High Density Three Dimensional Capacitors Based on Si Nanowires Array* Grown on a Metal Layer, Appl. Phys. Lett. **101**, 083110 (2012).
- [50] S. Wippermann, Y. He, M. Vörös, and G. Galli, Novel Silicon Phases and Nanostructures for Solar Energy Conversion, Appl. Phys. Rev. 3, 040807 (2016).
- [51] V. S.-Y. Lin, K. Motesharei, K.-P. S. Dancil, M. J. Sailor, and M. R. Ghadiri, *A Porous Silicon-Based Optical Interferometric Biosensor*, Science 278, 840 (1997).
- [52] K.-I. Chen, B.-R. Li, and Y.-T. Chen, *Silicon Nanowire Field-Effect Transistor-Based Biosensors for Biomedical Diagnosis and Cellular Recording Investigation*, Nano Today **6**, 131 (2011).
- [53] G. Korotcenkov and B. K. Cho, *Porous Semiconductors: Advanced Material for Gas Sensor Applications*, Crit. Rev. Solid State Mater. Sci. 35, 1 (2010).
- [54] J. P. Proot, C. Delerue, and G. Allan, *Electronic Structure and Optical Properties of Silicon Crystallites: Application to Porous Silicon*, Appl. Phys. Lett. **61**, 1948 (1992).
- [55] R. Ganatra and Q. Zhang, *Few-Layer MoS2: A Promising Layered Semiconductor*, ACS Nano **8**, 4074 (2014).
- [56] C. V. Raman and K. S. Krishnan, *A New Type of Secondary Radiation*, Nature **121**, 501 (1928).
- [57] C. V. Raman, A New Radiation, Indian J. Phys. 2, 387 (1928).
- [58] J. Penders, A. Nagelkerke, E. M. Cunnane, S. V. Pedersen, I. J. Pence, R. C. Coombes, and M. M. Stevens, *Single Particle Automated Raman Trapping Analysis of Breast Cancer Cell-Derived Extracellular Vesicles as Cancer Biomarkers*, ACS Nano 15, 18192 (2021).
- [59] K. Neeshu, C. Rani, R. Kaushik, M. Tanwar, D. Pathak, A. Chaudhary, A. Kumar, and R. Kumar, *Size Dependence of Raman Line-Shape Parameters Due to Confined Phonons in Silicon*

Nanowires, Adv. Mater. Process. Technol. 6, 669 (2020).

- [60] Y. Chen, B. Peng, and B. Wang, Raman Spectra and Temperature-Dependent Raman Scattering of Silicon Nanowires, J. Phys. Chem. C 111, 5855 (2007).
- [61] E. G. Barbagiovanni, D. J. Lockwood, P. J. Simpson, and L. V. Goncharova, *Quantum Confinement in Si and Ge Nanostructures*, J. Appl. Phys. **111**, 034307 (2012).
- [62] H. Richter, Z. P. Wang, and L. Ley, *The One Phonon Raman Spectrum in Microcrystalline Silicon*, Solid State Commun. **39**, 625 (1981).
- [63] P. Alfaro, R. Cisneros, M. Bizarro, M. Cruz-Irisson, and C. Wang, *Raman Scattering by Confined Optical Phonons in Si and Ge Nanostructures*, Nanoscale 3, 1246 (2011).
- [64] M. Jouanne, R. Beserman, I. Ipatova, and A. Subashiev, *Electron-Phonon Coupling in Highly Doped n Type Silicon*, Solid State Commun. 16, 1047 (1975).
- [65] M. Balkanski, K. P. Jain, R. Beserman, and M. Jouanne, *Theory* of Interference Distortion of Raman Scattering Line Shapes in Semiconductors, Phys. Rev. B **12**, 4328 (1975).
- [66] D. Abidi, B. Jusserand, and J.-L. Fave, Raman Scattering Studies of Heavily Doped Microcrystalline Porous Silicon and Porous Silicon Free-Standing Membranes, Phys. Rev. B 82, 075210 (2010).
- [67] F. Cerdeira, T. A. Fjeldly, and M. Cardona, *Effect of Free Carriers on Zone-Center Vibrational Modes in Heavily Doped p-Type Si. II. Optical Modes*, Phys. Rev. B 8, 4734 (1973).
- [68] S. K. Saxena, P. Yogi, S. Mishra, H. M. Rai, V. Mishra, M. K. Warshi, S. Roy, P. Mondal, P. R. Sagdeo, and R. Kumar, *Amplification or Cancellation of Fano Resonance and Quantum Confinement Induced Asymmetries in Raman Line-Shapes*, Phys. Chem. Chem. Phys. **19**, 31788 (2017).
- [69] J. Faist, F. Capasso, C. Sirtori, K. W. West, and L. N. Pfeiffer, *Controlling the Sign of Quantum Interference by Tunnelling from Quantum Wells*, Nature **390**, 589 (1997).
- [70] G. Faraci, S. Gibilisco, P. Russo, A. R. Pennisi, and S. La Rosa, Modified Raman Confinement Model for Si Nanocrystals, Phys. Rev. B 73, 033307 (2006).
- [71] B. P. Falcão, J. P. Leitão, H. Águas, and R. N. Pereira, *Raman* Spectrum of Nanocrystals: Phonon Dispersion Splitting and Anisotropy, Phys. Rev. B **98**, 195406 (2018).
- [72] 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 Commun. **58**, 739 (1986).
- [73] S. Bar-Ad, P. Kner, M. V. Marquezini, S. Mukamel, and D. S. Chemla, *Quantum Confined Fano Interference*, Phys. Rev. Lett. 78, 1363 (1997).
- [74] A. E. Miroshnichenko, S. Flach, and Y. S. Kivshar, *Fano Resonances in Nanoscale Structures*, Rev. Mod. Phys. 82, 2257 (2010).
- [75] E. Janzén, G. Grossmann, R. Stedman, and H. G. Grimmeiss,

Fano Resonances in Chalcogen-Doped Silicon, Phys. Rev. B **31**, 8000 (1985).

