Understanding the Effect of Anharmonicity and Fano Interaction in Solids using Raman Spectromicroscopy

Ph.D. Thesis

By Chanchal Rani



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE May 2023

Understanding the Effect of Anharmonicity and Fano Interaction in Solids using Raman Spectromicroscopy

A THESIS

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

of DOCTOR OF PHILOSOPHY

> *by* **Chanchal Rani**



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE May 2023



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled Understanding the Effect of Anharmonicity and Fano Interaction in Solids using Raman Spectromicroscopy in the partial fulfillment 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 2019 to May 2023 under the supervision of Professor Rajesh Kumar, Professor, Indian Institute of Technology 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. ∞

Chanchallani 02.105/2023

Signature of the student with date (Chanchal Rani)

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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Born' 30/06/23

Signature of Thesis Supervisor with date (Professor Rajesh Kumar)

Dedicated

to

my Family and Teachers

Acknowledgement

Without the encouragement of well-wishers, a doctoral journey that is an emotional rollercoaster of successes is never feasible. As I write this letter to thank everyone who has been with me to support and encourage me along this journey, the four-year adventure has finally come to an end, with the heavenly grace of ultimate power, I must state. Over the course of the last four years, many people have walked with me. They have led me, presented me with opportunities, and shown me the doors they might be able to help me unlock. I have a lot of people to thank for their assistance, generosity, and maybe insufficient words on this occasion.

First and foremost, my sincerest thanks and gratitude are extended to my guide Professor Rajesh Kumar, for his guidance and motivation to complete this journey. He has been a tremendous mentor for me. His constant support, patience, valuable advice, constructive criticism, and extensive discussion helped me in accomplishing my Ph.D. He has been inculcating inspiration, strength, knowledge, hard work, and confidence as qualities remain source of the light throughout my path of journey. His kindness, joy & enthusiasm which he has for research motivated me to keep going in this bumpy ride of Ph.D. He made me think differently and nourished me by reasoning, analytical and writing ability. He not only enriched my subject knowledge but also taught me about the challenges of life and to win over them. One of the most important things I want to acknowledge is that Professor Rajesh Kumar gave me mental strength to complete this journey and helped me to grow as a better person.

I must express a deep sense of gratitude to my PSPC member, Professor Preeti Bhobe and Professor Sanjay K. Singh for providing valuable suggestions and guidance during my research work.

I express my sincere gratitude to Director IIT Indore, who has been highly encouraging during the entire course of my doctoral work. I

would like to acknowledge all faculty members of the Physics department (IIT Indore) for their kind support and for providing me with experimental facilities. I want to thank the whole physics department which was like a family to me in these four years. I never felt alone due to the pleasant atmosphere here. This Ph.D. work would not have been possible without the help of my seniors Dr. Manushree Tanwar, Dr. Devesh K. Pathak, Dr. Anjali Chaudhary, Dr. Anil Garry, Dr. Aanchal Sati, Dr. Kamal Warsi, Dr. Rinki Singh. I am truly excited to reveal a sense of acknowledgement to Dr. Manushree Tanwar for guiding me to start this journey in my initial days. I was lucky to spend time with my lab mates and friends Tanushree Ghosh, Suchita Kandpal, Love Bansal, Bhumika Sahu, Deb Kumar rath, Nishchal, Meenal, Kailash, Neeshu, Ritika, Rachit. I would also like to thank my batchmates Komal, Jagjit, Koyal who helped me to settle here. I would also like to thank a few of my special friends in IIT Indore Tanushree, Neha, Love, Omkar, Anil, Apoorv for helping me and giving me joyful moments throughout this journey. I also want to thank my friends from badminton group Neha, Mahima, Anushka, Swarna for giving me stress-free and joyful moments.

I would also like to thank my friends Shubham Sharma, Prabhat Garg, Himanshu Srivastav, Keerthivasan, Anviksha, Santosh for their support, encouragement, criticism, and contributions that helped me to complete this journey. While writing this thesis I am feeling very happy and joyous and as well as wishful for leaving my friends.

I owe my deepest sense of gratitude to Dr. Hem Chandra Jha for helping me in various manners. I would also like to thank my supervisor for setting up external collaborations with Dr. Maxim M. Maximov (Peter the Great Saint-Petersburg Polytechnic University, Saint Petersburg, Russia), Dr. Himani Sharma (Doon University, Dehradun), Dr. Sameera (Guru Jambheshwar University, Hisar).

I would like to acknowledge academic staff, accounts and finance section staff, Murali Nair, Rahul Shrivas, Tapesh Parihar, Suresh thakur,

Rahul Geed, Roshan Bhatia, Pradeep Aggarwal for assisting me in every academic or financial issue. I would also like to thank SIC IIT Indore, most specifically Mr. Nitin Upadhyay, Mr. Kinny Pandey, Mr. Ghanshyam, Mr. Ved Prakash, Mr. Prashant for their kind help. I also acknowledge DST-INSPIRE for providing me with financial assistance. I would like to thank Dr. Bipin Joshi for help. I would also like to acknowledge Raman facilities by DST-FIST at IIT Indore.

I would like to thank Dr. Shilpa Raut and all staff members of IIT Indore dispensary for taking care of my health and keeping me fit so that only I could work efficiently. This journey would not have been possible without the help provided by staff and employees of the transport department, I am also thankful to them. I thank the estate section (IIT Indore) for providing me with research infrastructure. I would like to thank all housekeeping staff, especially Siyarama Ji (Daddu) for cleaning the lab every day. I want to thank all staff members of IIT Indore and all those persons whose names may have been missed here but contribute throughout the journey of four years to achieve this feat.

I owe my deepest gratitude to my parents and family for all the sacrifices they made on behalf of me and supported me in all the ups and downs of my life. I would like to thank from the depth of my heart to my mother who gave me mental strength to reach this milestone. I would like to thank my two strengths Rohit Goyal and Manika Goyal for always being with me and supporting me.

... Chanchal Rani

Abstract

Fano interaction is one of the most important phenomena which requires a focused study to observe the different properties of material. Fano interaction originates due to the mixing of the continuum of electronic state and discrete phonon in heavily doped systems or in complex systems. Due to Fano interaction, a material starts showing new properties which depend strongly on doping concentration and doping type in such a way that it becomes more prominent with slight change in doping or any external perturbation like temperature.

Raman spectroscopy, being a sensitive and non-destructive tool, can detect subtle scale phenomena and is thus indulges in the analysis of different systems. Various perturbations such as temperature effect, electron-phonon (Fano) interaction, quantum confinement effect etc., affect the Raman spectra by changing the various parameters of Raman lineshape and these effects are well-explored in various materials, especially in Si. The perturbations in heavily doped Si are manifested in terms of various Raman line-shapes, when analyzed temperature dependent Raman spectroscopy, yields interesting interplays of two physical phenomena for example temperature & Fano resonance. Thermally induced Fano interaction is an effect which shows completely different results and originates the different pathways for the decay of phonons in the different temperature range and needs to be explored. This thesis comprises the study of interplay of Fano interaction with temperature by using temperature dependent Raman spectro & microscopy along with the study of low dimensional materials.

The research work reported here deals with the temperature dependent Raman study of Fano intervened systems (degenerate Si) and transition metal oxides (TiO2). Temperature dependent Raman study in heavily doped p-type Si confirms that phonons adopt two different pathways to decay at different range of temperatures and deviate from the conventional anharmonic decay theory of Balkanski. The two pathways of phonon decay include: 1. Interferons mediated decay process and, 2.

Phonons mediated decay process. The same study has been done on differently doped Si (different doping concentrations, lightly doped & moderately doped) and it has been confirmed that only heavily doped Si shows nonlinear kind of behaviour. To prove that the given theory or process of nonlinearity is thermodynamically favorable phonon-self energy have been calculated. Another observation is to see the effect of excitation on the Fano intervened systems along with thermal perturbations. This theory reveals that, the required temperature to dissociate the interferons is different for different excitation wavelengths in same sample (same doping concentration) and both the perturbations temperature and excitation wavelengths are inversely proportional to each other. In addition to this, in this study, the required energy which is required to dissociate the interferons has been calculated which depends upon the excitation wavelength, an empirical relation has been proposed to calculate the interferon dissociation energy. Other than this, the presence of two different quasi-micro phases in the heavily doped p-type Si has also been revealed here by using temperature dependent Raman spectroscopy. Thermal hysteresis has been performed to check the stability of both the phases present in the heavily doped Si and thermal energy which is required for the transition from one state to another have also been calculated. And a theoretical calculation has been done in this study and developed a formula to observe the temperature dependent Fano strength parameter. Another study is to determine the temperature dependent Fermi level position in degenerate Si and the corresponding Fermi energy. Here Raman spectroscopy has been used as a simple yet effective tool to calculate Fermi energy. A simple formula has also been developed to calculate the Fermi energy in degenerate Si which depends on the Fano induced linewidth in the temperature dependent Raman spectra. Raman spectroscopy has also been used to analyze the low dimensional materials such as amorphous Si, Si nanowires, TiO2 nanorods.

List of Publications

A. (Publications from thesis work)

[1] Chanchal Rani, Suchita Kandpal, Tanushree Ghosh, Love Bansal, Manushree Tanwar, and Rajesh Kumar, "*Energy dispersive antianharmonic effect in a Fano intervened semiconductor: revealed through temperature and wavelength-dependent Raman scattering*[†]". Phys. Chem. Chem. Phys., 25, 1627-1631(2022).

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[8] Chanchal Rani, Km. Neeshu, Ritika Kaushik, Manushree Tanwar, Devesh k. Pathak, Anjali Chaudhary, Ashisha Kumar, and Rajesh Kumar, "Size dependence of Raman line-shape parameters due to confined phonons in silicon nanowires". Adv. Mater. Process. Technol., 6, 669-674 (2020).

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[13] Tanushree Ghosh, **Chanchal Rani**, Suchita Kandpal, Manushree Tanwar, Love Bansal, and Rajesh Kumar, "*Chronoamperometric deposition of transparent WO3 film for application as power efficient electrochromic auxiliary electrode*." **J. Phys. D., 55, (2022).**

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Abbreviations

Silicon	Si
Nanostructures	NSs
Silicon nanowires	SiNWs
Crystalline Si	c-Si
Amorphous Si	a-Si
Intrinsic Si	i-Si
Metal Assisted Chemical Etching	MACE
Metal Nanoparticles	MNPs
Phonon Confinement Model	PCM
Bond Polarization Model	BPM
Direct Matrix Method	DMM
Full Width at Half Maxima	FWHM
Electron-Phonon	e-ph
Semiconductor Quantum Dots	SQDs
TiO ₂ Nanorods	TNRs
Temperature Dependent	TD
P-type Si (resistivity $10^{-3} \Omega$ -cm)	P++
P-type Si (resistivity $10^{-2} \Omega$ -cm)	P ⁺
N-type Si (resistivity $10^{-3} \Omega$ -cm)	N ⁺⁺

Chapter 1

Introduction

In the world of technology, semiconductors [1-3] retain their position as one of the most important areas as they remain the backbone of the many devices such as electronic, optic, electric etc.[4–6]. The different types of semiconductors such as Si, Ge, GaAs, InP are the basic building blocks of the modern technological world[7–9]. The most important property of the semiconductor is the conductivity which can easily be controlled by the human being by simply giving some external energy in the form of voltage, temperature, current etc.[10-13]. The conductivity of the semiconductor lies between metals and insulator and at room temperature semiconductor behaves like an insulator and on giving some temperature or voltage it starts to behave like conducting materials[14-16]. The modern understanding of the properties of a semiconductor lies in quantum physics to explain the movement of electrons and holes inside a crystal structure and also in a lattice. Undoubtedly, tremendous amount of technological development has taken place around semiconductors, yet lot of scientific understanding remains to be discovered hence needs exploration.

Silicon (Si) makes up 27.7% of Earth's crust by mass and is the 2nd most abundant material semiconductor element (oxygen is the first) and lies in the 4th group of the periodic table[17,18]. In nature, however, Si is found in the form of compound with oxygen, aluminum and magnesium and thus is extracted and purified using various processes. Being an indirect bandgap semiconductor Si shows unique properties[19–22] such as in modern electronic devices that includes resistor, diodes, transistors etc., due to which scientists are still interested in this material and continuously getting new in this field. The properties of the intrinsic semiconductors can be used by adding some external impurities and on the basis of those impurities' semiconductors (extrinsic) are categorized in two categories i.e., n- type and p- type[23,24]. Both types of Si are being used in different applications depending upon the charge carriers taking part in the conduction process.

Apart from this, transition metal oxides [25-29] such as TiO₂, Co₃O₄, NiO, MnO₂ etc., are used as emerging materials in various fields. Transition metal oxides are generally used for catalytic activity and semiconductive properties[30,31]. Transition metal oxides have a wide variety of surface structures which affect the surface energy of these compounds and influence their chemical properties. The relative acidity and basicity of the atoms present on the surface of metal oxides are also affected by the coordination of the metal cation and oxygen anion, which alter the catalytic properties of these compounds. Transition metal oxides are mainly used as pigments in paints and plastics[32-34]. The most common transition metal oxides which are used in cosmetic products or in paints is titanium oxide (TiO₂)[35–37]. In comparison with the bulk counterpart, nanostructured TiO₂ shows exclusive properties due to its low toxicity and chemical stability. Under ambient conditions, TiO2 is known to exist in eight crystalline polymorphs, of which only three, namely, rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) phases occur naturally[38-40]. Though each of these polymorphs exhibit distinct properties, but rutile phase is the thermodynamically preferred form at all temperatures. There are various techniques to fabricate the nanostructure of rutile TiO₂ (nanorods)[41– 44] such as chemical vapor deposition (CVD), hydrothermal method, Sol-gel method, atomic layer deposition (ALD) etc.

Amongst all the techniques, the hydrothermal method is one of the easiest and most cost-effective techniques to fabricate the rutile TiO_2 nanorods. Using hydrothermal method, one can deposit the uniform layer of TiO_2 on different substrates like semiconductor substrate (Si,

Ge), Florine doped tin oxide (FTO), Indium tin oxide (ITO) etc., and can be fabricated the well- aligned nanorods. The hydrothermal process is a two-step process as discussed in chapter 3. After sample preparation, various techniques are used to characterize the prepared samples (bulk crystalline Si, Si nanowires, TiO₂ nanorods etc.,) such as scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), Atomic force microscopy (AFM) etc. These techniques are used to check the surface morphology of the sample, purity, or phase of the sample etc.

Raman spectroscopy[45–52] is one of the most widely used technique to investigate the vibrational properties of the molecule and phonons in solids. Raman spectroscopy emerged as a superior tool over the others for characterization of different materials especially where a quick and extremely sensitive technique is required. Raman spectroscopy[53–59] can be employed to observe any phenomenon at the microscopic level in the material like to assess phase, doping, strain/stress, and effect of various other perturbations in variety of materials. Raman effect was discovered in 1928 as "*a new kind of radiation*" resulting from inelastic scattering of light from molecules by Indian Physicists C.V. Raman and K.S. Krishnan using a very simple setup shown in Figure 1.1.



Figure 1.1 Sir C.V. Raman with the very first setup of the Raman spectrometer (Image courtesy, IISc Bangalore archives).

Since its discovery, the effect has made a journey from being a weak (low probability) scattering phenomenon to getting developed as one of the most widely used spectroscopic techniques "Raman spectroscopy" especially after the discovery of lasers. With the advent of better detectors and reliable computer engineering, interfacing, newer dimensions in terms of added capabilities make the Raman spectroscopic tools reach out to unexplored areas of science and technology. Very recent developments in the areas of machine learning and artificial intelligence can make this technique available for routine characterization purposes which once was only limited to very specialized scientists. Even though it is a spectroscopic tool that largely probes vibrational properties, it has advantages over infra-red (IR) spectroscopy due to flexibility in choosing the excitation source making it more appropriate for investigating biological samples as well. Due to its interdisciplinary nature, Raman spectroscopy, very often in combination with IR spectroscopy, finds application in almost all areas of science and technology including material science and technology[60–62].