- [76] Y. S. Joe, A. M. Satanin, and C. S. Kim, *Classical Analogy of Fano Resonances*, Phys. Scr. **74**, 259 (2006).
- [77] U. Fano, *Effects of Configuration Interaction on Intensities and Phase Shifts*, Phys. Rev. **124**, 1866 (1961).
- [78] R. Gajić, D. Braun, F. Kuchar, A. Golubović, R. Korntner, H. Löschner, J. Butschke, R. Springer, and F. Letzkus, *Boron-Content Dependence of Fano Resonances in p-Type Silicon*, J. Phys. Condens. Matter 15, 2923 (2003).
- [79] V. Magidson and R. Beserman, *Fano-Type Interference in the Raman Spectrum of Photoexcited Si*, Phys. Rev. B 66, 195206 (2002).
- [80] S. K. Saxena, R. Borah, V. Kumar, H. M. Rai, R. Late, V. g. Sathe, A. Kumar, P. R. Sagdeo, and R. Kumar, *Raman* Spectroscopy for Study of Interplay between Phonon Confinement and Fano Effect in Silicon Nanowires, J. Raman Spectrosc. 47, 283 (2016).
- [81] P. Yogi, D. Poonia, S. Mishra, S. K. Saxena, S. Roy, V. Kumar, P. R. Sagdeo, and R. Kumar, *Spectral Anomaly in Raman Scattering from P-Type Silicon Nanowires*, J. Phys. Chem. C 121, 5372 (2017).
- [82] X. Yin, Z. Ye, D. A. Chenet, Y. Ye, K. O'Brien, J. C. Hone, and X. Zhang, *Edge Nonlinear Optics on a MoS2 Atomic Monolayer*, Science **344**, 488 (2014).
- [83] H. Yorikawa, H. Uchida, and S. Muramatsu, *Energy Gap of Nanoscale Si Rods*, J. Appl. Phys. **79**, 3619 (1996).
- [84] N. Fukata, W. Jevasuwan, Y. Ikemoto, and T. Moriwaki, Bonding and Electronic States of Boron in Silicon Nanowires Characterized by an Infrared Synchrotron Radiation Beam, Nanoscale 7, 7246 (2015).
- [85] N. Fukata, *Impurity Doping in Silicon Nanowires*, Adv. Mater. 21, 2829 (2009).
- [86] N. Fukata, M. Mitome, Y. Bando, M. Seoka, S. Matsushita, K. Murakami, J. Chen, and T. Sekiguchi, *Codoping of Boron and Phosphorus in Silicon Nanowires Synthesized by Laser Ablation*, Appl. Phys. Lett. **93**, 203106 (2008).
- [87] N. Fukata, K. Sato, M. Mitome, Y. Bando, T. Sekiguchi, M. Kirkham, J. Hong, Z. L. Wang, and R. L. Snyder, *Doping and Raman Characterization of Boron and Phosphorus Atoms in Germanium Nanowires*, ACS Nano 4, 3807 (2010).
- [88] S. Luo, W. B. Yu, Y. He, and G. Ouyang, Size-Dependent Optical Absorption Modulation of Si/Ge and Ge/Si Core/Shell Nanowires with Different Cross-Sectional Geometries, Nanotechnology 26, 085702 (2015).
- [89] K. P. Jain, A. K. Shukla, S. C. Abbi, and M. Balkanski, *Raman Scattering in Ultraheavily Doped Silicon*, Phys. Rev. B 32, 5464 (1985).
- [90] M. L. Schultz, Silicon: Semiconductor Properties, Infrared Phys. 4, 93 (1964).