Raman spectroscopy mainly investigates the scattering of incident photon with optic or longitudinal phonons, any quasiparticles in the system or electronic transitions in the material[63–65]. In crystalline materials the Raman scattering, especially semiconductors, occurs from the zone centered phonons (follows momentum k = 0 selection rule) and resulting in a sharp symmetric Raman spectrum having peak position corresponding to zone center phonon frequency. In nanostructures (NSs), Raman spectroscopy is employed to investigate the phonons other than the zone centered ones, resulting in a red shifted and asymmetrically broadened Raman spectra. This happens due to the confinement of phonons within the physical boundary of the NSs[66– 69]. Any change in the lineshape of the Raman spectra is also important to the external perturbations like thermal effect, electron-phonon interaction, quantum confinement, etc. Raman spectrum from the crystalline Si (c- Si)[70–73] is generally symmetric having a Lorentzian line-shape. Any deviation from symmetry, shift in the peak position, or change in its full width at half maximum (FWHM) can be explained in terms of external perturbation. Raman spectroscopy also provides information about the crystallinity of the material whether it is crystalline, amorphous or nanocrystalline. Raman spectroscopy can also be used to confirm the presence of nonlinear effect of stimulated Raman scattering. Raman spectroscopy can also be used for other materials which are very sensitive to defects and cannot be stored directly like transition metal oxides (TiO₂).

Temperature dependent (TD) Raman spectroscopy[74-76] and microscopy is now widely used to explain the thermal effect on materials and how the different Raman active modes of the materials are responding to the thermal effects. Generally, the phonons which take part in the Raman scattering annihilate into two or three lower energy phonons due to temperature according to the theory given by Balkanski et al[77]., known as anharmonic decay theory of phonons. Due to the anharmonic effects the lifetime of the phonons gets decreased and resulting a broad lineshape of the Raman spectra. Apart from this, the Raman spectra gets shifted towards a lower frequency region (red shift) due to the thermal expansion of the covalent bonds between the molecules. On the contrary, a few Raman modes do not show any variation with temperature and act as thermally immune like in rutile TiO₂ due to the various reasons which need to be explored[78]. Apart from this, the materials which shows phase transition with temperature or shows some different phenomena like electron-phonon interaction are also do not follow Balkanski's anharmonic theory while show deviation and different results with temperature[79,80].

Other than the confinement effect, thermal effect, there exists other phenomena e.g., doping effect or electron-phonon interaction, also known as Fano interaction[81,82] which affects the Raman spectra and manifests itself in terms of asymmetry and antiresonance in the Raman lineshape. The perturbations caused by doping are different from the ones caused by thermal effects hence the way doping affects the Raman line-shape is different from the way it is affected by the temperature. Fano interaction is basically the interference between the continuum of the electronic state with the discrete state of phonons or it can be said that Fano interaction is caused by the matching of energies if one discrete phonon with continuum provided by heavy doping which can induce asymmetry in Raman spectral lineshape[83–86]. It was U. Fano who observed the asymmetric lineshape in Rydberg spectral atomic lines and gave the theory of Fano interaction which is based on the superposition principle of quantum mechanics. In heavily doped systems (degenerate semiconductor, doping order $\sim 10^{19}$ cm⁻³), Fermi level enters the respective band either valance (p-type) or conduction band (n-type) which gives rise to the continuous electronic Raman scattering due to interband transitions between the inter-conduction bands (n-type) Δ_1 and Δ_2 bands[87–91] along the (100) directions (Figure 1.2).

A continuum of transitions exists from the minimum energy ($\hbar\omega_{min}$) to the maximum energy ($\hbar\omega_{max}$) determined by the Fermi level E_F (Figure 1.2). In p-type Si, these interband transitions occur in valence band. These interband transitions in respective semiconductor (n or p type), cause asymmetry and broadening in the Raman lineshape. In n-type semiconductor, the broadening in the spectral linewidth occurs in the pre-maximum side of the spectra and asymmetry occurs in the opposite side i.e., pre-minimum side. While for p-type semiconductors, these changes in the Raman lineshape[92,93].



Figure 1.2: Conduction bands of heavily doped n-type c-Si. The figure has been reproduced with the permission of ref. (84).

(Broadening and asymmetry) appear on the pre-minimum and premaximum side, respectively.

The Fano interaction is also affected by the external perturbations such as temperature and excitation wavelength of the laser. Thermally induced Fano interaction in heavily doped systems behaves differently in comparison to the Fano interaction and act as a nonlinear Fano interaction[94–96]. Nonlinear Fano interaction basically has been observed in hybrid systems which is made up of semiconductor quantum dots and metal nanoparticles in the presence of external perturbation electric field[97–99]. There is no restriction for exhibiting nonlinear Fano interaction in single systems such as heavily doped semiconductors in the presence of thermal effect as external perturbation. There is no such report reported (before this current thesis study) on nonlinear Fano interaction in single systems. A TD Raman spectroscopy can be used as a tool to investigate the nonlinear or linear Fano effect in the different materials.

Therefore, various perturbations such as temperature effect (anharmonicity), electron-phonon interaction (Fano interaction), quantum confinement, thermally induced Fano interaction (nonlinear Fano interaction) etc., affects. the Raman spectra in different manner (Figure 1.3) which can be observed by analyzing the parameters of the Raman spectrum such as shift in the Raman peak position, change in spectral linewidth measured through full width at half maxima (FWHM), asymmetry ratio, antiresonance dip etc. The effect of the some of the perturbations are well explored in various systems, especially in Si like anharmonic effect, Fano interaction etc., but few effects such as nonlinear Fano interaction need to be explored in the semiconductors and in other materials as well.



Figure 1.3: Schematic represents the effect of different perturbations on the Raman spectra.

The main objective of the current thesis is to study the thermally induced electron phonon interaction or Fano interaction in crystalline semiconductors i.e., for Si. To observe this effect, TD Raman spectroscopy & microscopy (spectromicroscopy) has been used for experimental section and theoretical analysis has also been done for the validation of the obtained result from experiments. In heavily doped Si, where the doping concentration is very high, the electronic bands present in the valance band or conduction band (depending on the doping type) make continuum of the bands. This continuum interferes with the phonons (discrete) while performing the Raman spectroscopy and makes a bound state of electron-phonon i.e., interferon. Due to this interaction between electron-phonon (interferon), heavily doped p-type Si shows deviation from the Balkanski's anharmonic decay theory of

phonons with temperature which has been analyzed in this thesis. In heavily doped p type Si, the Raman spectral parameters i.e., spectral linewidth behaves nonlinearly under thermal perturbations, first decrease, and then increases with increasing temperature, has been explained in this thesis study. This study explains that in heavily doped systems, phonons adopt different pathways to decay in different temperature range apart from the anharmonic effect. To validate that these phonon decay processes in the heavily doped p-type Si are thermodynamically favorable, phonon self-energy has been calculated by using some theoretical simulations and proves that this theory follows all the thermodynamic rules. Therefore, the presence of nonlinear Fano effect in single systems (heavily doped p-type Si) under external thermal perturbation is studied in this thesis. On the other hand, the presence of two different quasi-micro phases has also been revealed using temperature dependent Raman spectroscopy and for theoretical validation, a formula has been developed to calculate the TD Fano strength parameter. The variation of TD Fano strength parameter reveals that at lower temperatures, heavily doped p-type Si system remains in the interferonic rich state while at higher temperatures, the system has another phase in which all the interferons convert into the phonons i.e., phononic rich state. The stability of these phases present in the p-type Si has been observed by performing thermal hysteresis by performing temperature dependent Raman spectroscopy in both the ranges i.e., from low to high and high to low temperature. The effect of excitation wavelength of laser has also been observed on the nonlinear Fano interaction by using three different excitation laser wavelengths and it has been confirmed that, at higher wavelength the bound state energy of the interferons is very much higher in compared to the other low excitation wavelengths. And in this study, the thermal energy required to dissociate the bound state of interferons has also been calculated which depends upon the excitation wavelength and the given temperature. To calculate interferon dissociation energy, an empirical relation has been proposed and got results that at different excitation

different techniques. This study also covers the advantages of DMM-BPM method over already existing model i.e., phonon confinement model (PCM) and explain that why phonon confinement model cannot generate the Raman lineshape for very short range (amorphous) ordered materials. Other than this, an empirical relation has also been proposed to calculate the size dependent Raman peak position variation in short range ordered materials and in long range materials as well. This study can easily be used to any short range ordered materials and can remove the discrepancies of the phonon confinement model.

All the results, discussions and conclusions which have been presented in this current thesis as per the following chapter wise plan:

Chapter 1 (current chapter): This chapter gives an introduction about the semiconductor world and Raman spectroscopy and discusses the current status of the problem which is dealt here and defines the objective.

Chapter 2: This chapter gives the overview of Si along with its basic properties and how it is affected by various perturbations such as quantum confinement effect, electron-phonon interaction etc. Other relevant theoretical backgrounds, helpful in explaining the results, are also included here.

Chapter 3: This chapter summarizes the different experimental methods which are used to different nanomaterials such as Si nanowires and rutile TiO_2 nanorods. This chapter also explains the different characterization techniques such as scanning electron microscope (SEM), Raman spectroscopy, X-ray diffraction (XRD) which are used to characterize the prepared samples.

Chapter 4: This chapter explains the presence of nonlinear Fano interaction in the single system i.e., in heavily doped p type Si under external perturbation by using temperature dependent Raman spectroscopy and also give the theoretical validation for the abovementioned phenomena. **Chapter 5:** This chapter reveals the presence of two different quasi microphase in the heavily doped p-type Si and also explains the effect of excitation wavelength on thermally induced Fano interaction.

Chapter 6: This chapter deals with the application of nonlinear Fano interaction in the heavily doped Si by estimating temperature dependent Fermi energy and Fermi level positioning. This chapter explains how only temperature dependent Raman spectro and microscopy can be used to calculate the Fermi energy in heavily doped Si.

Chapter 7: This chapter deals with the Raman study of low dimensional materials such as rutile TiO_2 nanorods, Si nanowires and amorphous Si. This chapter explains the effect of temperature on rutile TiO_2 nanorods and degree of anharmonicity in the rutile TiO_2 nanorods has also been calculated in this chapter.

Chapter 8: This chapter summarizes all the conclusions drawn from the reported study which has been listed above. This chapter also discussed possible future scope on work that can be carried out for further developments in this research field.

Chapter 2

General Overview and Theoretical Background

This chapter deals with the general properties and theoretical background of silicon (Si). The basic overview of Si is presented in section 2.1 in terms of its crystalline structure, band structure etc. The effects of different phenomena such as quantum confinement effect and electron-phonon coupling have been discussed in this chapter. At the end, the general theory of Raman scattering from semiconductors is also discussed.

2.1 Overview of Si

Silicon[100–102] is a nonmetallic chemical element in the carbon family (Group IVth of the periodic table). It makes up 27.7 percent of the Earth's crust and it is the second most abundant element in the crust, being surpassed only by oxygen. Pure Si is a hard and dark gray solid with a metallic luster. It possesses a crystalline structure the same as that of the diamond form of carbon due to which Si shows many chemical and physical similarities with diamond[103]. Highly purified Si, doped with such elements 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 Si are known: Si-28, which makes up 92.21 percent of the element in nature; Si-29, 4.70 percent; and Si-30, 3.09 percent.

2.1.1 Crystal Structure of Silicon

The atomic structure of Si[104–107] makes it an extremely important semiconductor. The basic unit of crystalline Si consists of five Si atoms, which are capable of forming a "primitive unit cell". The unit cell of a crystalline Si is a diamond structure, which consists of two interpenetrating face centered cubic (FCC) lattices, displaced along the body diagonal of the cubic cell by one-fourth of the diagonal length. It is regarded as an FCC lattice with a two-point basis. The bonding structure in Si is tetrahedral, i.e., each atom lies at the center of a tetrahedral configuration defined by four atoms with which it is bounded. The Si unit cell has a lattice parameter of 0.543 nm and tetrahedral angle of 109.2°. The basic FCC unit cell of the Si atom has been shown in Figure 2.1.



Figure 2.1: FCC unit cell structure of Si.

2.1.2 Band Structure of Si

Figure 2.2 shows the Brillouin-zone of Si, which is defined in the reciprocal lattice as the volume enclosed within a Wigner-Seitz cell. The important

symmetrical points of the Brillouin-zone[108–110], which are determined by the symmetry of the crystal lattice, are also shown in Figure 2.2. Si is an indirect band gap material having a band gap of 1.1 eV[111–113]. Knowledge of Brillouin zone is important for better understanding of the band structure of any crystal because the band gap energy depends on different direction in the lattice.



Figure 2.2: First Brillouin zone of Face cubic centered lattice.

Different approaches are used to calculate the band structure of crystalline solids. The pseudopotential method[114,115] and **k.p** methods are two of them. In the first method, the electronic states in a crystal are obtained by solving the non-relativistic Schrodinger equation in the one-electron approximation. The empirical pseudopotential method is based on the approximation that the Fourier coefficients of the pseudopotential are empirically chosen so that the shape of the critical points and their energies show good agreement with experimental observation. Figure 2.3 represents the energy band structure of the Si obtained by empirical pseudopotential method.



Figure 2.3: Energy band structure calculated by using the empirical pseudopotential method for Si.

The other approach for band structure determination is **k.p** method[116,117]. This method was used to calculate the detailed structure of the valance band of germanium (Ge). Cardona and Pollak *et al.* have used this method in combination with experimental data obtained by cyclotron resonance and optical studies to determine the energy bands of Ge and Si throughout the entire Brillouin zone. The **k.p** method includes spin-orbit interactions and is valuable for materials with large relativistic effects as these corrections are incorporated into the energy gaps and band parameters at k = 0, which are readily determined by fitting experimental data. Cardona and Pollak's result for Si is shown in Fig. 2.4.



Figure 2.4: Si band structure obtained by using **k.p** method.

2.1.3 Optical properties of Si

As mentioned earlier, Si is an indirect band gap material. Transitions at the band edge must therefore involve a change in the electron wave vector. Optical frequency photons only have a very small k vector, and it is not possible to make this transition by absorption of a photon alone: the transition must involve a phonon to conserve momentum. The interband transitions in a direct and indirect band gap are shown in Fig. 2.5. Figure 2.5 shows that indirect transitions involve both photons and phonons.



Figure 2.5: (a & b) Direct and indirect bandgap interband transition in Si, respectively. The vertical arrow represents the photon absorption while wiggly arrow represents the absorption or emission of a phonon.

In quantum mechanical terms, this is a second-order process: a photon must be destroyed, and a phonon must be either created or destroyed. This is in contrast with the direct transitions, which are first-order processes because no phonons are involved. The transition rate for indirect absorption is therefore much smaller than that for direct absorption. The smaller transition rate for indirect process is clearly shown from the absorption coefficient verses photon energy spectrum of Si[118–121] in Fig. 2.6. The absorption rise is slow because of the indirect nature of band of Si having band gap of 1.1 eV.



Figure 2.6: The absorption coefficient vs photon energy at room temperature.

Figure 2.6 shows the absorption spectra of Si only in the range near the band gap. The absorption coefficients in the spectral region around these two values are extremely large as compared to its value near band edge (as in Fig. 2.6). This is a consequence of the following two factors. Firstly, the band edge absorption is weak because it is indirect, 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.

2.1.4 Phonon Dispersion Curve in Si

The phonon dispersion curve for crystalline Si[122–126] is shown in Figure 2.7 along with high symmetry directions. Since there are two atoms per primitive unit cell in these crystals, there are six phonon branches. These branches are divided into three acoustic phonon branches (the three lower energy curves) and three optical phonon curves. Along high-symmetry directions (such as the [k00], [0qq] and [kkk] directions), the phonons can

be classified as transverse and longitudinal depending on whether their displacements are perpendicular or parallel to the direction of wave vector, respectively. Transverse optical (TO) and the longitudinal optical (LO) phonons of Si degenerate at the zone center because of the identical atoms in the unit cell and the purely covalent nature of bonding. The TA dispersion curves are relatively flat near the zone edge and their energies are much lower than the LA phonon energy near the zone edge.



Figure 2.7: Phonon dispersion curve for crystalline Si along high symmetry directions.

2.2 Quantum Confinement Phenomenon in Si

When the size or dimension of a material is continuously reduced from a large or macroscopic size to a very small size (of the order of few nanometer), dramatic changes in the properties of these nanomaterials can be observed[127–130]. Confinement in one, two or three dimensions leads to structures termed as quantum well, quantum wire and quantum dot, respectively. The word quantum is associated with these three types of nanostructures because the changes in material properties arise from the

quantum-mechanical nature of physics in the domain of ultra-small dimensions. Quantum confinement effect is a general word used for any effect seen caused by the reduction in the dimensionality of the material, which is not observable from its bulk counterpart.

Quantum confinement in semiconductors results from the geometric confinement of electrons and holes as independent 'wave-particles' or bound pairs known as excitons. The normal size of an exciton in a bulk crystal, expressed as the exciton Bohr radius, provides an approximate dimension for the onset of quantum-confinement effects. When the dimensions of a nanomaterial approach the size of the exciton Bohr radius in bulk semiconductor, the effective band gap of the semiconductor increases. The smaller the dimension, the larger is the effective band gap. As a consequence, most of the bulk semiconductor properties such as electronic band structure, linear and nonlinear optical properties, excitonic properties and phonon propagation etc. are drastically changed.

2.2.1 Bandgap Enhancement in Confined Si

Quantum confinement leads to an increase in the band gap of semiconductors[131,132]. In very small sized NSs, the energy levels in conduction and valance band are separated and become discrete and can be calculated using the analogy to the problem of a particle within a suitable potential barrier. Considering the general case of 3-D confinement within a particle having sizes d_x , d_y and d_z in x-, y- and z-directions respectively, the modified band gap can be written as Eq 2.1:

$$E_{confined} = E_{bulk} + \frac{\hbar^2 \pi^2}{2} \left[\frac{1}{d_x^2} + \frac{1}{d_y^2} + \frac{1}{d_z^2} \right] \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right],$$
(2.1)

where, m_e^* and m_h^* are effective masses of electron in conduction band and hole in valance band respectively and is the Plank's constant. For the energy levels to be discrete, the sizes d_x , d_y and d_z should be larger than the lattice parameter and comparable to the Bohr exciton radius. The Eq. (2.1) can be used to calculate the band gap for the case of 1-D or 2-D confinement by using the limiting value of one or more sizes tending to infinity. According

For Bulk semiconductor:

$$\rho_{Bulk}(E) = \left(\frac{m^*}{\hbar^2}\right)^2 \frac{v}{\pi^2} \sqrt{2E},$$
(2.2)

Where V is the crystal volume in Eq 2.2.

For One dimensional confinement:

$$\rho_{1D}(E) = \left(\frac{Sm^*}{\pi\hbar^2}\right)^2 \sum_l \Theta(E - E_l), \qquad (2.3)$$

where S is the surface area of the quantum well, $\boldsymbol{\Theta}(x)$ is the Heaviside function: $\boldsymbol{\Theta}(x) = 1$ for x > 0 and $\boldsymbol{\Theta}(x) = 0$ for x < 0.

For Two-dimensional confinement:

$$\rho_{2D}(E) = \frac{L_x}{\pi} \sqrt{\left(\frac{2m^*}{\hbar^2}\right)} \frac{1}{\sqrt{E - E_{l,m}}} \sum_l \Theta(E - E_l)$$
(2.4)

Where L_x is the length of the wire.

For Three-dimensional confinement:

$$\rho_{3D}(E) = \sum_{V} \delta(E - E_V), \qquad (2.5)$$

where V= (1, m, n). Figure 2.9 shows the plot of $\rho(E)$ versus energy E for bulk and confined semiconductors in various dimensions. In bulk semiconductors, $\rho_{Bulk}(E)$ increases by factor of, while it takes a step function in case of one-dimensional confinement. For two-dimensional confinement, $\rho_{1D}(E)$ decreases by whereas it consists of a series of delta functions in three-dimensional confinement. The density of states is used to determine various electronic and optical properties. Since $\rho(E)$ varies differently in all the three cases of confinement, the properties of a material can be drastically different for different degrees of confinement.



Figure 2.9: The density of states in different confinement configurations (a) bulk, (b) quantum well, (c) quantum wire and (d) quantum dot. The conduction and valence bands split into overlapping sub-bands that become successively narrower as the electron motion is restricted in multiple dimensions.

2.3 Raman Scattering

In the year 1928 a new kind of radiation resulting from inelastic scattering of light from molecules was discovered by Indian Physicists C.V. Raman and K.S. Krishnan which is now popularly known as the "Raman effect"[133]. Since its discovery, the effect has made a journey from being a weak (low probability) scattering phenomenon to getting developed as one of the most widely used spectroscopic techniques especially after the discovery of lasers. When a high intensity beam of monochromatic light illuminates a gas, a liquid or a transparent solid, a small fraction of light is scattered in all directions. The scattered energy consists of almost entirely the incident frequency, known as Rayleigh lines. Additional Raman frequencies above and below the incident frequencies are also present. The lines on the low frequency side of the exciting line are called 'Stokes' line, while those on the high frequency components along with the incident frequency in the scattered radiation is known as the Raman effect. There are two approaches to understand the Raman effect. Classical theory[134] was the first to understand this effect. Later quantum theory[135] was proposed because of some discrepancies in the classical theory. Both the theories are discussed here in the following subsections.

2.3.1 Raman Scattering in Semiconductors

When incident light of angular frequency ω_i interacts with a semiconductor crystal, the scattered light has frequency ω_s , which may have value higher or lesser than the incident light frequency ω_i . The observation of higher or lower frequency in the scattered light is due to the creation or destruction of one or more lattice vibration quanta, known as phonon. Following energy and momentum conservation have to be followed during the first order scattering process, where one phonon participates:

$$\omega_i = \omega_s \pm \omega_0, \tag{2.6}$$

$$\boldsymbol{k_i} = \boldsymbol{k_s} \pm \boldsymbol{k}, \tag{2.7}$$

Where, \mathbf{k}_i , \mathbf{k}_s and \mathbf{k} are wave-vectors of the incident light, scattered light and phonon respectively and ω_0 is the phonon frequency.

Raman interaction between photon and phonon in the semiconductor takes place through the involvement of the electronic virtual states as shown in Figure 2.10. Figure 2.10 shows the Hamiltonian for the electron-radiation and electron-lattice interaction as H_{E-R} and H_{E-L} , respectively. For homopolar semiconductors (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 the atoms. The electronic dipole moment M produced by an electric vector of the incident light can be written as:

$$M_{\rho} = \sum_{\sigma} \alpha_{\rho\sigma} E_{\sigma}, \qquad (2.8)$$

Where $\alpha_{\rho\sigma}$ is the polarizability tensor associated with electrons in the crystal. The electronic polarizability can be extended in a power series of r:

$$\alpha_{\rho\sigma} = \alpha_{\rho\sigma}(0) + \sum_{\mu} \alpha_{\rho\sigma,\mu} r_{\mu} + \sum_{\mu\nu} \alpha_{\rho\sigma,\mu\nu} r_{\mu} r_{\nu} + \cdots, \qquad (2.9)$$

$$\alpha_{\rho\sigma,\mu} = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial r_{\mu}}\right)_{r=0}, \text{ and } \alpha_{\rho\sigma,\mu\nu} = \left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial r_{\mu}\partial r_{\nu}}\right)_{r=0}, \tag{2.10}$$

In Eq 2.10, 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 2.10a 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 \mathbf{k}_i and \mathbf{k}_s (105 cm⁻¹) are negligible in comparison to the width of the Brillouin zone (3*10⁸ cm⁻¹), momentum conservation allows the first order Raman scattering for the phonon frequency at k = 0 (i.e., wavelength of the phonon is very large compared to the lattice).



Figure 2.10 Raman scattering processes in terms of elementary interactions H_{E-L} (electron-lattice Hamiltonian interaction), 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) second order Raman scattering.

The second order Raman scattering[136–138] results due to the involvement of two phonons in the scattering process. Involvement of two phonons can be in two ways as shown in Figure 2.10 (b & c). In one case, the second order Raman spectra (Raman line spectrum) is due to two successive first-order Raman scattering as depicted in Figure 2.15 (b). In this case the frequency of the scattered photon is the sum or the difference of shifts occurring in the first-order spectrum. The line nature of the second order Raman scattering. In the other case, a couple of phonons participate as a single event as shown in Figure 2.15 (c). According to the conservation of wavevectors, the wavevectors of the two phonons should be equal and opposite because wavevectors of incident and scattered photons are negligible as compared to the Brillouin zone dimension. As a result, the second order continuous Raman spectrum reflects a combined density of phonon pair with equal and opposite wavevectors.

2.3.2 Raman Scattering in c-Si

Raman spectrum from c-Si[139] shows only the zone-centered phonons because of the selection rules as discussed in the above section. Phonons present in the diamond structured Si can be investigated by one-phonon and two-phonon Raman scattering. Phonon frequencies present in c-Si can be known from the phonon dispersion curve shown in Figure 2.7. Figure 2.11 shows the Raman spectrum recorded from c-Si. The Raman peak at 520.5 cm⁻¹ with Lorentzian line-shape has the maximum intensity. This Lorentzian Raman line reflects the first-order Raman active phonon having Γ_{25} symmetry located at the zone center in Figure 2.7. This zone center phonon (ZCP) has a tendency to decay to other sets of phonons. The coupling of the ZCP with other sets of phonons is reflected as the width of this one-phonon Raman line-shape at 520.5 cm⁻¹. Natural linewidth of first order Raman line is 3.5 cm⁻¹. In the frequency range 200-500 cm⁻¹, Figure 2.11 shows two peaks at 300 cm⁻¹ and 350 cm⁻¹ with a kink at 230 cm⁻¹. Temple et al. have associated these peaks with the 2TA phonons from the critical points X and Σ respectively. The kink at 230 cm⁻¹ is associated with the 2TA phonon from L point in the phonon dispersion curve. Weak scattering from the phonons along and near Σ direction is reflected as a weak peak at 460 cm⁻¹. Two-phonon Raman spectra associated with a combination of the acoustic and optic phonons in the Σ direction is seen near 610 cm⁻¹ in Figure 2.11.



Figure 2.11: Raman spectra of c-Si, recorded using 514.5 excitation wavelength laser.

The scattering in the frequency range 900-1050 cm⁻¹ has been identified with two TO phonon overtones from the critical points at X. The shoulders at 940 cm⁻¹ and 975 cm⁻¹ are associated with two TO phonon overtones at W and L points respectively.

2.4 Electron-Phonon (Fano) Interaction

Doping concentration and doping type also affects the Raman spectrum in terms of change in the spectral parameters such as change in the spectral peak position and linewidth but not necessarily in the same way[140–142].

Doping of atoms like boron (p-type), phosphorous (n-type), arsenic (n-type) etc. in semiconductors (e.g., silicon, germanium etc.) or in two-dimensional materials affects the band structure which affects the charge carrier's distribution in the electronic levels. This change in the solids may cause asymmetry, redshift and change in linewidth in the Raman spectra. Such changes in the Raman spectra can be explained with the Fano type interaction model based on a discrete continuum interaction.



Figure 2.12: Schematic diagram shows the phenomena of Fano resonance. Figure represents the interference process in which the direct ionization of a deep inner shell electron and autoionization of two excited electrons followed by the Auger effect.

The theory given by U. Fano for the asymmetrical lineshape is constructed on the interference phenomena between the discrete states of the atoms and the available electronic continuum in the same energy level. It is wellknown that in any material if a photon of very high energy is incident, then the atoms present in that material get ionized. This ionization process can be done in two different ways, (1) if electron direct reaches to the excited state (unbound) from its ground state (bound) and other is just like the Auger ionization process in which electrons gets excited through the intermediate bound state. The direct excitation process of electron is non-resonant, meaning the electron only ejects from the ground state if the energy of the incident photons is more than the ionization threshold where $A + hv \rightarrow$ $A^+ + e$). On the contrary, Auger ionization process (indirect excitation process) is resonant because the two electrons must be excited into a welldefined auto ionizing state $(A + hv \rightarrow A^* \rightarrow A^+ + e)$ and responsible for the autoionization.

The process of authorization can be explained as the interference between the discrete spectrum with continuum spectrum and this process can be considered as a mechanism that couples bound states of one channel with continuum of the other (Figure 2.12). An electron comes to the lower energy state and the second electron is gone into the continuum, by taking the energy of the relaxed electron and because of the superposition principle, wherever two states are coupled or interfere by different modes, the phenomena of interference may occur.

U Fano used quantum mechanical theory to explain the asymmetric lineshape of the absorption spectra. In which he considered an atomic system with a number of zero-approximation states, and among these states one belongs to the discrete configuration and other belongs to the continuum of states.

$$\sigma(E) = \frac{(\varepsilon + q^2)}{1 + \varepsilon^2},\tag{2.11}$$

By using q as a shape parameter of the lineshape & a reduced energy $\varepsilon = [2(E-E_F)/\Gamma)$, E_F is the resonant energy and Γ is the spectral width. Above Eq. 2.11 explains that in the Fano lineshape, the minima & maxima obtained at the following points:

$$\sigma_{\min} = 0$$
 at $\varepsilon = -q$
and $\sigma_{\max} = 1 + q^2$ at $\varepsilon = 1/q$

U. Fano used q (shape parameter or asymmetry parameter) as a ratio of the


transition probabilities of the discrete state and to the continuum as can be easily understood using a schematic (Figure 2.13).

Figure 2.13: Schematic shows the function of the Fano resonance.

2.4.1 Fano Interaction in c-Si

In well-tailored c-Si, the electron-phonon coupling in terms of interference between electronic continuum and optic phonon results in an asymmetric Raman lineshape. Manifestation of the Fano interference is one of the wellstudied properties in the heavily doped Si wafer[143–147]. In heavily doped p-type semiconductors, electronic continuum is created in the valance band due to the transition of light hole to heavy hole while created in the conduction band in heavily doped n-type[148–151]. In p-type Si, incident light ω excites from the light hole band (light) to the conduction band an electron, which, by emitting a scattered photon ω' , deexcites to the heavy hole band (heavy), leaving a net transition light to heavy. These intervalence band transitions give a Raman spectrum, as depicted in the energy band diagram as shown in Figure 2.14.



Figure 2.14: Transitions of electrons in electronic bands.

Fano interaction 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 around. As a result, any of the spectral half widths, towards lower or higher frequency side, of the Raman peak may dominate over the other. Figure 2.15 shows the Fano Raman lineshapes expected from heavily doped (Figure 2.15a & 2.15b).



Figure 2.15: Theoretical generated Raman line-shape for the different (positive & negative) values of electron-phonon coupling parameter q.

In Figure 2.15, in both the cases (A & B), a deviation from symmetry is evident on increasing the Fano coupling (decreasing q value).

2.5 Anharmonic Effect in c-Si

Crystal lattice dynamics of many systems has been explained on the basis of atomic vibrations, interacting waves from the atoms, and corresponding quasi-particle generated due to the vibrations i.e., phonons. The light getting inelastically scattered from lattice vibrating anharmonically behaves differently with temperature and contains information about various interconnected phenomena like scattering, anharmonicity, phonons[152]. Particularly in pure materials, the Raman line position and linewidth both vary with temperature as quantified and explained by M Balkanski *et. al.* This kind of temperature behavior in any material can be explained by the vibrational potential energy and the change in vibrational energy due to anharmonicity and can be observed in the terms of lattice vibrations in Raman spectra. The theory for the anharmonic effects influencing the Raman line-shape parameters was first given by Hart, Aggarwal and

Lax[153] who observed the cubic anharmonicity in Raman peak position and Raman spectral linewidth of Si. Hart & Aggarwal recorded the temperature dependent (TD) Raman spectra of c-Si over a broad spectrum of the temperatures from 20K to 770K and it was found that data for the Raman peak position agree with the theoretical observation given by Cowley et. al. [154], based on the second order cubic anharmonicity in the vibrational potential energy, but it the variation in linewidth was showing deviation from the Cowley's result. To remove this ambiguity in Raman spectral linewidth, M. Balkanski et. al., gave a new anharmonic theory in that he included both the anharmonic terms of vibrational energy i.e., cubic anharmonicity and quartic anharmonicity. Balkanski explained in his theory that at higher temperature range, inclusion of higher-order terms means involving cubic and quartic anharmonicity both are necessary to obtain a good data as only second order cubic anharmonic terms are not sufficient to make a satisfactory fit. Hence to explain the effect of temperature on Raman spectra, Balkanski considered an intrinsic Si (ρ ~100 Ω -cm, oriented with a (111) face). At low temperature range, Balkanski regulated the temperature of c-Si sample by He cryostat, for intermediate temperatures, an electrically heated furnace has been used, and by laser heating at higher temperatures. Therefore, the Raman spectrum obtained from the c-Si seems to be involved in the absorption of an incident photon, the emission of a photon (scattered photon), and the creation of an optical phonon (lattice vibration). The generated optical phonons decay into two phonons via temperature effect or anharmonicity into, and three phonons of lower energy. The process of annihilation of one phonon into two and three phonons is shown in Figure 2.15. Balkanski explained that the mechanism of production or annihilation of phonons can also occur by some other means which has been shown in Figure 2.15b & 2.15c:



Figure 2.15 (a-d): Schematic diagram represents the three and four phonon annihilation process of one optical phonon due to the anharmonic processes.

The phonon decay process with temperature affects the Raman spectra shows some changes in the lineshape which can be observed in the terms of the parameters of Raman spectrum i.e., shift in the position of the Raman peak and linewidth of the spectra. A comparison of Raman spectra at two different temperatures clearly shows how distinctly photons get scattered through the lattice phonons with changing temperatures. Balkanski has shown the two Raman spectra recorded from c-Si at two different temperatures 295K and 1140K which shows that the values of spectral parameters vary with temperature. The Raman peak position shows redshift as the temperature is increased, and the spectral linewidth gets broadened which has been explained by Balkanski very well as discussed below in detail.