- [91] E. Burstein, E. E. Bell, J. W. Davisson, and M. Lax, *Optical Investigations of Impurity Levels in Silicon*, J. Phys. Chem. 57, 849 (1953).
- [92] Kittel, *INTRODUCTION TO SOLID STATE PHYSICS, 7TH ED* (John Wiley & Sons, 2007).
- [93] S. Wei and M. Y. Chou, *Phonon Dispersions of Silicon and Germanium from First-Principles Calculations*, Phys. Rev. B **50**, 2221 (1994).
- [94] R. Tubino, L. Piseri, and G. Zerbi, Lattice Dynamics and Spectroscopic Properties by a Valence Force Potential of Diamondlike Crystals: C, Si, Ge, and Sn, J. Chem. Phys. 56, 1022 (1972).
- [95] V. Yu. Davydov, A. A. Klochikhin, A. N. Smirnov, I. Yu. Strashkova, A. S. Krylov, H. Lu, W. J. Schaff, H.-M. Lee, Y.-L. Hong, and S. Gwo, Selective Excitation of \${E}_{1}(\text{LO})\$ and \${A}_{1}(\text{LO})\$ Phonons with Large Wave Vectors in the Raman Spectra of Hexagonal InN, Phys. Rev. B 80, 081204 (2009).
- [96] S. Wei and M. Y. Chou, Phonon Dispersions of Silicon and Germanium from First-Principles Calculations, Phys. Rev. B 50, 2221 (1994).
- [97] A. Marcus, *Gallium Arsenide Band Structure Calculation*, Phys. Rev. **135**, A527 (1964).
- [98] L. C. O. Dacal and A. Cantarero, Ab Initiocalculations of Indium Arsenide in the Wurtzite Phase: Structural, Electronic and Optical Properties, Mater. Res. Express 1, 015702 (2014).
- [99] A. M. Fox, *Optical Properties of Solids* (Oxford University Press, 2001).
- [100] S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (John Wiley & Sons, 2006).
- [101] A. Kole and P. Chaudhuri, *Growth of Silicon Quantum Dots by* Oxidation of the Silicon Nanocrystals Embedded within Silicon Carbide Matrix, AIP Adv. **4**, 107106 (2014).
- [102] S. Lu, B. Wu, Y. Sun, Y. Cheng, F. Liao, and M. Shao, *Photoluminescence of Pure Silicon Quantum Dots Embedded in an Amorphous Silica Wire Array*, J. Mater. Chem. C 5, 6713 (2017).
- [103] N. S. Mohammad, Understanding Quantum Confinement in Nanowires: Basics, Applications and Possible Laws, J. Phys. Condens. Matter 26, 423202 (2014).
- [104] N.-M. Park, C.-J. Choi, T.-Y. Seong, and S.-J. Park, *Quantum Confinement in Amorphous Silicon Quantum Dots Embedded in Silicon Nitride*, Phys. Rev. Lett. **86**, 1355 (2001).
- [105] H. Yorikawa and S. Muramatsu, Logarithmic Normal Distribution of Particle Size from a Luminescence Line-Shape Analysis in Porous Silicon, Appl. Phys. Lett. 71, 644 (1997).
- [106] A. P. Alivisatos, *Perspectives on the Physical Chemistry of Semiconductor Nanocrystals*, J. Phys. Chem. **100**, 13226 (1996).
- [107] Y. Zhu and J. Appenzeller, On the Current Drive Capability of Low Dimensional Semiconductors: 1D versus 2D, Nanoscale Res. Lett. 10, (2015).

- [108] H. (何海平) He, C. (刘超) Liu, L. (孙陆威) Sun, and Z. (叶志镇) Ye, Temperature-Dependent Photoluminescence Properties of Porous Silicon Nanowire Arrays, Appl. Phys. Lett. 99, 123106 (2011).
- [109] L. Z. Zhang, H. Z. Song, B. R. Zhang, Z. H. Xu, and G. G. Qin, Evolution of Photoluminescence in Laser Illuminating Porous Silicon, Mater. Res. Bull. 29, 603 (1994).
- [110] J. M. Perez, J. Villalobos, P. McNeill, J. Prasad, R. Cheek, J. Kelber, J. P. Estrera, P. D. Stevens, and R. Glosser, *Direct Evidence for the Amorphous Silicon Phase in Visible Photoluminescent Porous Silicon*, Appl. Phys. Lett. **61**, 563 (1992).
- [111] H. Tsuchiya and Y. Kamakura, *First-Principles Calculations* for Si Nanostructures, in Carrier Transport in Nanoscale MOS *Transistors* (IEEE, 2016), pp. 12–40.
- [112] S. Chattopadhyay, X. Li, and P. W. Bohn, *In-Plane Control of Morphology and Tunable Photoluminescence in Porous Silicon Produced by Metal-Assisted Electroless Chemical Etching*, J. Appl. Phys. **91**, 6134 (2002).
- [113] A. J. Read, R. J. Needs, K. J. Nash, L. T. Canham, P. D. J. Calcott, and A. Qteish, *First-Principles Calculations of the Electronic Properties of Silicon Quantum Wires*, Phys. Rev. Lett. 69, 1232 (1992).
- [114] T. Ito, T. O. T. Ohta, and A. H. A. Hiraki, *Light Emission from Microcrystalline Si Confined in SiO2 Matrix through Partial Oxidation of Anodized Porous Silicon*, Jpn. J. Appl. Phys. **31**, L1 (1992).
- [115] W. Ding, J. Zheng, W. Qi, W. Yu, and G. Fu, Dependence of the Photoluminescence from Silicon Nanostructures on the Size of Silicon Nanoparticles, in Vol. 7135 (2008), pp. 713508-713508–9.
- [116] O. Demichel, V. Calvo, P. Noé, B. Salem, P.-F. Fazzini, N. Pauc, F. Oehler, P. Gentile, and N. Magnea, *Quantum Confinement Effects and Strain-Induced Band-Gap Energy Shifts in Core-Shell Si-SiO\${}_{2}\$ Nanowires*, Phys. Rev. B 83, 245443 (2011).
- [117] M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, *Electronic States and Luminescence in Porous Silicon Quantum Dots: The Role of Oxygen*, Phys. Rev. Lett. 82, 197 (1999).
- [118] T. Suemoto, K. Tanaka, A. Nakajima, and T. Itakura, Observation of Phonon Structures in Porous Si Luminescence, Phys. Rev. Lett. 70, 3659 (1993).
- [119] R. Loudon, *Theory of the First-Order Raman Effect in Crystals*, Proc R Soc Lond A 275, 218 (1963).
- [120] R. Loudon, *The Raman Effect in Crystals*, Adv. Phys. **13**, 423 (1964).
- [121] Dynamical Theory of Crystal Lattices by M. Born and K. Huang, Acta Crystallogr. 8, 444 (1955).
- [122] M. V. Klein, *Electronic Raman Scattering*, in *Light Scattering in Solids*, edited by M. Cardona (Springer, Berlin, Heidelberg, 1975), pp. 147–204.
- [123] M. Cardona, *Introduction*, in *Light Scattering in Solids*, edited by M. Cardona (Springer, Berlin, Heidelberg, 1975), pp. 1–22.