2.5.1 Anharmonic Effect on the Raman spectra of c-Si

Balkanski has performed the temperature dependent (TD) Raman spectroscopy on c-Si and found that Raman spectra shows redshift and broadening in the Raman spectra with increasing temperature. Figure 2.16 shows the Raman spectra of c-Si at two different temperatures 295K and 1140K. From Figure 2.16 it can be observed that, at low temperature (295K, room temperature) the Raman peak position of the c-Si is at 520 cm⁻¹ but while increasing the temperature i.e., at 1140K, the Raman peak position gets shifted towards the lower frequency side and shows redshift (495 cm⁻¹) with broadening in the spectral linewidth.



Figure 2.16: Raman spectra of c-Si at different temperatures 295K and 1140K.

As mentioned in the above section that redshift in the peak position and broadening in the spectral linewidth arises due to the anharmonic decay of one optical phonon into two or three lower energy phonons. This theory is true for almost all the materials but there are few materials which do not follow this theory and show opposite results. In this thesis study, TD Raman study has been done for those materials which do not follow conventional anharmonic decay theory of phonons given by Balkanski and explored the reason behind non-anharmonic nature of those materials.

Chapter 3

Experimental Methodology and Sample Preparation

In this chapter, the fabrication techniques of different materials such as nanowires of the silicon substrate and nanorods of the rutile TiO_2 have been discussed. The characterization techniques used to characterize the materials have also been discussed in the current chapter. The instrumentation details of different characterization techniques have also been explained here. The sample preparation technique and specifications of all the samples under investigation are discussed in this chapter.

3.1 Material Synthesis Techniques

The sample used in the current thesis study i.e., silicon nanowires (SiNWs) and rutile TiO_2 nanorods (TNRs) have been fabricated using metal assisted chemical etching (MACE) and hydrothermal method. The detailed discussion about both the fabrication techniques is discussed below:

3.1.1 Metal Assisted Chemical Etching Process (MACE)

There are various techniques which are used to fabricate the SiNWs such as electron beam lithography[155], ion implantation, laser induced etching etc. Metal assisted chemical etching[156–163] (MACE) is one of the easiest and cost-effective techniques and it provides well aligned wire like structure of the silicon substrate. Basically, MACE is a two-step process in which the first is the deposition of metal nanoparticles such as Ag, Au, Pt, etc. onto the silicon substrate and the second step is the etching process. In the deposition process, metal nanoparticles are mixed with an acid like HF and make a solution and then the silicon substrate is dipped into that solution. In etching process, a solution is made up of an oxidizing agent (mostly H_2O_2) with HF and then the deposited substrate is dipped into that solution.

The metal nanoparticles deposited on the silicon substrate act as a catalyst in the etching process. These metal nano particles help the oxidizing agent to remove the silicon atom and make an etched surface faster. In this study, the chemicals used in the MACE process are AgCl₃ and as metal nano particles, HF to make chemical solutions, H₂O₂ & KMnO₄ as oxidizing agents. Apart from this distilled water (DI) water has been used to make the dilute solution and HNO₃ to remove additional layers from the etched surface.

Cutting & Cleaning of the Silicon Substrate

The well oriented silicon substrate of both the types i.e., n-type and p-type silicon has been cut with the help of a diamond cutter to the required dimensions. After cutting the substrate, the sample undergoes the cleaning process to remove any dirt deposited from the surface of the substrate. To clean the surface, DI, iso propyl alcohol (IPA) and acetone have been used. First, the substrate is dipped into the IPA and put into the ultrasonicator for 10 min and after that substrate is dipped into the acetone and again put into the ultrasonicator for 10 min followed by cleaning by DI water.

The Deposition of the Metal Nanoparticles: First Step of MACE

Before deposition process, the cleaned substrate is further cleaned in the piranha solution to remove the oxide layer formed on the surface of the silicon substrate. The piranha solution is made up in 3:1 ratio of H_2O_2 and H_2SO_4 . The substrate is dipped in this solution for 1 min and then washed with DI water. After this process, the wafer is kept into the HF solution for further cleaning. Then finally the wafer is washed by DI water and now the sample is ready for the deposition process.

For the deposition process, first the solution is made by mixing chemicals in the proper ratio. To make deposition solution, 4.8M HF and 5mM AgCl₃ have been mixed together. The Si substrate is then dipped into the solution for the deposition of the Ag metal nanoparticle for 1 minute and then rinsed with the DI water to remove additional layer of Ag metal nanoparticles.

Etching Process: Second Step of MACE

In the etching process, an oxidizing agent is used to oxidize the surface of the substrate. The main work of the oxidizing agent is to inject the holes into the valance band of the Si which depends upon the electrochemical potential of oxidizing agent. Generally, H_2O_2 is used as oxidizing agent to etch the Si substrate due to its high electrochemical potential. A detailed discussion about the electrochemical potential has been done in chapter 7. The solution for the etching process is prepared by using 4.6M HF and 0.5M H_2O_2 . The Si substrate has also been etched by using KMnO₄ (oxidizing agent, 0.5mM) instead of H_2O_2 to fabricate the SiNWs.

After that, metal nanoparticles deposited Si substrate is dipped into the etching solution and kept for 60 minutes. Figure 3.1 shows the etching process of Si substrate by using different oxidizing agents.



Figure 3.1: Etching mechanism of metal nanoparticles deposited Si substrate using different oxidizing agents, H₂O₂ (left panel) & KMnO₄ (right panel).

The oxidizing agent gets reduced at the metal sites and generates a large number of holes, the chemical reactions takes part into the etching process are discussed below:

$$H_2O_2 + 2H^+ \xrightarrow{\text{yields}} 2H_2O + 2h^+, \qquad (3.1)$$

This is accompanied by the oxidation of silicon surface and further gets dissolved in HF solution, causing the formation of SiF₄ followed by further hydrolysis to SiF_6^{-2} :

$$Si + 4h^+ + 4HF \xrightarrow{\text{yields}} SiF_4 + 4H^+,$$
 (3.2)

$$SiF_4 + 2HF \xrightarrow{yields} H_2SiF_6,$$
 (3.3)

$$Si + 4HF_2^{-} \xrightarrow{\text{yields}} SiF_6^{-2} + 2HF + H_2 + 2e^{-}, \qquad (3.4)$$

When H_2O_2 is used instead of KMnO₄, the hole generation step can be written as Eq. 3.5 below:

$$MnO_4^- + 8H^+ \xrightarrow{yields} Mn^{+2} + 4H_2O + 5h^+,$$
 (3.5)

By following these chemical steps in the etching solution, SiNWs has been formed and characterized by various techniques like scanning electron microscopy (SEM) to see the surface morphology of the prepared SiNWs and Raman spectroscopy to investigate the size of the SiNWs.

3.1.2 Hydrothermal Method

The hydrothermal method is one of the synthesis processes to fabricate the nanomaterials of different morphologies like thin film, nanotubes, nano powder, nanorods, etc. Hydrothermal method is a temperature-controlled process in which temperature can be reached from room temperature to high temperature (desired). This process is also a two-step process in which the first step is to put the chemical solution in the furnace and the second step is thermal annealing of prepared sample at high temperature.

The chemical solution required to fabricate the nanomaterials is put into the autoclave with the substrate on which the desired thin film needs to be deposited. Then the autoclave is kept in the furnace at the required temperature for a certain time period and after that the autoclave is left to

cool down for some time. And in the second step, the prepared sample is kept for the thermal annealing at a certain temperature for some time i.e., for one hour (usually). In this study, rutile TiO₂ nanorods[164–167] have been prepared by using hydrothermal method for further study.

Preparation of Chemical Solution

To prepare the chemical solution for the rutile TNRs, initially 15 ml of HCL and 15ml of DI water has been mixed in a glass beaker and stirred for 10 minute to make a uniform mixture. Then after stirring, 2 ml of Titanium Butoxide was added dropwise in the solution by using capillary tube and stirred the solution for one hour to make a homogenous solution of precursors present in an aqueous medium. The prepared solution and FTO substrate are kept into the teflon beaker where the conducting side of the FTO substrate is facing down, and this beaker is then kept into the autoclave of stainless steel.

Temperature Treatment

The whole setup i.e., autoclave with teflon beaker then kept into the furnace at 180°C for five hours to deposit a uniform thin film of the rutile TNRs on the FTO substrate. After that the autoclave is left to cool down for some time. Then the prepared sample has been rinsed with the DI water to remove residuals of the chemical from the substrate and then sample has been again kept into the furnace for thermal annealing. For annealing process, the sample has been kept at 180°C for two hours. The complete hydrothermal setup has been shown in Figure 3.2.



Figure 3.2: Schematic diagram represents the setup of the hydrothermal process with an autoclave and teflon beaker.

After the annealing process, the sample is ready for the further characterizations for which different techniques have been used such as SEM, Raman spectroscopy, and X-ray diffraction.

3.2 Characterization Techniques

The different characterization techniques which have been used to characterize the prepared samples in the current study are:

- a) Scanning electron microscope (SEM)
- b) Raman Spectroscopy
- c) X-ray diffraction (XRD)

The detailed discussion about the instrumentation of these techniques is discussed below.

Instrumentation Details

3.3 Scanning Electron Microscope

Using a high energy electron beam as a source, scanning electron microscopy (SEM) is a method for examining the surface morphology of

any material. Figure 3.2 represents a graphic representation of the entire setup. Different electron and photon signals are emitted from the specimen when it is exposed to these powerful electrons. These two emitted signals include X-rays (through thickness and compositional information), cathodoluminescence (electrical information), augur electrons (surface sensitive compositional information), secondary electrons (topographic information), backscattered electrons (atomic number and topographic information), and secondary electrons (topographic information). These signals are used to obtain various pieces of information about the specimen.

3.3.1 Secondary electrons

To determine the surface morphology, secondary electrons that are released after the specimen and incident electron contact are used. Due to inelastic scattering from the valence electron, secondary electrons with energies less than 50 eV are released from the object surface. Since the energy of the secondary electrons is very small (less than 50 keV) are occurred in the abundance.

3.3.2: Backscattered Electrons

After elastic interactions between the beam and the sample, the backscattered electrons are mirrored back. However, secondary electrons come from the sample's atoms. Depending on the element's weight, different backscattered electrons are produced. Heavier metals typically have a stronger ability to deflect incident electrons than lighter ones due to their larger nuclei. So, in contrast to lighter elements like silicon (atomic number 14), heavy elements like silver (atomic number 47), look brighter in a SEM image because more backscattered electrons are released from the sample surface.

3.3.3: X-Rays

In the sample, when an electron of the inner shell gets excited, then this electron gets displaced which attracts another electron from an outer shell to

fill the vacancy. As the electron moves from the outer higher-energy to the inner lower-energy shell of the atom, this energy difference can be released in the form of an X-ray. These generated X-rays are basically used for elemental analysis in SEM such as EDX.

3.3.4 Imaging in SEM

The size of the space where the electron beam interacts with the sample depends on the energy of the beam, the shape of the interaction volume, and the atomic number.



Figure 3.2: Schematic diagram represent the ray diagram of scanning electron microscope (SEM).

3.3.5 Different Components of the SEM

Electron Gun

A SEM instrument with a FE electron gun creates images with higher resolution than others. For this, a single tungsten crystal is placed inside a tungsten filament that serves as the cathode. The emitter portion of this tungsten crystal has a 100 nm curvature at its apex. The crystal responsible for firing the electron stream from the gun is given a high potential (negative). The entire electron cannon setup is maintained at a high pressure of about 10^{-8} Pa.

Condenser Lens

To change the diameter of the electron beam, lenses are used below the electron gun. When a strong or weak field is applied, the condenser lens's strength determines whether the electron beam will be narrower or wider. A small hole on the aperture plate, which is maintained between the condenser lens and objective lenses, allows this electron beam to pass through.

Scanning Coils

The impact of a magnetic field can deflect a travelling electron beam because it has an electric charge. The electron beam travels through the scanning coil and may sweep over the samples because the field is created and varied by passing the variable current in the coil. It is possible to scan a larger area of the material by sweeping the electron beam. Lower resolution and more noise are the outcomes of faster scanning.

Detector

There are many detectors available inside the chamber to detect various emissions, discussed above. The detector detects secondary and backscattered electrons coming from the material at various angles and with varying velocities and densities. Produced photon from the screen is amplified by an attached transducer and given to the display as a video signal. In this work SEM images were recorded using Supra55 Zeiss, an oxford instrument.

3.4 X-Ray Diffraction (XRD)

X-Rays are electromagnetic radiation having shorter wavelengths, typically of the order of 1Å, and diffracts when interact with the crystal where the lattice planes act as diffraction element. In crystallography, XRD is a main characterization technique to get the composition and purity of samples. A brief mechanism of XRD from a sample is shown in Figure 3.3 and the same is being described here.

3.4.1 Generation of X-Ray

X-rays are generated when sample is irradiated by a beam of high-energy charged particles such as electrons. In the laboratory, a filament is heated to produce electrons which are then accelerated in vacuum by a high electric field in the range 20-60 kV towards a metal target, which being positive is called the anode. When electrons lose their energy, an electromagnetic radiation emits which is known as the continuous X-ray. Higher shell electron fills the vacancies on lower shell and emits the electromagnetic radiation corresponds to the transition energy levels' difference, called characteristic (monochromatic) X-ray. These X-ray consist of high energy K_{α} and K_{β} radiations having wavelength near about 1.54 Å, a typical value for the copper target. The most widely used target material for X-ray generation is copper, which fulfils the engineering as well as crystallographic conditions.

3.4.2 Diffraction Pattern

The X-rays coming from the source interact with the electron cloud of atom of material placed at sample holder over the goniometer. All atoms behave

as diffraction centre and the crystal behave as a grating to diffract X-rays. A diffraction pattern is formed by following the Bragg's diffraction condition.

$$2d\sin\theta = n\lambda,\tag{3.6}$$

$$\frac{n\lambda}{2d} \le 1,\tag{3.7}$$

where, λ , d and θ are wavelength, interplanar spacing and diffraction angle respectively (Figure 3.4).



Figure 3.4 Schematic diagram represents an X-ray diffraction spectrometer.

3.4.3 Detector

The source, sample stage and detector are kept in a spherical geometry (called Ewald sphere), in which both source and detector can vary between 0^0 to 90^0 . All the constructive interference signals coming from the sample is detected by the detector and plotted as a function of diffraction angle (2 θ). This diffraction pattern contains information about different miller indices, corresponding to a lattice plane and thus used to draw the information about the sample phase purity, interatomic spacing, bond length/angle etc. In this work XRD pattern was taken using D8, advance Bruker instrument.

3.5 Raman Spectroscopy

When a monochromatic beam of visible light illuminates any material, a fraction of light gets scattered in all directions. The scattered radiation consists almost entirely of the incident frequency, known as Rayleigh below the incident frequency which is called the Raman component. The lines on the low frequency side of the exciting line are called 'Stokes' lines, whereas those on the high frequency side are called 'antistokes' lines. Therefore, Raman process is a weak and inelastic process. Though a weak process, Raman spectroscopy has now been used as a versatile tool to investigate the different physical phenomena taking place at microscopic levels like confinement, chemical compositions, defect states etc. Various components of a typical Raman spectrometer, schematically represented in Figure 3.5, is being discussed below.

3.5.1 Excitation Source

A high intense monochromatic laser beam is used to illuminate the samples for measuring the Raman bands. Appropriate laser source is chosen based on the nature of samples. Most used lasers include argon laser (514 nm and 488nm), He-Ne laser (633 nm), and diode lasers (532 nm, 785nm, 976 nm etc.) with an option of variation in power.



Figure 3.5: Schematic diagram represents the setup of the Raman spectrometer.

3.5.2 Microscope

For focusing the laser on samples at various areas, optical lenses with various magnification and numerical aperture are used, and high magnification reveals lenses with high resolution. The backscattered light originates from that particular sample region and is collected for further use using the same optical lens.

3.5.3 Grating

Grating is a gathering of various line spacings or grooves from which light is scattered; the resolution depends on the density of the grooves. High dispersion amount used to compromise decreased intensity to achieve higher resolution.

3.5.4 Filter

Raman spectrometers use optical filters with Rayleigh notches to cut and pass the intended scattering wavelength. Rayleigh filtering is used to eliminate the Rayleigh component from the dispersing light because the spectrometer operates in the backscattering mode, allowing all Raman bands to pass. In addition to the Stokes Raman line, notch filters are used to produce the anti-Stokes Raman line.

3.5.5 Detector

Due to their great quantum efficiency and low signal to noise ratio, CCD detectors are currently used in the design of Raman spectrometers. Small light-sensitive CCD pixels are exposed to scattered light from the sample, which produces the corresponding signal strength at various positions. (Called Raman shift). A CCD is a multi-channel array detector built on silicon that operates with a Peltier device at a temperature of about -70°C. **Model used:** Horiba LabRam Jobin Micro-Raman spectrometer.

Chapter 4

Nonlinear Temperature Dependent Fano Interaction in Heavily Doped p- type Silicon

This chapter reports nonlinear temperature dependent (TD) Fano interaction in heavily doped p-type Si. A parabolic temperature-dependent Raman spectral parameter behavior has been seen. To investigate the behavior of anharmonic phonon decay in Si systems where Fano interactions are present inherently, temperature-dependent Raman spectroscopic studies have been carried out on differently doped crystalline silicon. It has been revealed that in heavily doped systems an interferon mediated decay route exists for cold phonons present at lower temperatures. To validate the theory of nonlinear decay of phonons through interferon mediation and to prove that this process is thermodynamically favorable, temperature-dependent phonon self-energy have been calculated using experimentally observed Raman line-shape parameters. This study has been published in the peer reviewed journal of ACS publication[168]^{\$}.

^{\$}Chanchal Rani et al. J. Phys. Chem. Lett., 13, 23, 5232-5239, 2022

4.1 Nonlinear Phonon Decay in Heavily Doped Semiconductor

In heavily doped semiconductors, high charge carrier density can induce a thermal (lattice) phonon distribution at zone boundaries and may cause a nonlinear decay of phonons with increasing temperature. These lattice phonons are generated in abundance because of the slower anharmonic decay in comparison with faster generation rate and cause a bound state of charge carrier and phonon or electron-phonon interaction and converts into interferons. As mentioned earlier, Fano interaction is the mixing of a configuration belonging to a discrete spectrum with a continuous spectrum configuration meeting a certain energy requirement for such interaction to be thermodynamically favorable. It can be observed through spectroscopic tools when the quantum interference takes place between two competing optical pathways, one connecting the energy ground state and an excited discrete state, the other connecting the ground state with a continuum of energy states.

Fano interaction in nonlinear regime (Nonlinear Fano effect) has been explored in hybrid systems made up by metal nano particles and semiconductor quantum dots[169–171]. There is no thermodynamic restriction that prohibits its occurrence in semiconductors provided appropriate variables are probed under suitable perturbations of course if the energy compatibility required for this interaction is met. In view of this, it would be interesting to explore semiconductors, a technologically important material, under suitable perturbations that may lead to observations of nonlinear Fano interaction. A thorough analysis of TD Raman spectral behavior has been carried out as reported below.

4.2 Temperature-Dependent Raman Spectra and phonon decay channel in heavily doped p-Si

A TD Raman spectroscopy have been carried out (Figures 4.1 A & B) from p-type Si wafers doped with different dopant (boron) concentrations (samples P⁺⁺ and P^{+,} in abbreviations) to investigate the thermal response of phonons through possible phonon-phonon and electron-phonon interactions in sample P⁺⁺ and P⁺. The obtained TD Raman spectra for both the samples have been compared with the existing undoped system (Balkanski's experimental Raman spectra, say i-Si).



Figure 4.1: (A) Temperature dependent Raman spectra from heavily doped (sample P⁺⁺) and, (B) Temperature dependent Raman spectra from moderately doped c-Si (sample P⁺).

From Figure 4.1, a typical redshift in Raman peak position for both the samples ($P^{++} \& P^{+}$) with increasing temperature can be seen. To observe these changes in Raman spectra with temperature, Raman spectral parameters i.e., peak position and linewidth have been calculated for both

the samples (Figure 4.2A) and have been compared with the undoped (i-Si) samples (taken from literature). From Figure 4.2A, the TD Raman red-shift variation of moderately doped sample (P⁺, red curve) is similar to the variation predicted for an intrinsic Si, (Balkanski *et. al.*,), the latter predicts an underestimated values of Raman red shift in comparison with the experimentally observed values.



Figure 4.2 (A) Variation in Raman peak-position with temperature for i-Si (blue), P^+ (red) and P^{++} (green) sample, respectively. (B) Variation in spectral-linewidth with temperature for i-Si (blue), P^+ (red) and P^{++} (green) sample, respectively.

Since sample P⁺ is moderately doped with boron dopant atoms, therefore at a given temperature an additional redshift (in comparison with the i-Si) is expected due to Fano interaction which is responsible for the abovementioned difference between the relative TD red-shift variation (red & blue curves, Figure 4.2A). On the other hand, the TD Raman peak redshift exhibited by heavily doped sample (P⁺⁺, green curve Figure 4.2A) shows additional Raman shift with respect to the i-Si (blue curve, Balkanski theory) as well as P⁺ (red curve). It is important to notice that the overall TD variation of Raman peak position remains same meaning for all the three samples i.e., i-Si, P⁺, and P⁺⁺. Apart from this, another observation from Figure 4.2A is the different TD variation trend of Raman peak position for sample P⁺⁺ which shows the same trend as of the sample P⁺ at higher temperatures (T>475K) but in low temperature range, Raman peak position is more shifted towards lower frequency region. This indicates that the thermal effect on the e-phonon interaction in moderately doped and heavily doped Si is not only different from each other but also has different TD trends.

To further confirm the presence of Fano interaction in both the samples P⁺ & P⁺⁺ (Figure 4.2B), the phonon energy variation with temperature has been calculated and observed that whether the phonon lifetime follows the Balkanski theory of TD behavior or otherwise. Sample P⁺ shows increasing linewidth with increasing temperature (Figure 4.2B) similar to the predictions of anharmonic decay theory, with the former showing an additional linewidth likely due to contribution form the Fano interaction, inherently present in doped Si. More interestingly, a nonlinear TD variation in linewidth is observed for sample P⁺⁺ showing a parabolic nature where the linewidth decreases with increasing temperature in the range of 150K-475K (say low temperature range) and reaches a minimum value of 13.5 cm⁻¹ (Figure 4.2B) corresponding to 475K temperature. On increasing the temperature above 475K, linewidth starts increasing again following similar trend as predicted by Balkanski's anharmonic theory with some additional linewidth due to the somewhat presence of Fano interaction at higher temperatures.



Figure 4.3: Fitting of experimentally observed Raman spectra with theoretically generated spectra using Fano lineshape function at room temperature.

To confirm the presence of Fano interaction in sample P^{++} , a theoretical line-shape function has been used to fit the experimentally observed Raman data at different temperatures as shown in Figure 4.3A for Raman data recorded at 300K for representation with the established Fano-Raman line-shape function given as in chapter 2, Eq 2.11.

Figure 4.3 shows the theoretical fitting (solid line, Eq. 2.11) of experimental Raman data (discrete points) from sample P⁺⁺ recorded at room temperature and shows a very good fitting further confirming the presence of Fano interaction in the heavily doped sample.



Figure 4.4: The zoomed view of Raman spectra of P^{++} sample at room temperature to show the antiresonance dip.

Further confirmation of Fano interaction can be obtained by looking at the antiresonance which is very clear from Figure 4.4 showing the zoomed portion of Raman data from sample P^{++} at room temperature. The asymmetric Raman lineshape (right side, Figure 4.4) and accompanying antiresonance dip (left side, Figure 4.4) confirms the presence of Fano interaction. It is important to mention here that in the present case, the antiresonance is on the low energy side of the peak whereas the spectral half width is more on the higher energy side of the peak making it asymmetric which is a typical observation from p-type material.

The TD Raman data of sample P^{++} (Figure 4.1A) have been fitted by using the Fano strength parameter, q, as the fitting variable and the variation of Fano strength parameter (1/q) with temperature has been observed (Figure 4.5).



Figure 4.5: Variation of inverse of Fano strength parameter 1/q with temperature.

Figure 4.5 shows that at a given temperature, in addition to the anharmonic effect, Fano interaction is also present which weakens with increasing temperature. The TD variation of Fano strength parameter reveals the following.

At temperatures below 475K, cold phonons are strongly bound in the interferons form which is consistent with the existing theories used to understand the origin of Fano interaction.

4.3 Observation of Nonlinear Decay of Phonons in p-Si

The non-linear TD variation in the Raman line width of sample P⁺⁺ shown in Figure 4.2, can be understood as follows which reveals interesting facts:

In the low temperature range (green curve, Figure 4.2B) due to the high concentration of dopant atoms, the phonons are bound to the charge carriers i.e., electrons and convert into interferons (the e⁻ph bound state) hence Fano effect dominates. In the high temperature range, most of the interferons break, and anharmonic effects start to dominate. In other words, in the higher temperature region, typical anharmonic three- and/or four- phonon process dominates due to weaker Fano interaction.



Figure 4.6: (A) Schematic diagram of phonon decay process in intrinsic semiconductor. (B) Schematic diagram of non-linear phonon decay process in heavily doped semiconductor.

It is clear that in heavily doped systems two types of phonon decay routes are possible namely, through interferon formation and through decay into multiple phonons. Figure 4.6 shows schematic representation of the two abovementioned different pathways of phonon decay in different systems. In systems where no Fano-interaction is possible (e.g., intrinsic semiconductors), increasing phonon-phonon interaction on increasing temperatures leads to the typical anharmonic phonon decay as shown using the schematic in Figure 4.6A which leads to the linear trend of Raman spectral linewidth with temperature (Figure 4.2B, T> 475 K). On the other hand, systems with inherent Fano interaction, has an additional pathway by following which phonons can get annihilated through a process mediated by interferons (Figure 4.5B) upto a certain temperature and after that temperature, conventional anharmonic phonon decay is followed.

4.4 Validation through Phonon-Self Energy of p-Si

To validate the nonlinear phonon decay in heavily doped systems (P^{++}), a theoretical analysis of phonon self-energy has been carried out. Phonon self-energy is the associate self-energy of phonons which is a complex function of peak shift and linewidth of the Raman spectra[172–176]. Hence the total change in linewidth and Raman peak position due to both the effects i.e., phonon-phonon interaction or anharmonic effect and e-phonon interaction or Fano effect has been calculated using experimental TD Raman spectral parameters and consequently the phonon self-energy has been calculated. From the nonlinear trend (with temperature) of the Raman spectral linewidth of P^{++} sample (Figure 4.2), the total linewidth can be expressed as the combination of linewidth due to anharmonic effect and Fano effect which can be written as Eq. 4.1:

$$\Gamma = \Gamma_{an} + \Gamma_{Fano}, \tag{4.1}$$

where, Γ_{an} is the anharmonic phonon linewidth and Γ_{Fano} is the linewidth due to Fano effect. To calculate the perturbed parameters of Raman spectra due to both the perturbations, the atoms of the system are at positions **R**_s, where 's' labels the different atoms of unit cell and **R** is the direct lattice vector, at equilibrium, has been considered by Balkanski *et. al.*

On considering the phonon-phonon interaction due to temperature, the spectral linewidth has been affected according to the Balkanski's anharmonic theory which can be written as Eq. 4.2:

$$\Gamma_{an} = \frac{1877}{\hbar^2} \sum_{\mathbf{k}_1, j_1} \sum_{\mathbf{k}_2, j_2} |V(0, j; \mathbf{k}_1, j_1, \mathbf{k}_2, j_2)|^2 \times [(n_1 + n_2 + 1)\{\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)\} + (n_1 - n_2)\{\delta(\omega + \omega_1 - \omega_2) - \delta(\omega - \omega_1 + \omega_2)\}],$$
(4.2)

Eq. 4.3 can be solved to obtain Eq. 4.3

$$\Gamma_{an} = \frac{\pi}{2\hbar^2} \sum_{\mathbf{k}_1, j_1, \mathbf{k}_2, j_2} |V(0, j; \mathbf{k}_1, j_1, \mathbf{k}_2, j_2)|^2 \Delta(-k + k_1 + k_2) \left[\{ n(\mathbf{k}_1, j_1) + n(\mathbf{k}_1, j_1) + 1 \} \{ \delta \left(\omega - \omega_{j_1}(\mathbf{k}_1) - \omega_{j_2}(\mathbf{k}_2) \right) \} + 2 \{ n(\mathbf{k}_1, j_1) - n(\mathbf{k}_1, j_1) + 1 \} \{ \delta \left(\omega + \omega_{j_1}(\mathbf{k}_1) - \omega_{j_2}(\mathbf{k}_2) \right) \} \right],$$

$$(4.3)$$

On solving the perturbation expansion of the total energy with respect to the phonon amplitude, the total anharmonic width in a phonon frequency ω and wave vector k in jth branch, which is the sum of cubic and quartic anharmonicities can be written as Eq 4.4:

$$\Gamma_{an} = \frac{2 \Pi}{\hbar} \sum_{f} |\langle i|E_{tot}|f\rangle|^2 \delta(E_i - E_f), \qquad (4.4)$$

Similarly, the linewidth induced by the Fano interaction depends upon the electron-phonon matrix element and density of states explained by Cardona *et. al*[177].

Therefore, the Fano induced linewidth can be given as Eq. 4.5[84]:

$$\Gamma_{Fano} = \Pi V^2 D(\omega), \qquad (4.5)$$

Replacing the terms including $D(\omega)$ and V, the function for Γ_{Fano} is given as Eq. 4.6:

$$\Gamma_{Fano} = \frac{a \Pi D_0^2}{\omega_0 \kappa \hbar^2} \bigg[E_F - \frac{\hbar^2}{2m_l} \Big(K - \frac{\omega m_l}{2\kappa \hbar} \Big)^2 \bigg], \tag{4.6}$$

where D_0 is the deformation potential, m_l is the longitudinal mass of the band. Hence, total spectral-linewidth due to the anharmonic effect and Fano interaction is given by Eq. 4.7:

$$\Gamma = \frac{2 \Pi}{\hbar} \sum_{f} |\langle i|E_{tot}|f\rangle|^2 \delta\left(E_i - E_f\right) + \frac{a \Pi D_0^2}{\omega_0 K \hbar^2} \left[E_F - \frac{\hbar^2}{2m_l} \left(K - \frac{\omega m_l}{2K \hbar}\right)^2\right],$$
(4.7)

The perturbed Raman peak-position by both the perturbations i.e., anharmonic effect and Fano interaction has also been calculated. Since the

anharmonicity arises due to the decay of phonons through three- or fourphonon process therefore $\Delta \omega_{an}$ can be written as Eq 4.8[77]:

$$\Delta \omega_{an} = \Delta_j^{(0)} + \Delta_j^{(3)}(\omega) + \Delta_j^{(4)}(\omega),$$
(4.8)

In Eq 4.9, 3^{rd} term is real and related with the fourth order derivative of the total energy and the first two terms represent the change in frequency due to the thermal expansion of lattice. Therefore, the expression for the $\Delta \omega_{an}$ can be written as Eq. 4.9:

$$\Delta\omega_{an} = \omega_j \left\{ exp\left[-3\gamma_j \int_0^T \propto (T')dT' \right] - 1 \right\} - \frac{2}{\Pi} P \int_0^\infty \frac{\omega' \Gamma_j(\omega')}{\left(\omega'^2 - \omega^2\right)} d\omega' + \frac{12}{\hbar} \sum_{q_1, j_1} \frac{\partial^4 E_{tot}[2n(\mathbf{k}_1, j_1) + 1]}{\partial e(\mathbf{k}; j) \partial e(-\mathbf{k}_1; j_1) \partial e(-\mathbf{k}_1; j_1)},$$

$$(4.9)$$

Apart from this, the Fano induced shift depends upon the electron-phonon and Raman matrix element given be Cardona *et. al.* Therefore, the Fano induced shift can be given as $\Delta \omega_{Fano} = V^2 R(\omega)$

By putting the values of electron phonon matrix element V and Raman matrix element $R(\omega)$, the expression will take the form given in Eq. 4.10:

$$\Delta\omega_{Fano} = \frac{4D_0^2}{a^2} \frac{\hbar}{4MN\omega_0} \int D(\omega') \left[\frac{1}{(\omega - \omega')} + \frac{1}{(-\omega - \omega')} \right] d\omega', \qquad (4.10)$$

The total change in Raman peak-position due to the combination of anharmonic effect and Fano interaction can be given as Eq. 4.11:

$$\Delta \omega = \Delta_j^{(0)} + \Delta_j^{(3)}(\omega) + \Delta_j^{(4)}(\omega) + \frac{4D_0^2}{a^2} \frac{\hbar}{4MN\omega_0} \int D(\omega') \left[\frac{1}{(\omega - \omega')} + \frac{1}{(-\omega - \omega')}\right] d\omega', \qquad (4.11)$$

Hence, in heavily doped system (P^{++}) where nonlinear Fano interaction exists and dominates in a particular temperature region and the parameters of Raman spectra varies as predicted by the above equations.