- [124] P. A. Temple and C. E. Hathaway, *Multiphonon Raman* Spectrum of Silicon, Phys. Rev. B **7**, 3685 (1973).
- [125] H. Weller, Quantum Size Colloids: From Size-Dependent Properties of Discrete Particles to Self-Organized Superstructures, Curr. Opin. Colloid Interface Sci. 3, 194 (1998).
- [126] V. H. Grassian, Size-Dependent Properties and Surface Chemistry of Oxide-Based Nanomaterials in Environmental Processes, in Nanoscale Materials in Chemistry: Environmental Applications, Vol. 1045 (American Chemical Society, 2010), pp. 15–33.
- [127] M. L. Brongersma, P. G. Kik, A. Polman, K. S. Min, and H. A. Atwater, *Size-Dependent Electron-Hole Exchange Interaction in Si Nanocrystals*, Appl. Phys. Lett. **76**, 351 (2000).
- [128] G. Faraci, S. Gibilisco, P. Russo, A. R. Pennisi, and S. La Rosa, *Modified Raman Confinement Model for Si Nanocrystals*, Phys. Rev. B 73, 033307 (2006).
- [129] K. W. Adu, H. R. Gutierrez, and P. C. Eklund, *Raman-Active Phonon Line Profiles in Semiconducting Nanowires*, Vib. Spectrosc. 42, 165 (2006).
- [130] A. K. Shukla and K. P. Jain, *Raman Scattering from Ultraheavily-Ion-Implanted and Laser-Annealed Silicon*, Phys. Rev. B 34, 8950 (1986).
- [131] M. Chandrasekhar, J. B. Renucci, and M. Cardona, *Effects of Interband Excitations on Raman Phonons in Heavily Doped \$n-\mathrm{Si}\$*, Phys. Rev. B **17**, 1623 (1978).
- [132] E. Burstein, D. L. Mills, and R. F. Wallis, *Interband Electronic Raman Scattering in Semimetals and Semiconductors*, Phys. Rev. B 4, 2429 (1971).
- [133] S. K. Saxena, P. Yogi, S. Mishra, H. Mohan Rai, V. Mishra, M. Kamal Warshi, S. Roy, P. Mondal, P. R. Sagdeo, and R. Kumar, *Amplification or Cancellation of Fano Resonance and Quantum Confinement Induced Asymmetries in Raman Line-Shapes*, Phys. Chem. Chem. Phys. **19**, 31788 (2017).
- [134] K. W. Adu, Q. Xiong, H. R. Gutierrez, G. Chen, and P. C. Eklund, *Raman Scattering as a Probe of Phonon Confinement and Surface Optical Modes in Semiconducting Nanowires*, Appl. Phys. A 85, 287 (2006).
- [135] B. Li, D. Yu, and S.-L. Zhang, *Raman Spectral Study of Silicon Nanowires*, Phys. Rev. B 59, 1645 (1999).
- [136] 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 Commun. **58**, 739 (1986).
- [137] R. Kumar, G. Sahu, S. K. Saxena, H. M. Rai, and P. R. Sagdeo, *Qualitative Evolution of Asymmetric Raman Line-Shape for NanoStructures*, Silicon 6, 117 (2014).
- [138] J. Zi, K. Zhang, and X. Xie, *Comparison of Models for Raman* Spectra of Si Nanocrystals, Phys. Rev. B 55, 9263 (1997).
- [139] K. W. Adu, H. R. Gutierrez, and P. C. Eklund, *Raman-Active Phonon Line Profiles in Semiconducting Nanowires*, Vib. Spectrosc. 42, 165 (2006).

- [140] R. Gupta, K. P. Jain, S. C. Abbi, and M. Balkanski, *Alloy Contribution to Phonon Softening in Ultra-Heavily Doped Si:As*, Solid State Commun. 55, 285 (1985).
- [141] J. Zi, H. Büscher, C. Falter, W. Ludwig, K. Zhang, and X. Xie, *Raman Shifts in Si Nanocrystals*, Appl. Phys. Lett. 69, 200 (1996).
- [142] F. J. Bartoli and T. A. Litovitz, Analysis of Orientational Broadening of Raman Line Shapes, J. Chem. Phys. 56, 404 (1972).
- [143] M. P. Chamberlain, C. Trallero-Giner, and M. Cardona, *Theory of One-Phonon Raman Scattering in Semiconductor Microcrystallites*, Phys. Rev. B **51**, 1680 (1995).
- [144] C. Trallero-Giner, A. Debernardi, M. Cardona, E. Menéndez-Proupín, and A. I. Ekimov, *Optical Vibrons in CdSe Dots and Dispersion Relation of the Bulk Material*, Phys. Rev. B 57, 4664 (1998).
- [145] M. I. Vasilevskiy, A. G. Rolo, and M. J. M. Gomes, One-Phonon Raman Scattering from Arrays of Semiconductor Nano-Crystals, Solid State Commun. 104, 381 (1997).
- [146] R. Kumar and A. K. Shukla, *Quantum Interference in the Raman Scattering from the Silicon Nanostructures*, Phys. Lett. A 373, 2882 (2009).
- [147] T. Lopez and L. Mangolini, Low Activation Energy for the Crystallization of Amorphous Silicon Nanoparticles, Nanoscale 6, 1286 (2014).
- [148] R. Al-Salman, J. Mallet, M. Molinari, P. Fricoteaux, F. Martineau, M. Troyon, S. Z. E. Abedin, and F. Endres, *Template Assisted Electrodeposition of Germanium and Silicon Nanowires in an Ionic Liquid*, Phys. Chem. Chem. Phys. **10**, 6233 (2008).
- [149] K. W. Adu, H. R. Gutiérrez, U. J. Kim, and P. C. Eklund, Inhomogeneous Laser Heating and Phonon Confinement in Silicon Nanowires: A Micro-Raman Scattering Study, Phys. Rev. B 73, (2006).
- [150] P. Yogi, S. K. Saxena, S. Mishra, H. M. Rai, R. Late, V. Kumar, B. Joshi, P. R. Sagdeo, and R. Kumar, *Interplay between Phonon Confinement and Fano Effect on Raman Line Shape for Semiconductor Nanostructures: Analytical Study*, Solid State Commun. 230, 25 (2016).
- [151] C. Gérard, A. Martinez, and D. Robert, *Breit-Wigner Formulas* for the Scattering Phase and the Total Scattering Cross-Section in the Semi-Classical Limit, Commun. Math. Phys. **121**, 323 (1989).
- [152] U. Fano, *Effects of Configuration Interaction on Intensities and Phase Shifts*, Phys. Rev. **124**, 1866 (1961).
- [153] S.-J. Xiong and Y. Yin, Asymmetric Line Shape and Fano Interference in the Transport of Electrons through a Multilevel Quantum Dot in the Coulomb Blockade Regime, Phys. Rev. B 66, 153315 (2002).
- [154] M. Kroner, A. O. Govorov, S. Remi, B. Biedermann, S. Seidl, A. Badolato, P. M. Petroff, W. Zhang, R. Barbour, B. D. Gerardot, R. J. Warburton, and K. Karrai, *The Nonlinear Fano Effect*, Nature 451, 311 (2008).
- [155] L. E. Calvet, J. P. Snyder, and W. Wernsdorfer, Fano Resonance

in Electron Transport through Single Dopant Atoms, Phys. Rev. B **83**, 205415 (2011).

- [156] D. M. Cardamone, C. A. Stafford, and S. Mazumdar, *Controlling Quantum Transport through a Single Molecule*, Nano Lett. 6, 2422 (2006).
- [157] J. R. Lombardi and R. L. Birke, *The Theory of Surface-Enhanced Raman Scattering*, J. Chem. Phys. **136**, 144704 (2012).
- [158] Y. G. Wang, S. P. Lau, B. K. Tay, and X. H. Zhang, *Resonant Raman Scattering Studies of Fano-Type Interference in Boron Doped Diamond*, J. Appl. Phys. **92**, 7253 (2002).
- [159] K. Jin and S. J. Xu, Fano Resonance in the Luminescence Spectra of Donor Bound Excitons in Polar Semiconductors, Appl. Phys. Lett. 90, 032107 (2007).
- [160] D. Pröpper, A. N. Yaresko, T. I. Larkin, T. N. Stanislavchuk, A. A. Sirenko, T. Takayama, A. Matsumoto, H. Takagi, B. Keimer, and A. V. Boris, *Fano Resonances in the Infrared Spectra of Phonons in Hyperkagome* \$\{\mathrm{D}\]_{3}\{\mathrm{Ir}\}_{3}\{\mathrm{O}\}_{8}\\$, Phys.

Rev. Lett. 112, 087401 (2014).