Figure 4.7: (A) Phonon self-energy of $P^{++}(\text{green})$, P^{+} (red) and i-Si (blue) sample with temperature, respectively. (B) Difference of phonon-self energies of $P^{++}(\text{green})$ and $P^{+}(\text{red})$ with respect to the thermal phonon energy (i-Si, blue), respectively.

To explain and validate this nonlinear decay of phonons phenomenon in heavily doped systems, phonon self-energy has been calculated (Figure 4.7) by using experimentally observed Raman spectral parameters (peak shift and linewidth, Figure 4.2). As mentioned above, Phonon self-energy (Σ) is written as the amplitude of the complex function of Raman parameters as $[\Sigma = \Delta(\omega) - i\Gamma(\omega)]$, where the real part $\Delta(\omega)$ represents the Raman shift and the imaginary part $\Gamma(\omega)$ represents the Raman spectral linewidth. The values of $|\Sigma|$ have been calculated for samples P⁺⁺ and P⁺ and i-Si shown in Figure 4.7.

From Figure 4.7, it is clear that the phonon self-energy increases monotonically for sample P⁺ (red curve), similar to the predictions of the Balkanski theory (i-Si, blue curve, Figure 4.7A) which means that in the moderately doped c-Si phonons decay through a process similar to the anharmonic decay. It means that anharmonic perturbations in undoped and moderately doped samples affects the Raman spectra as discussed above in the context of TD variation of Raman peak shift & peak width (Figure
4.2A). On the other hand, for heavily doped c-Si (sample P⁺⁺) self-energy decreases with increasing temperature (green curve, Figure 4.7A) showing a trend similar to the Raman spectral width (Figure 4.2B) in the low temperature regime (150K-475K). At temperature higher than the Tn (=375K), self-energy increases like the one seen for moderately doped samples (P⁺) which is also similar to the pure anharmonic type of behavior. It is clear from Figure 4.7A that in heavily doped samples, at temperatures other than 375K, the phonon decay rates are higher as compared to the rate at 375K.

Therefore, to understand the nonlinear trend of phonon self-energy for P⁺⁺ sample and different pathways for phonon decay in the temperatures higher and lower than 375K, individual process specific self-energies have been estimated by subtracting the anharmonic contribution (blue curve, Figure 4.7A) from the total contributions (Red and green curves for sample P⁺ and P⁺⁺ respectively, Figure 4.7A) obtained experimentally. To understand the above-mentioned phenomena, phonon self-energies have been added and subtracted linearly which can be explained by considering the wavevector of incident and scattered photon can be written as follows:

$$|\psi^{i}\rangle = |\Psi^{i}_{T}\rangle + |\Psi^{i}_{\beta}\rangle \& |\psi^{s}\rangle = |\Psi^{s}_{T}\rangle + |\Psi^{s}_{\beta}\rangle$$

where $\Psi_T \& \Psi_\beta$ are the wavevectors of thermal and electron-phonon interaction respectively. Hence, the eigen value of Hamiltonian can be written in the form of phonon-self energies as given by Eq. 4.12:

$$\widehat{H} \mid \Psi_{\beta}^{i} \rangle = \Sigma_{\beta} \mid \Psi_{\beta}^{s} \rangle \qquad \& \qquad \widehat{H} \mid \Psi_{T}^{i} \rangle = \Sigma_{T} \mid \Psi_{T}^{s} \rangle \tag{4.12}$$

Here in Eq 4.12, $\Sigma_{\beta} \& \Sigma_{T}$ are the Fano and thermal phonon-self energies. In order to the perturbation expansion, the average value of Hamiltonian has been calculated to understand the relation between total self-energy with individual thermal & Fano self-energies which can be shown in following Eq:

$$\left\langle \Psi^{s} \middle| H \middle| \Psi^{i} \right\rangle = \left(\left\langle \Psi^{s}_{T} \middle| + \left\langle \Psi^{s}_{\beta} \middle| \right\rangle \middle| \widehat{H} \middle| \left(\middle| \Psi^{i}_{T} \right\rangle + \left| \Psi^{i}_{\beta} \right\rangle \right), \tag{4.13}$$

$$\Sigma\langle\Psi^{s}\mid\Psi^{s}\rangle = \left(\langle\Psi_{T}^{s}\mid+\langle\Psi_{\beta}^{s}\mid\right)\left(\Sigma_{T}\langle\Psi_{T}^{s}\mid+\Sigma_{\beta}\langle\Psi_{\beta}^{s}\mid\right),\tag{4.14}$$

$$\Sigma = \Sigma_T \langle \Psi_T^s \mid \Psi_T^s \rangle + \Sigma_\beta \langle \Psi_\beta^s \mid \Psi_\beta^s \rangle, \tag{4.15}$$

$$\Sigma_0 = \Sigma_T + \Sigma_{\beta'} \tag{4.16}$$

From Eq. 4.16, it is clear that Fano related self-energies (Σ_{β}) can be obtained by simply subtracting the thermal self-energy (Σ_{T}) from the total self-energy (Σ_{0}). As mentioned above, to validate the non-linear decay of phonons thermodynamically, the difference of self-energies of P⁺⁺ & P⁺ has been taken (Figure 4.7B) with respect to the self-energy of i-Si sample (Balkanski theory) which has been considered as the thermal self-energy due to no doping. Therefore, from Figure 4.7B, the observations have been made that:

- For sample P⁺⁺ Fano self-energy is more than the thermal selfenergies in the low temperature range which confirms that phonon annihilation is mediated by interferons.
- And in the high temperature range thermal self-energy has higher values than the Fano self-energy which means that phonon annihilation is dominated by the phonon-phonon interaction or anharmonic decay of phonons.
- For P⁺ sample, the thermal self-energies are more than the Fano selfenergies at every temperature which confirms that phonon are annihilated via anharmonic channel only.
- An elaborate and consolidate analyses confirms that in heavily doped semiconductor system like Si, there exists multiple phonon decay pathways unlike moderately doped or undoped semiconductor due to a Fano interaction responding non-linearly under thermal perturbations.

4.5 Fano interaction at Ultra-Low Temperatures

Above discussions show that at lower temperatures, strong Fano interaction is observed. It will be interesting to see the strength at ultra-low temperatures below liquid N₂ temperatures. To observe this TD Raman spectra has been recorded upto ultra-low temperature $\sim 6K$ of heavily doped p-Si with resistivity 0.0001 Ω -cm. Figure 4.8 shows the TD Raman spectra of p-Si at different temperatures 6K (blue curve), 50K (green curve) and 100K (red curve). It can be seen from Figure 4.8 that, at very low temperatures the Raman spectra become completely asymmetric where the Raman peak is completely replaced by the anti-resonance dip in the lower frequency side (similar to Figure 4.3). This is consistent with the studies reported by K. P. Jain *et al.*, which shows that Raman lineshape broadens appreciably, becomes asymmetric and develops an antiresonance on the low energy side of the resonance as the boron acceptors or the wavelength of the incident photons is increased, or the temperature is lowered.



Figure 4.8: Low temperature Raman spectra of p type c-Si with resistivity (0.0001 Ω -cm).

Figure 4.9 shows the fitting of the experimentally observed TD Raman data at different temperatures with the theoretically generated Raman lineshape using Eq 2.11 (chapter 2) and Fano strength parameter "q" has been calculated. From Figure 4.9A, it is clear that at high temperature (100K), the Raman spectra has high value of $q\sim0.58$ which means less Fano interaction present while at low temperature (6K, Figure 4.9B), $q\sim0.42$ has a small value which confirms the very high strength of Fano interaction.



Figure 4.9: (A & B) Fitting of experimentally observed Raman spectra with theoretically generated spectra using Fano lineshape function at 100K (red curve) and 6K (green curve), respectively.

To explain this temperature dependence of Raman spectra the intensity of Raman spectra due to interband electronic Raman scattering was considered as below[178]:

$$I_{el} = \sum_{bb'}^{k} f_{bk} (1 - f_{b'k}) |\hat{e}_{l} A \hat{e}_{s}|^{2} \delta\{\omega - [(E_{b'k} - E_{bk})/\hbar]\}, \qquad (4.17)$$

where $\hat{e}_l \& \hat{e}_s$ are the polarization directions for incident photon and scattered photon during Raman scattering, and f_{bk} is the occupation probability of electrons given by Fermi distribution function.

According to previous studies, the lineshape depends upon the temperature and the doping concentration. It means that temperature plays a role in Raman scattering in the following two ways[179]:

- (a) The Bose factor giving the phonon occupation number
- (b) The Fermi factor f_{bk} affecting the joint density of states.

It is known that the variation of electronic Raman scattering with doping concentration comes in through the chemical potential in the Fermi functions[180,181]. As doping concentration increases, chemical potential increases and together with the intervalence band structure of Si, this leads to an overall enhancement of the electronic Raman scattering. The Fermi function also plays an important role in temperature dependence through chemical potential. As temperature decreases, chemical potential increases which leads to increase the electronic Raman scattering in silicon which results the high strength of interference effect. In ultra-low temperature range, dominant electronic Raman scattering dictates the Raman line-shape due to scarce phonon mediated Raman scattering.

4.6 Summary & Conclusion

The heavily doped p-Si shows a deviation from the established pureanharmonic type TD variation in Raman line width in the low temperature range (150-475K) showing an increasing line width with decreasing temperature meaning a faster phonon decay at lower temperatures. This atypical faster decay of cold phonons is observed due to the annihilation of these cold phonons through interferon mediated process. At low temperatures, the Fano coupling is strong thus leading to a faster phononinterferon conversion providing an alternate path for phonon decay other than the known anharmonic three- (four-) phonon decay process. Fano coupling strength decreases with increasing temperature revealing weakening of Fano coupling at higher temperatures allowing the phononphonon decay process to dominate over the interferon mediated phonon decay. Furthermore, process free-energies, estimated from the experimental TD Raman data reveals that in the low temperature range, interferon mediated decay of (cold) phonons is thermodynamically more probable whereas hot phonons prefer to decay through typical phonon-phonon process. Investigations reveal the presence of an alternate phonon decay process where annihilation of cold phonons takes place through an interferon mediated decay process.

On the other hand, Fano interaction gets stronger in ultra-low temperature range in heavily doped p-Si due to the high electronic Raman scattering. At ultra-low temperatures, the Raman peak disappears and a prominent anti-resonance dip in the lower energy side is present exclusively. At ultra-low temperatures, the Fano effect is stronger due to the electronic continuum excitations which leads to the autoionization of the charge carriers. The Raman spectral line width, thus the phonon lifetime, varies non-linearly with temperature in c-Si heavily doped with boron.

Chapter 5

Existence of Quasi-Microphase and Energy-Dispersive Anti-Anharmonic Effect in Degenerate Silicon

This chapter deals with two very important observations firstly, existence of interferon and phonon rich quasi stable microphases and secondly an energy dispersive anti-anharmonic effect in heavily doped Si. An unusual anti-anharmonic effect has been investigated by temperature and wavelength dependent Raman spectromicroscopy. Additionally, a temperature dependent quasi phase transition in heavily doped Si has also been studied using TD Raman spectroscopy and Raman microscopy. The experimentally observed TD Raman data has been used to propose an empirical formula has been proposed to calculate thermal energy for dissociating an interferon. The work reported here has been published in the following journals[182,183][§].

^{\$}Chanchal Rani *et al.* Phys. Chem. Chem. Phys., 25, 3, 1627-1631, (2022) ^{\$}Chanchal Rani *et al.* J. Phys. Chem. C, 126, 46, 19858-19865, (2022)

5.1 Interplay Between Two Perturbations in Heavily Doped Si

It is always interesting to understand how interplay between two perturbations, affecting any physical process, get manifested in a semiconductor. Fano coupling strength varies as a function of excitation wavelength in addition to the temperature of the system which makes it likely that the overall process ends up being energy dispersive when both of these are present in a system. Under different thermal perturbations, changes in Raman spectral position (phonon energy) and spectral width (phonon lifetime) in the Raman spectra of heavily doped Si have been reported previously using Balkanski's anharmonic theory or non-linear Fano interaction and also explained in chapter 4, but the change in strength of Fano interaction with excitation wavelength and temperature together needs to be explored which can also be identified using Raman scattering. It is well-known that at longer excitation wavelengths electron-phonon makes a strong bound state of interferons apparently requires higher thermal energy to dissociate the interferon. Any variation in temperature may directly affect the strength of these interferons which equally get affected by wavelength. A TD Raman spectroscopy carried out at different excitation wavelengths will reveal important phenomena taking place in heavily doped Si as discussed below.

5.2 Wavelength and Temperature Dependent Raman Spectroscopy of P⁺⁺ Sample

To understand the effect of thermally induced Fano interaction at different excitation wavelengths, and the strength of bound state electron-phonon (i.e., interferon) binding energy, TD Raman spectra from P⁺⁺ sample with two different excitation wavelengths 785 nm & 532nm has been recorded

(Figure 5.1). The presence of Fano interaction in P^{++} sample can be confirmed from the anti-resonance dip and asymmetry present in the obtained TD Raman spectra as discussed in chapter 4.



Figure 5.1: Raman spectra recorded at different temperatures from sample P⁺⁺ at different wavelengths (A) 532nm, (B) 785nm.

As it is known and reported that, at longer excitation wavelength, Fano interaction is more prominent, means the strength of Fano interaction is directly proportional to the excitation wavelength. This can also be confirmed from the TD Raman spectra of P⁺⁺ sample recorded at different wavelengths 532nm and 785nm. In Figure 5.1A, it can be seen that at shorter wavelength i.e., 532nm, the Raman spectra is less asymmetric and shows a less prominent anti-resonance dip while at higher wavelength i.e., at 532nm (Figure 5.1B), the Raman spectra is comparatively very high asymmetric and shows a high prominent anti-resonance minimum.

On the other hand, as explained in chapter 4, temperature plays a different role in the different systems. In intrinsic systems, where no doping is present, temperature provides thermal energy to annihilate the phonons into lower energy phonons i.e., phonon-phonon interaction. In heavily doped systems or Fano intervened systems, where all the phonons are bound with the electrons present in the sample due to high doping and makes interferons, the thermal energy provided by temperature has been used to break the bound state. This phenomenon can also be understood by the schematic diagram shown in Figure 5.2. From Figure 5.2, it is clear that in intrinsic or lightly doped systems, one phonon get annihilated into two- or three- phonons of lower frequency (top panel) according to the Balkanski anharmonic theory while in Fano intervened system where phonons are in the form of interferons (middle panel), the phonon decay is intermediated by interferons (bottom panel) and with the help of thermal energy, interferon dissociate in electron and phonon.



Figure 5.2: Schematic diagrams of different pathways for the phonon decay in different systems.

A typical redshift with increasing temperature in both the samples (P^{++} and i-Si) at different excitation wavelengths has been observed (Figure 5.3). From Figure 5.3A, it can be seen that at 785nm excitation wavelength (orange curve), shift in Raman peak position shows an overestimated value than the intrinsic one (green curve), means at a given temperature an additional Raman peak shift is obtained in P^{++} sample at 785nm due to the

high Fano interaction in it. While the TD Raman spectra, when recorded using shorter excitation wavelength i.e., 532nm (red curve, Figure 5.3B) also shows redshift with increasing temperature but the values are somewhat near to the i-Si sample. Hence from Figure 5.3, it is confirmed that for P⁺⁺ sample the Raman peak position is redder shifted (Figure 5.3A) in comparison with the i-Si sample and shorter excitation wavelength which is likely due to the contribution of high Fano interaction at higher exciting wavelength.



Figure 5.3: Variation in Raman peak position with temperature (A) heavily doped Si, P^{++} at 785nm excitation wavelength and i-Si, (B) at 532nm excitation wavelength.

Therefore, it can be concluded here that the overall TD variation of Raman peak position remain same for both the samples (P⁺⁺ and i-Si) meaning that their TD lattice expansion, responsible for such decreasing phonon energy on increasing temperature, is similar irrespective of the exciting wavelength and doping level. On the other hand, to see the change in Raman peak position more vividly at different excitation wavelengths, Raman microscopy has also been used. The shift in Raman peak position with temperature while using 785nm excitation wavelength can be seen in the Raman thermal image in Figure 5.4A (no post processing of Raman image

has been done). The thermal Raman image at 785nm (Figure 5.4A) which shows redshift by showing different intensity at different temperatures. Similar has been shown in Figure 5.4B while TD Raman spectra has been recorded when using 532nm excitation wavelength.



Figure 5.4: Thermal Raman imaging of P⁺⁺ sample at different excitation wavelengths, (A) 785nm and, (B) 532nm, respectively.