- [161] J. Humlíček, Ellipsometric Study of Fano Resonance in Heavily Doped P-Type Si and SiGe Alloys, Thin Solid Films 313–314, 656 (1998).
- [162] V. A. Volodin and M. D. Efremov, *Electron-Phonon Interaction in Boron-Doped Silicon Nanocrystals: Effect of Fano Interference on the Raman Spectrum*, J. Exp. Theor. Phys. Lett. 82, 86 (2005).
- [163] B. G. Burke, J. Chan, K. A. Williams, Z. Wu, A. A. Puretzky, and D. B. Geohegan, *Raman Study of Fano Interference in P-Type Doped Silicon*, J. Raman Spectrosc. **41**, 1759 (2010).
- [164] R. Kumar, H. S. Mavi, A. K. Shukla, and V. D. Vankar, *Photoexcited Fano Interaction in Laser-Etched Silicon Nanostructures*, J. Appl. Phys. **101**, 064315 (2007).
- [165] R. Gupta, Q. Xiong, C. K. Adu, U. J. Kim, and P. C. Eklund, *Laser-Induced Fano Resonance Scattering in Silicon Nanowires*, Nano Lett 3, 627 (2003).
- [166] 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, *Porosity Control in Metal-Assisted Chemical Etching of Degenerately Doped Silicon Nanowires*, Nanotechnology 23, 305304 (2012).
- [167] K. Peng, X. Wang, and S.-T. Lee, *Silicon Nanowire Array Photoelectrochemical Solar Cells*, Appl. Phys. Lett. **92**, 163103 (2008).
- [168] J. Gonzalez-Hernandez, G. H. Azarbayejani, R. Tsu, and F. H. Pollak, *Raman, Transmission Electron Microscopy, and Conductivity Measurements in Molecular Beam Deposited Microcrystalline Si and Ge: A Comparative Study*, Appl. Phys. Lett. 47, 1350 (1985).
- [169] N. Hondow, R. Brydson, and A. Brown, *The Use of Transmission Electron Microscopy in the Quantification of Nanoparticle Dose*, J. Phys. Conf. Ser. **522**, 012055 (2014).

- [170] C. V. Raman, A New Radiation [Reproduced from Indian J. Phys., 1928, 2, 387–398], Curr. Sci. 74, 382 (1998).
- [171] V. J. Cadarso, N. Chidambaram, L. Jacot-Descombes, and H. Schift, *High-Aspect-Ratio Nanoimprint Process Chains*, Microsyst. Nanoeng. **3**, 17017 (2017).
- [172] P. Yogi, D. Poonia, S. Mishra, S. K. Saxena, S. Roy, V. Kumar, P. R. Sagdeo, and R. Kumar, *Spectral Anomaly in Raman Scattering from P-Type Silicon Nanowires*, J. Phys. Chem. C 121, 5372 (2017).
- [173] P. Yogi, S. K. Saxena, A. Chaudhary, D. K. Pathak, S. Mishra, P. Mondal, B. Joshi, P. R. Sagdeo, and R. Kumar, *Porous Silicon's Fractal Nature Revisited*, Superlattices Microstruct. **120**, 141 (2018).
- [174] P. Kubelka, New Contributions to the Optics of Intensely Light-Scattering Materials. Part I, JOSA **38**, 448 (1948).
- [175] V. Mishra, A. Sagdeo, V. Kumar, M. K. Warshi, H. M. Rai, S. K. Saxena, D. R. Roy, V. Mishra, R. Kumar, and P. R. Sagdeo, *Electronic and Optical Properties of BaTiO3 across Tetragonal to Cubic Phase Transition: An Experimental and Theoretical Investigation*, J. Appl. Phys. **122**, 065105 (2017).
- [176] J. H. Nobbs, *Kubelka—Munk Theory and the Prediction of Reflectance*, Rev. Prog. Color. Relat. Top. **15**, 66 (1985).
- [177] A. P. Bonifas and R. L. McCreery, Solid State Spectroelectrochemistry of Redox Reactions in Polypyrrole/Oxide Molecular Heterojunctions, Anal Chem 84, 2459 (2012).
- [178] M. Abouda-Lachiheb, N. Nafie, and M. Bouaicha, *The Dual Role of Silver during Silicon Etching in HF Solution*, Nanoscale Res. Lett. 7, 455 (2012).
- [179] S. K. Saxena, P. Yogi, P. Yadav, S. Mishra, H. Pandey, H. M. Rai, V. Kumar, P. R. Sagdeo, and R. Kumar, *Role of Metal Nanoparticles on Porosification of Silicon by Metal Induced Etching (MIE)*, Superlattices Microstruct. **94**, 101 (2016).
- [180] Y. Qi, Z. Wang, M. Zhang, F. Yang, and X. Wang, A Processing Window for Fabricating Heavily Doped Silicon Nanowires by Metal-Assisted Chemical Etching, J. Phys. Chem. C 117, 25090 (2013).
- [181] V. Lehmann and H. Föll, Formation Mechanism and Properties of Electrochemically Etched Trenches in N-Type Silicon, J. Electrochem. Soc. 137, 653 (1990).
- [182] X. Li and P. W. Bohn, Metal-Assisted Chemical Etching in HF/H2O2 Produces Porous Silicon, Appl. Phys. Lett. 77, 2572 (2000).
- [183] M. Tanwar, D. K. Pathak, A. Chaudhary, P. Yogi, S. K. Saxena, and R. Kumar, *Mapping Longitudinal Inhomogeneity in Nanostructures Using Cross-Sectional Spatial Raman Imaging*, J. Phys. Chem. C **124**, 6467 (2020).
- [184] P. Yogi, M. Tanwar, S. K. Saxena, S. Mishra, D. K. Pathak, A. Chaudhary, P. R. Sagdeo, and R. Kumar, *Quantifying the Short-Range Order in Amorphous Silicon by Raman Scattering*, Anal. Chem. 90, 8123 (2018).

- [185] P. Yogi, S. Mishra, S. K. Saxena, V. Kumar, and R. Kumar, Fano Scattering: Manifestation of Acoustic Phonons at the Nanoscale, J. Phys. Chem. Lett. 7, 5291 (2016).
- [186] C. M. Hessel, J. Wei, D. Reid, H. Fujii, M. C. Downer, and B. A. Korgel, *Raman Spectroscopy of Oxide-Embedded and Ligand-Stabilized Silicon Nanocrystals*, J. Phys. Chem. Lett. **3**, 1089 (2012).
- [187] Z. Huang, X. Zhang, M. Reiche, L. Liu, W. Lee, T. Shimizu, S. Senz, and U. Gösele, *Extended Arrays of Vertically Aligned Sub-10 Nm Diameter [100] Si Nanowires by Metal-Assisted Chemical Etching*, Nano Lett. 8, 3046 (2008).
- [188] M. Tanwar, A. Chaudhary, D. K. Pathak, P. Yogi, S. K. Saxena, P. R. Sagdeo, and R. Kumar, *Deconvoluting Diffuse Reflectance Spectra for Retrieving Nanostructures' Size Details: An Easy and Efficient Approach*, J. Phys. Chem. A **123**, 3607 (2019).
- [189] P. Yogi, S. K. Saxena, A. Chaudhary, D. K. Pathak, S. Mishra, P. Mondal, B. Joshi, P. R. Sagdeo, and R. Kumar, *Porous Silicon's Fractal Nature Revisited*, Superlattices Microstruct. **120**, 141 (2018).
- [190] P. Yogi, D. Poonia, P. Yadav, S. Mishra, S. K. Saxena, S. Roy, P. R. Sagdeo, and R. Kumar, *Tent-Shaped Surface Morphologies of Silicon: Texturization by Metal Induced Etching*, Silicon 10, 2801 (2018).
- [191] S. K. Saxena, P. Yogi, S. Mishra, H. M. Rai, V. Mishra, M. K. Warshi, S. Roy, P. Mondal, P. R. Sagdeo, and R. Kumar, *Amplification or Cancellation of Fano Resonance and Quantum Confinement Induced Asymmetries in Raman Line-Shapes*, Phys. Chem. Chem. Phys. **19**, 31788 (2017).
- [192] H. Richter, Z. P. Wang, and L. Ley, *The One Phonon Raman Spectrum in Microcrystalline Silicon*, Solid State Commun. **39**, 625 (1981).
- [193] U. Fano, *Effects of Configuration Interaction on Intensities and Phase Shifts*, Phys. Rev. **124**, 1866 (1961).
- [194] F. Cerdeira and M. Cardona, *Effect of Carrier Concentration on the Raman Frequencies of Si and Ge*, Phys. Rev. B **5**, 1440 (1972).
- [195] H. S. Mavi, A. K. Shukla, R. Kumar, S. Rath, B. Joshi, and S. S. Islam, *Quantum Confinement Effects in Silicon Nanocrystals Produced by Laser-Induced Etching and Cw Laser Annealing*, Semicond. Sci. Technol. **21**, 1627 (2006).
- [196] S. M. Sze, Physics of Semiconductor Devices, 3rd Edition / Wiley, https://www.wiley.com/enus/Physics+of+Semiconductor+Devices%2C+3rd+Edition-p-9780471143239.
- [197] F. Cerdeira, T. A. Fjeldly, and M. Cardona, *Raman Study of the Interaction between Localized Vibrations and Electronic Excitations in Boron-Doped Silicon*, Phys. Rev. B 9, 4344 (1974).
- [198] N. Fukata, K. Sato, M. Mitome, Y. Bando, T. Sekiguchi, M. Kirkham, J. Hong, Z. L. Wang, and R. L. Snyder, *Doping and Raman Characterization of Boron and Phosphorus Atoms in Germanium Nanowires*, ACS Nano 4, 3807 (2010).