On the contrary, the variation of Raman spectral linewidth (FWHM) has also been observed from the TD Raman spectra (Figure 5.1) at different excitation wavelengths and compared with the Raman spectral linewidths of the i-Si sample and Balkanski theory of phonon decay which can be seen in Figure 5.5. From the Balkanski's anharmonic decay theory of phonons, it is well-known that due to the annihilation of phonons, the lifetime decreases with increasing temperature which results in increasing linewidth. The increasing FWHM for i-Si can be seen in Figure 5.5A, yellow curve. Apart from this, for P⁺⁺ sample, where Fano interaction is present, the spectral linewidth shows some interesting trend with temperature at different excitation wavelengths. At longer wavelengths i.e., 785nm, the FWHM is continuously decreasing with temperature (Figure 5.5A, red curve) and shows completely opposite trend with the i-Si. On the other hand, at shorter excitation wavelengths i.e., 532nm, FWHM varies nonlinearly with temperature (Figure 5.5B) which has been explained previously in chapter 4 as nonlinear temperature dependent behaviour of Raman parameters in the P⁺⁺ sample. Figure 5.5A shows that at lower temperatures, phonons have longer lifetime therefore the TD behaviour of FWHM directly means that at lower temperatures the phonons decay faster making it inconstant with the anharmonic theory which says that phonons decay slower at lower temperatures. The decreasing TD variation of FWHM while using 785nm excitation wavelength for P⁺⁺ sample is decreasing from 35 cm⁻¹ to 12 cm⁻¹ in the temperature range 150K to 625K while for i-Si sample, FWHM increases from 3 cm⁻¹ to 8 cm⁻¹ with increasing temperature. The opposite TD variation and broader spectral width for P⁺⁺ sample (in comparison with i-SI) confirm that all the phonons present in the sample are bound with the electrons and make a bound state of electron phonon i.e., interferons.



Figure 5.5: Variation in spectral linewidth with temperature (A) heavily doped Si, P⁺⁺ at 785nm excitation wavelength and i-Si, (B) at 532nm excitation wavelength.

At shorter wavelengths where less Fano component is expected as the Fano process is dispersive in nature as mentioned above. Interestingly, the behaviour of FWHM of P⁺⁺ sample when excited with 532nm laser while performing Raman Spectromicroscopy (Figure 5.5B) shows a nonlinear(parabolic) TD variation in FWHM. It is important to mention here that the strength of the bound state of electron-phonon i.e., interferon gets weaker with the increasing temperature and similar trend is seen with deceasing wavelength (or increasing excitation energy).



Figure 5.6: Temperature gradient of FWHM for (A) heavily doped Si, P^{++} and i-Si at 785nm excitation wavelength, (B) for sample P^{++} at 532nm excitation wavelength, respectively.

This has also been confirmed from the slope of the FWHM with temperature. The slope of the FWHM while using 785nm excitation wavelength yields negative values (Figure 5.6A, red curve), in comparison with the intrinsic one (green curve), which might be associated with a quantum of binding energy of interferons at lower temperatures. Similarly, for shorter wavelength (532nm), the slope of the FWHM, first have the negative values in the low temperature region which is due to the bound state of interferons but after a certain temperature (~400K), slope reaches to the positive values and shows the similar behavior to the Balkanski's anharmonic theory. Therefore, it can be said from the above slope behavior that the strength of the bound state of electron-phonon i.e., interferon in the

P⁺⁺ sample gets weaker with the increasing temperature which shows that the effect of temperature is inversely proportional to the strength of the Fano interaction. And for excitation wavelength, the Fano interaction behaves differently and shows directly proportional behavior. In other words, the strength of the Fano interaction increases with the increasing excitation wavelength or decreasing excitation energy.

From the TD variation of FWHM it can be said that at a certain temperature (say transition temperature (T_G), all the interferons dissociate into electron and phonon separately and then start to follow Balkanski anharmonic theory. Here the T_G has been explained as the temperature at which interferons dissociate because this is the temperature above which the TD behaviour follows the Balkanski-type behaviour which is valid for systems where interferons are not present thus the electrons and phonons remain uncoupled. It is apparent from the FWHM vs Temperature behaviour for excitation wavelength 532nm (Figures 5.5B) that the interferons appear to break around 400K, and this temperature is different for 785nm excitation wavelength.

5.3 Calculation of Interferon Dissociation Energy

As explained above, the electron-phonon bound states or interferons dissociate into electron and phonon under sufficient thermal energy. Therefore, to calculate the required thermal energy for dissociating interferons at a particular excitation wavelength, an empirical relation has been proposed in this work which explains the dispersive nature of interferons in P⁺⁺ sample. From Figure 5.5B, T_G (transition temperature) for P⁺⁺ sample while excited by 532nm laser wavelength is 400K and T_G while excited by using 633nm (chapter 4, Figure 4.2) is 475K. For 785nm excitation wavelength T_G has been assumed 700K (hypothetical) which is required to dissociate the bound state of interferons. As the TD variation of

FWHM of P⁺⁺ sample while excited by 785nm laser reaches to almost close to the FWHM (excited by 532nm) at maximum temperature (625K), therefore it is reasonable to consider that at \sim 700K all the interferons dissociate.

Using the values of T_G and excitation wavelength energies (table 5.1), the following empirical relation can be obtained:

$$E_{\theta}(\lambda) = E_{\theta}^{0} + \alpha e^{-\left(\frac{E_{\lambda}}{\beta}\right)}, \qquad (5.1)$$

where, $E_{\theta}(\lambda)$ is interferon dissociation energy at a given excitation wavelength (λ) (calculated from the thermal energy corresponding to temperature T_G). E_{θ}^{0} (= 32.23 meV) is the inherent non-dispersive interferon dissociation energy and E_{λ} is the excitation photon energy, α (=3.25 eV) and β (=0.3 meV) are constants obtained by fitting the experimental data with Eq. 5.1. The (thermal) energy required to dissociate the interferons at different wavelengths can be seen in Figure 5.7.



Figure 5.7: Variation in thermal energy with interferon dissociation energy at different excitation wavelengths.

Table 5.1: List of experimentally obtained transition temperature and corresponding interferon dissociation energies (error ± 2 meV) for given excitation wavelength.

Excitation	Transition temperature	Interferon
wavelength (energy)	Т _б (К)	Dissociation Energy (meV)
532nm (2.33eV)	400	35
633nm (1.95eV)	475	41
785nm (1.57eV)	700	60

Therefore, at different excitation wavelengths, different thermal energies are required to dissociate the interferons in P⁺⁺ sample. From table 5.1, the interferon dissociation energy for P⁺⁺ sample when excited by 532nm is 35meV and for 633nm the interferon dissociation energy is 41meV corresponding to the transition temperature provided by external temperature perturbations. For 785nm, the interferon dissociation energy is 60meV (assuming T_G is 700K) which means that with higher excitation wavelength, the strength of the bound state of interferons becomes stronger and requires high energy to break the bound between electron phonons.



Figure 5.8: Schematic diagram of wavelength dependent Fano interaction.

The wavelength dependent Fano interaction can be depicted schematically by a diagram shown in Figure 5.8 which shows how Raman lineshape changes with exciting wavelength. With the increasing wavelength, the Raman lineshape becomes highly asymmetric or vice versa. On the other hand, as the effect of temperature, when the temperature increases band to band transition increases resembling the material to be more intrinsic which flattens the electronic continuum thus weakening the Fano interaction at a given excitation wavelength. The systems where Fano effects are inherently present, the interplay between excitation wavelength & temperature (both affecting the Fano coupling) decides the overall Fano strength and it may eventually lead to an anti-anharmonic type of temperature dependent behaviour in Raman line-shape. In brief, it is evident from the above discussion that strength of Fano interaction increases with increasing excitation wavelength which also affects the temperature dependent Raman line-shape behaviour.

5.4 Presence of Quasi Microphases in P⁺⁺ Sample

Phase transition of material can be categorized based on their properties such as structural phase transition, quantum phase transition etc.[184–187].

The very basic material Si under compression transforms the diamondcubic structure at low pressure to a high-pressure phase to tetragonal β -Sn structure[188,189]. The analysis of this pressure dependent phase transition has been mostly concerned with energy-volume calculations and the thermodynamic criterion of free energies. Other than this, under thermal perturbations, Si exhibits several changes at microscopic levels and properties. Though no change at macroscopic structure is reported, existence of stable microscopic phases at different temperature domains cannot be ruled out thus will be interesting to explore such quasi phases and possible transitions between such phases. In heavily doped systems, temperature induces a non-uniform phonon distribution which may lead to the different micro phases in the system. Since electronic properties affect the overall application of semiconductors, the role of interferons and their behavior under different temperatures cannot be ignored and must be investigated using an appropriate tool.

Further extending the TD Raman study in P⁺⁺ sample and to investigate the different quasi micro phases in the P⁺⁺ sample, TD Raman spectra shown in chapter 4 (Figure 4.1) has been analyzed in a different context and for the further validation of TD Raman data, the Raman experiment has been performed again by using 633nm excitation wavelength in the temperature range 150K to 625K. Here the 3D view of the TD Raman spectra from P⁺⁺ sample has been shown (Figure 5.9), a typical redshift in the Raman peak position can also be observed with increasing temperatures. The origin of redshift with increasing temperature has been explained in chapter 4, section 4.2. In the TD spectra of P⁺⁺ sample, a peak appears at approx. 620 cm⁻¹ which is due to boron doping in the p-Si, and also gets affected by the temperature. The boron peak also gets broadened with the increasing temperature (Figure 5.9).



Figure 5.9: Raman spectra of heavily doped p-Si recorded at different temperatures.

As explained in chapter 4, the Raman spectra from P⁺⁺ sample behaves abnormally with temperature, hence, to confirm this, a zoomed version of TD Raman spectra has also been shown in Figure 5.10. Figure 5.10 shows the TD Raman spectra in the range of 480 cm⁻¹ to 560 cm⁻¹ to observe the shift in Raman peak position and change in Raman spectral linewidth with temperature. Figure 5.10 clearly shows that, at lower temperature i.e., at 175K (blue curve), the Raman peak position is at higher frequency side and have the large spectral linewidth while at higher temperature i.e., at 625K (red curve), The Raman peak position shifts towards the lower frequency side and spectral linewidth also shows some contraction.



Figure 5.10: Zoomed portion to see TD peak shift and Raman spectral width variation in the TD Raman spectra of heavily doped silicon p-Si.

It is important here to mention that such a temperature dependence is inconsistent with the predictions of the Balkanski's anharmonic decay theory of phonons with temperature in intrinsic Si and the explanation of these deviations in Raman parameters has been explained in chapter 4. To confirm the Fano interaction in P^{++} sample, experimentally observed Raman spectra has been fitted and shown in chapter 4 (section 4.2) by using Eq 4.1 given by U. Fano.

5.5 Calculation of TD Fano strength parameter q(T)

As already explained in the previous chapter 4, the trend of the TD spectral width (Figure 5.11A) is quite different from the one shown by i-Si or lightly doped Si which shows a monotonically increasing spectral width with increasing temperature. The nonlinear TD variation of FWHM for P⁺⁺ is parabolic in nature, can be seen in Figure 5.11A. This parabolic nature

appears due to the high Fano interaction in the sample due to the high doping of boron dopant atoms. The FWHM of the P⁺⁺ decreases with the increasing temperature in the low temperature range (150K-475K, Region I) and reaches a minimum value and at a certain temperature (475K, T_G), FWHM starts to increase with the increasing temperature (Region II) and follow the trend predicted by Balkanski's anharmonic theory. Interestingly, though the trend is similar to the anharmonic theory given for lightly doped Si in region II, the values of FWHM is much higher which is because of less strength of Fano interaction at high temperature.



Figure 5.11: (A) TD variation of Raman spectral linewidth, where discrete points show the experimental data and solid red line represents Eq. 5.6, (B) Variation of Fano coupling parameter (q) with temperature observed from theoretical model.

Since the obtained Raman spectral linewidth is associated with both the effects i.e., Fano and anharmonic in the different temperature region therefore, to fit the nonlinear TD FWHM, a careful analysis has been done in this study and the strength of Fano interaction has also been calculated. As already discussed in Eq 4.1 (chapter 4), the total FWHM of P⁺⁺ sample can be written as the combination of Fano induced linewidth and anharmonicity induced linewidth. Hence, the separate FWHM due to both

the effects have been calculated here by using previously established theories. Therefore, in Fano interaction, a phonon with wavevector **s** excites an electronic state $\langle \mathbf{k}_i |$ with wavevector **k** into the state $\langle (\mathbf{k} + \mathbf{s})_j |$. Thus, the scattering probability is given by the electron-phonon coupling matrix element $V_{(\mathbf{k}+\mathbf{s})_i,\mathbf{k}_i}$ which can be expressed as Eq. 5.1:

$$\Gamma_{Fano}(T) = \frac{4\Pi}{N_k} \sum_{k,i,j} |V_{(k+s)_i,k_i}|^2 \left[f_{k_i}(T) - f_{(k+s)_j}(T) \right] \Delta \left[E_{k_i} - E_{(k+s)_j} + \hbar \omega_0 \right],$$
(5.1)

where, ω_0 is the phonon frequency, the sum is on N_k, **k** vectors, $f_{k_i}(T)$ is the Fermi-Dirac occupation at temperature T for an electron with energy E_{k_i} and Δ is the Dirac-delta function. On rationalizing, this result in a simplified equation for the temperature dependence of Fano induced FWHM, $\Gamma_{Fano}(T)$ can be expressed as Eq. 5.2[190]:

$$\Gamma_{Fano}(T) = \Gamma_0 \left[f\left(-\frac{\hbar\omega_0}{2K_B T} \right) - f\left(\frac{\hbar\omega_0}{2K_B T} \right) \right],\tag{5.2}$$

where, Γ_0 is the temperature independent Fano induced linewidth which is calculated from experimentally observed FWHM of Raman lineshape $\Gamma(T)$ and the value of $\Gamma_{an}(T)$ as predicted by Balkanski's anharmonic model. The Fermi-Dirac function $f\left(\frac{\hbar\omega_0}{2KT}\right)$ which depends upon Boltzmann constant " k_B " and Planck's constant "h" can be given as Eq. 5.3:

$$f\left(\frac{\hbar\omega_0}{2K_BT}\right) = \frac{1}{e^{\left(\frac{\hbar\omega_0}{2K_BT}\right)} + 1},$$
(5.3)

where $\hbar\omega_0$ is the phonon energy (520.5 cm⁻¹) which is nearly equal to 65 meV can be calculated by simply putting the values of parameters. But in case of weak electron-phonon coupling (at high temperature range), phonons' decay is dominated by the anharmonic effect i.e., a zone center phonon decays into two phonons. Hence, the temperature dependence of

spectral linewidth responsible for the anharmonic effect process can be expressed as Eq. 5.4[174]:

$$\Gamma_{an}(T) = \left[1 + \frac{\gamma}{e^{(\frac{\hbar\omega_0}{2k_B T})} - 1}\right],$$
(5.4)

where γ is the fitting parameter. Hence by replacing the Fermi-Dirac function into Eq. 5.2 the simplified equation for TD Fano linewidth $\Gamma_F(T)$ can be written as Eq. 5.5:

$$\Gamma_{Fano}(T) = \Gamma_0 \left[\frac{1}{e^{(-\frac{\hbar\omega_0}{2k_B T})} + 1} - \frac{1}{e^{(\frac{\hbar\omega_0}{2k_B T})} + 1}} \right],$$
(5.5)

Hence the total spectral linewidth due to the combination of Fano interaction and anharmonic effect which has been used to generate the theoretical TD FWHM can be given as Eq. 5.6:

$$\Gamma(T) = \Gamma_0 \left[\frac{1}{e^{\left(-\frac{\hbar\omega_0}{2k_B T}\right)_{+1}}} - \frac{1}{e^{\left(\frac{\hbar\omega_0}{2k_B T}\right)_{+1}}} \right] + \left[1 + \frac{\gamma}{e^{\left(\frac{\hbar\omega_0}{2k_B T}\right)_{-1}}} \right],\tag{5.6}$$

Therefore, Eq. 5.6 (solid red line, Figure 5.11A) has been used to fit the experimentally observed TD Raman spectral linewidth for P^{++} sample which shows a good agreement with the experimental data (scattered points, Figure 5.11A). From Eq. 5.6, in which first part explains the domination of Fano interaction, and second part explains the domination of anharmonic effect in the P^{++} sample. Hence the fitting confirms that Fano interaction or anharmonic effect does not behave linearly in heavily doped systems while dominating in a particular temperature region which can be seen in Figure 5.11A.