- [199] N. Fukata, W. Jevasuwan, Y. Ikemoto, and T. Moriwaki, Bonding and Electronic States of Boron in Silicon Nanowires Characterized by an Infrared Synchrotron Radiation Beam, Nanoscale 7, 7246 (2015).
- [200] S. K. Saxena, G. Sahu, V. Kumar, P. K. Sahoo, P. R. Sagdeo, and R. Kumar, *Effect of Silicon Resistivity on Its Porosification* Using Metal Induced Chemical Etching: Morphology and Photoluminescence Studies, Mater. Res. Express 2, 036501 (2015).
- [201] G. Korotcenkov and B. K. Cho, *Silicon Porosification: State of the Art*, Crit. Rev. Solid State Mater. Sci. **35**, 153 (2010).
- [202] L. Koker and K. W. Kolasinski, *Photoelectrochemical Etching* of Si and Porous Si in Aqueous HF, Phys. Chem. Chem. Phys. 2, 277 (2000).
- [203] L. Koker and K. W. Kolasinski, Laser-Assisted Formation of Porous Si in Diverse Fluoride Solutions: Reaction Kinetics and Mechanistic Implications, J. Phys. Chem. B 105, 3864 (2001).
- [204] H. Föll, M. Christophersen, J. Carstensen, and G. Hasse, *Formation and Application of Porous Silicon*, Mater. Sci. Eng. R Rep. **39**, 93 (2002).
- [205] S. K. Saxena, P. Yogi, P. Yadav, S. Mishra, H. Pandey, H. M. Rai, V. Kumar, P. R. Sagdeo, and R. Kumar, *Role of Metal Nanoparticles on Porosification of Silicon by Metal Induced Etching (MIE)*, Superlattices Microstruct. **94**, 101 (2016).
- [206] H. Richter, Z. P. Wang, and L. Ley, *The One Phonon Raman Spectrum in Microcrystalline Silicon*, Solid State Commun. **39**, 625 (1981).
- [207] 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 Commun. **58**, 739 (1986).
- [208] S. V. Koniakhin, O. I. Utesov, I. N. Terterov, A. V. Siklitskaya, A. G. Yashenkin, and D. Solnyshkov, *Raman Spectra of Crystalline Nanoparticles: Replacement for the Phonon Confinement Model*, J. Phys. Chem. C 122, 19219 (2018).
- [209] S. V. Koniakhin, O. I. Utesov, and A. G. Yashenkin, Lifetimes of Confined Optical Phonons and the Shape of a Raman Peak in Disordered Nanoparticles. II. Numerical Treatment, Phys. Rev. B 102, 205422 (2020).
- [210] M. Tanwar, P. Yogi, S. Lambora, S. Mishra, S. K. Saxena, P. R. Sagdeo, A. S. Krylov, and R. Kumar, *Generalisation of Phonon Confinement Model for Interpretation of Raman Line-Shape from Nano-Silicon*, Adv. Mater. Process. Technol. 4, 227 (2018).
- [211] G. Faraci, S. Gibilisco, P. Russo, A. R. Pennisi, and S. La Rosa, *Modified Raman Confinement Model for Si Nanocrystals*, Phys. Rev. B 73, 033307 (2006).
- [212] R. Kumar and A. K. Shukla, *Quantum Interference in the Raman Scattering from the Silicon Nanostructures*, Phys. Lett. A 373, 2882 (2009).
- [213] G. Sahu, R. Kumar, and D. P. Mahapatra, *Raman Scattering* and Backscattering Studies of Silicon Nanocrystals Formed Using Sequential Ion Implantation, Silicon **6**, 65 (2014).

- [214] R. Kumar, A. Shukla, H. Mavi, and V. Vankar, Size-Dependent Fano Interaction in the Laser-Etched Silicon Nanostructures, Nanoscale Res. Lett. 3, 105 (2008).
- [215] R. Kumar, H. S. Mavi, A. K. Shukla, and V. D. Vankar, *Photoexcited Fano Interaction in Laser-Etched Silicon Nanostructures*, J. Appl. Phys. **101**, 064315 (2007).
- [216] K. W. Adu, Q. Xiong, H. R. Gutierrez, G. Chen, and P. C. Eklund, *Raman Scattering as a Probe of Phonon Confinement and Surface Optical Modes in Semiconducting Nanowires*, Appl. Phys. A 85, 287 (2006).
- [217] G. D. Mahan, R. Gupta, Q. Xiong, C. K. Adu, and P. C. Eklund, *Optical Phonons in Polar Semiconductor Nanowires*, Phys. Rev. B 68, 073402 (2003).
- [218] N. Begum, A. S. Bhatti, F. Jabeen, S. Rubini, and F. Martelli, Lineshape Analysis of Raman Scattering from LO and SO Phonons in III-V Nanowires, J. Appl. Phys. 106, 114317 (2009).
- [219] R. Gupta, Q. Xiong, G. D. Mahan, and P. C. Eklund, Surface Optical Phonons in Gallium Phosphide Nanowires, Nano Lett. 3, 1745 (2003).
- [220] P. Yogi, D. Poonia, S. Mishra, S. K. Saxena, S. Roy, V. Kumar, P. R. Sagdeo, and R. Kumar, *Spectral Anomaly in Raman Scattering from P-Type Silicon Nanowires*, J. Phys. Chem. C 121, 5372 (2017).
- [221] B. G. Burke, J. Chan, K. A. Williams, Z. Wu, A. A. Puretzky, and D. B. Geohegan, *Raman Study of Fano Interference in P-Type Doped Silicon*, J. Raman Spectrosc. **41**, 1759 (2010).
- [222] S. K. Saxena, R. Borah, V. Kumar, H. M. Rai, R. Late, V. G. Sathe, A. Kumar, P. R. Sagdeo, and R. Kumar, *Raman* Spectroscopy for Study of Interplay between Phonon Confinement and Fano Effect in Silicon Nanowires, J. Raman Spectrosc. 47, 283 (2016).
- [223] 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, *Quantum Confined Electron–Phonon Interaction in Silicon Nanocrystals*, Nano Lett. **15**, 1511 (2015).
- [224] P. Yogi, S. K. Saxena, S. Mishra, H. M. Rai, R. Late, V. Kumar, B. Joshi, P. R. Sagdeo, and R. Kumar, *Interplay between Phonon Confinement and Fano Effect on Raman Line Shape for Semiconductor Nanostructures: Analytical Study*, Solid State Commun. 230, 25 (2016).
- [225] K. P. Jain, A. K. Shukla, S. C. Abbi, and M. Balkanski, *Raman Scattering in Ultraheavily Doped Silicon*, Phys. Rev. B 32, 5464 (1985).
- [226] M. Tanwar, D. K. Pathak, A. Chaudhary, S. K. Saxena, and R. Kumar, Unintended Deviation of Fermi Level from Band Edge in Fractal Silicon Nanostructures: Consequence of Dopants' Zonal Depletion, J. Phys. Chem. C 124, 16675 (2020).