From the previous studies it is known that as temperature increases, the phonon self-energy of electron-phonon bound state (interferons) decreases (explained in chapter 4, section 4.4) and interferons break into separate entities near the T_G (475K in the present case). On the other hand, in the

region II, the Raman spectral width is contributed mostly by the anharmonic effect (phonon-phonon interaction) where one phonon is annihilated into two phonons of same frequency and opposite momenta i.e., three phonons scattering, a known process as predicted by anharmonic theory.

From the above theoretical Eq. 5.6 for the fitting of the TD FWHM, the TD Fano coupling parameter has been calculated by using some already existing theories. The relation of Fano strength parameter and FWHM can be written as Eq. 5.7:

$$q = \frac{\Gamma_l + \Gamma_h}{\Gamma_l - \Gamma_h'} \tag{5.7}$$

where, $\Gamma_l \&$, Γ_h are the half width at half maxima towards lower and higher frequency regions of Raman spectra, respectively. Hence by replacing the value of $\Gamma_0(F) = \Gamma_l + \Gamma_h = q(\Gamma_l - \Gamma_h)$ in the Eq. 5.5, Fano induced spectral width can be given as Eq. 5.9:

$$\Gamma_{Fano}(T) = q(T)(\Gamma_l - \Gamma_h) \left[\frac{1}{\left\{ e^{(-\frac{\hbar\omega_0}{2K_B T})} + 1 \right\}} - \frac{1}{\left\{ e^{(\frac{\hbar\omega_0}{2K_B T})} + 1 \right\}} \right], \quad (5.8)$$

By rearranging the above equation, the temperature dependent coupling parameter can be expressed as Eq. 5.9:

$$q(T) = \frac{\Gamma_{Fano}(T) \left\{ e^{\left(\frac{\hbar\omega_0}{2K_B T}\right)} + e^{\left(-\frac{\hbar\omega_0}{2K_B T}\right)} + 2\right\}}}{(\Gamma_l - \Gamma_h) \left\{ e^{\left(\frac{\hbar\omega_0}{2K_B T}\right)} + e^{\left(-\frac{\hbar\omega_0}{2K_B T}\right)} \right\}},$$
(5.9)

Eq. 5.9 explains the TD Fano coupling parameter q(T) which confirms that in P⁺⁺ sample, q(T) increases as the temperature increases and the strength of the Fano interaction decreases. The variation of the q(T) has been shown in Figure 5.11B.

From Figure 5.11B, it can be observed that, in the region I (upto 475K), the value of coupling parameter increases with a very slow rate while in the

region II (after 475K), the coupling parameter abruptly increases to a very high value and then becomes constant. This kind of variation in the coupling parameter looks like a first order phase transition. Therefore, from Figure 5.11B, it can be said that:

For the region where coupling parameter varies linearly with temperature, is the region where electron-phonon interaction is strong, and all the phonons are in the form of interferons (region-I, 150K-475K). This region can be known as the interferonic rich state. In region II where anharmonic effect dominates, the change in coupling parameter is entirely different and increases abruptly with temperature. In this region, all the interferons get converted into the phonons, hence this region can be known as the phononic rich state. Hence, these two phases present in the heavily doped sample need to be confirmed whether these phases are stable or not. Therefore, to confirm the stability and reversibility of the thermal hysteresis has been performed by performing the cyclic TD Raman spectroscopy from low to high (heating process) then high to low temperature (cooling process). The observed TD Raman spectral width for the cyclic Raman spectra has been shown in Figure 5.12.



Figure 5.12: Raman spectral linewidth obtained from Raman spectra recorded by cycling the temperature first recorded while heating followed by cooling.

From Figure 5.12, it is clear that, in both the process i.e., heating, and cooling process, TD Raman spectral linewidth is same and shows the same T_G (475K). Therefore, the transition of states from interferon rich to phonon rich state is stable and this behavior also confirms that all the interferons present in P⁺⁺ sample require constant energy to break the interferons and convert into the phonons.

5.6 Estimating Activation Energy associated with Phase Transition

It is evident from Figure 5.12 that thermal hysteresis is absent in the system which reveals that the activation energy required for transition between the either phase is same thus both the microphases, namely interferon rich and phonon rich, are equally stable though they are prevalent at low and high temperatures respectively. This has been represented schematically in Figure 5.13.



Figure 5.13: Schematic diagram of (with y-axis as energy) proposed microphase transition in P^{++} sample between two equally stable interferonic rich phase to phononic rich phase.

Figure 5.13 shows that, at low temperature region, the heavily doped system (P^{++} sample) remains in the state which has abundance of interferons (say, interferonic rich phase) and phonon decay process is intermediated with interferons. At higher temperature region (>475K) due to high thermal energies, the interferons are not stable, and number of phonons increase due to breaking of interferon bound state. Thus, the phonons decay process is dominated by phonons through annihilating into two lower energy phonons which means that phonon-phonon interaction leading to the dominance of anharmonic annihilation process.

The minimum energy required to cross the barrier of interferonic rich phase to reach the phononic rich phase is δE (Figure 5.13) which can be provided only beyond a certain temperature. To break the interaction

between electron and phonons, interferons require a minimum of 41 meV energy. Hence, when the sample temperature reaches the transition temperature i.e., 475K, most of the interferons acquired the minimum required thermal energy (41meV) and interaction between electron-phonon by and large weakens, thus all the interferons convert to the phonons and reaches to the "phononic rich phase". In phononic state, phonons already high energy due to high temperature and anhelation of phonons, hence for the bound state of electron-phonon some energy has to be removed from the sample. This theory explains the presence of quasi-phases in the heavily doped p-Si and their transitions from one phase to another and hysteresis nature.

5.7 Summary and Conclusion

Temperature excitation wavelengths dependent Raman and spectromicroscopic study from heavily doped p type Si reveals the interplay of Fano effect which depends on wavelength as well as temperature. This study reveals that both the perturbation i.e., temperature and excitation wavelength affect differently and shows opposite relation with the Fano interaction. The temperature dependent variation in Raman line width exhibited an atypical negative temperature coefficient for heavily doped P type Si when an excitation wavelength of 785nm was used. For low excitation wavelengths where weak Fano coupling are present, it was observed that anti-anharmonic behaviour was present only till a certain temperature beyond which anharmonic effects prevail which reveals that these are the temperatures where the interferons get dissociated. In this study, an empirical relation to calculate the required thermal energy correspond to interferon dissociation energy has been proposed and explained. Apart from this, two different quasi micro phases of heavily doped Si were observed by performing the cyclic temperature dependent

Raman spectroscopy using 633nm excitation wavelength. The low temperature phase was found to be rich in interferons (electron-phonon bound state) whereas the high temperature phase was phonon rich. A theoretical temperature dependent function, proposed to see the variation of Raman spectral linewidth induced by Fano interaction and anharmonic effect, was found to be in good agreement with the experimental observations. Using this theoretical function of Fano induced linewidth, coupling strength parameter has been calculated which confirms that the Fano interaction dominates at the low temperatures allowing the phononphonon decay process to dominate over the Fano interaction process at higher temperatures.

Chapter 6

Using Raman Spectromicroscopy as a tool to estimate Fermi Level and Temperature-Dependent Shift in Heavily Doped Silicon

This chapter deals with developing Raman spectroscopy as a tool to estimate Fermi energy which is known to be dependent on doping concentration in sample and temperature. In this study TD Raman spectromicroscopy has been used and proves to be a technique to determine the position and temperature associated Fermi shift in an extrinsic semiconductor. The inherently present Fano interaction in heavily doped n and p type Si contains the information about Fermi level and to quantify the values of Fermi energy, TD Raman scattering experiments have been carried out and the obtained line-shape has been analyzed to find out the Fermi-energy and corresponding thermally induced shift in Fermi level. This work discussed here has been published in the following journal[191]^{\$}.

^{\$}Chanchal Rani *et al.* Anal. Chem. 94, 3, 1510-1514, (2022)

6.1 Fermi Energy and Temperature-Dependent Fermi Level in Heavily doped Silicon

Fermi energy[192-196] is one of the most important concepts in semiconductor world and contains all the information about material. To find accurate information about the position of Fermi level, one needs to do a lot of quantum mechanics or sample preparation to find experimentally. Existing techniques to probe the Fermi-energy including Ultra-violet Photoelectron spectroscopy, X-ray photoelectron spectroscopy, Valance band spectroscopy, Electro reflectance spectroscopy, etc.[197] using which, one can determine its value at a given temperature. All these techniques have limitations and require lots of sample preparation and tedious calculations that restrict it to being used by non-experts. In heavily doped semiconductors, electron-phonon coupling or Fano resonance is one such phenomenon which strongly depends on the position of Fermi level. The electron-phonon coupling, so does the Fermi level position, is very sensitive to doping type and gets manifested in terms of asymmetrically broadened Raman spectral line-shape with the presence of resonance maxima and antiresonance minima. Therefore, temperature or doping perturbed changes in the position of Fermi level position directly affects the underlying electronic continuum and gets identified using Raman scattering through simple observables like peak position (and corresponding shift), asymmetry and/or spectral width (quantified using full width at half maximum or FWHM). Thus, Raman spectroscopy may be explored for developing it as a simple and effective tool to get accurate information about Fermi-energy and its temperature and doping dependence.

6.2 Temperature Dependent Raman Spectromicroscopy from Heavily doped Silicon

To calculate the TD Fermi energy in heavily doped P^{++} and N^{++} samples (table xxx, chapter 3), TD Raman spectroscopy has been performed (Figures 6.1A & B) in the temperature range 150K to 450K. The thermal response of Raman spectra of both the samples has been investigated by observing the Raman spectral parameters i.e., Raman peak position and phonon linewidth.



Figure 6.1: Temperature dependent Raman spectra from (A) sample P⁺⁺ and (B) sample N⁺⁺.

The TD Raman spectra (Figures 6.1A & B) of both the sample P^{++} & N^{++} show the typical anharmonicity induced red shift with increasing temperature irrespective of the doping type which can be seen in the thermal Raman imaging (Figure 6.2).



Figure 6.2: Raman spectromicroscopic thermal images from heavily doped (A) p-type and (B) n-type Si respectively.

Figure 6.2A shows the thermal Raman image of sample P⁺⁺ obtained by Raman microscopy which shows the typical redshift in Raman peak position with temperature which has been explained in chapter 4 (section 4.2). Here, the sample N⁺⁺ also shows a similar trend (Figure 6.2B) for the Raman peak position (redshift) with temperature. On the other hand, The FWHM shows the opposite trend for both the samples with respect to the temperature. From Figure 6.3A, P⁺⁺ sample FWHM shows opposite trend with temperature and varies inversely while for sample N⁺⁺ the FWHM varies linearly (increasing) (Figure 6.3B) with temperature and follows the conventional Balkanski's anharmonic phonon decay theory. As mentioned above the TD trend (Figure 6.3) in FWHM and Raman line-shape (Figure 6.1) are sensitive to the doping which in turn depends on Fermi energy, these data has been used to estimate the value of Fermi energy and their TD variation as discussed below.



Figure 6.3: Variation of FWHM with temperature, from heavily doped Si for (A) sample P^{++} and (B) sample N^{++} .

6.3 Calculation of Temperature Dependent Fermi Level Position in Heavily doped Silicon

As per the previous studies explained in chapter 4 and 5, the atypical TD behavior of FWHM for P⁺⁺ sample is due to the inherently present Fano interaction, taking place between the doping induced electronic continuum and discrete phonons in the doped Si wafer. The presence of Fano interaction, in sample P⁺⁺, can be confirmed from the observed asymmetric broadening and antiresonance in the Raman spectra (Figure 6.1A). It means that, at a given temperature, both the anharmonic and Fano related effects contribute to the observed Raman spectral width. Since the inherently present Fano coupling exhibits the information about electronic continuum and Fermi level present in the sample. Therefore, to calculate the Fermi positioning in the heavily doped Si, the contribution due to Fano interaction has been extracted from the total experimentally observed Raman spectral
linewidth of both the samples. The total FWHM can be expressed as Eq 6.1 (using Eq 4.1, chapter 4):

$$\Gamma_{total} = \Gamma_{an} + \Gamma_{Fano}, \tag{6.1}$$

where, Γ_{an} is the anharmonic phonon linewidth and can be obtained from Balkanski theory of phonon decay due to temperature in i-Si. Γ_{Fano} , Fano induced linewidth, can be obtained from experimentally observed value of total linewidth Γ_{total} and the values of Γ_{an} as predicted using the Balkanski's anharmonic theory.

As explained by Cardona *et al.*, Fano interaction depends upon the electronphonon matrix element and is associated with density of states in the heavily doped semiconductor. Therefore, the Fano induced linewidth Γ_{Fano} , in the Raman spectra can be written as the combination of[84]:

$$\Gamma_{Fano} = \Pi V^2 D(\omega) \tag{6.2}$$

Where, $D(\omega)$, density of states depends upon the Fermi energy of the material which can be given as Eq. 6.3 and electron phonon matrix element, V, can be written in the terms of deformation potential (Eq. 6.4) given by M. Cardona *et al*[84].

$$D(\omega) = \frac{1}{4 \Pi^2} \frac{m_l m_t}{K \hbar^4} \left[E_F - \frac{\hbar^2}{2m_l} \left(K - \frac{\omega m_l}{2K \hbar} \right)^2 \right], \tag{6.3}$$

$$V = \left(\frac{2}{a}\right) D_0 \left(\frac{\hbar}{4MN\omega_0}\right)^{\frac{1}{2}},\tag{6.4}$$

where, $m_l = 0.9163m_e$ and $m_t = 0.1905m_e$ are the longitudinal and transverse masses of the bands, m_e is the electronic mass; M is the atomic mass of Si; $N = \frac{4}{a^3}$ is the number of unit cells per unit volume; K (= 0.14x $2\Pi/a$) is the distance of maximum of the valance band from the edge of the Brillion zone, and a = 5.43 nm is lattice constant; ω_0 is Raman peak position and D_0 is the deformation potential. Deformation potential is linear displacement coefficient of single electron band energy, or it can be defined as the expectation value of electron-phonon interaction potential. By replacing all these expressions in Eq. 6.2, following relation for Fermienergy can be obtained:

$$\Gamma_{Fano} = \frac{1}{4 \Pi} \frac{m_l m_t}{K \hbar^4} \left[E_F - \frac{\hbar^2}{2m_l} \left(K - \frac{\omega m_l}{2K \hbar} \right)^2 \right] \left(\frac{2}{a} \right)^2 D_0^2 \left(\frac{\hbar}{4MN\omega_0} \right), \tag{6.5}$$

As for Si samples, all the information like masses of the atoms, lattice constant is very well explored. The value of deformation potential for silicon is -8.08 eV which has been calculated by Cardona *et al.* The mass of the Si atom is 4.66 Kg. Hence by putting all the values in Eq. 6.5, a simple relation for Fermi energy in the terms of Γ_{Fano} can be given as:

$$E_F = -\left(\frac{\Gamma_{Fano}}{3.497} \times 10^{-18}\right),$$
 (6.6)

From Eq. 6.6, the value of Fermi energy (E_F) returns in *Joules* if Γ_{Fano} (the experimental observable) is substituted in wavenumber (cm⁻¹) units.

Using above relation of Fermi energy Eq. 6.6, the position of fermi level and corresponding thermal shift in fermi level can be calculated by simply putting the value of $\Gamma_{Fano.}$

Very basic understanding of Fermi energy tells that its position in the heavily doped semiconductors is governed under following facts:

(a) For p-type semiconductors Fermi level is closer to the valance band edge and for very high doping Fermi level enters the valance band.

(b) For n type semiconductor, Fermi level moves forward from the intrinsic position to reach closer to the conduction band. It may also enter the conduction band depending upon the doping concentration under degenerate state.

(c) The temperature dependence of the Fermi level in p-type semiconductor

is also known which can be understood using band diagram (Figure 6.4).

In semiconductors, for a given doping concentration, Fermi level shifts towards the intrinsic Fermi level with increasing temperature and behaves like an intrinsic semiconductor.



Figure 6.4: Schematic diagram of variation of Fermi level with temperature in heavily doped p type semiconductor under different temperature regimes.

Therefore, the typical TD variation in Fermi level shift can be seen for both the types of doping which indicates the effectiveness of the proposed method to estimate Fermi energy by Raman spectroscopy as demonstrated for extrinsic Si (Figure 6.5).



Figure 6.5: Temperature-dependent Fermi-energy variation for heavily doped n- and p-type Si.

The obtained TD $(E_F - E_{F_i})$ values for both the samples N⁺⁺ & P⁺⁺ reveals that, at low temperatures Fermi level enters into the conduction and valance bands, respectively and as temperature increases, the Fermi level starts to move towards the intrinsic position. The TD Fermi level shift can also be understood using the schematic shown in Figure 6.6 which shows how Fermi-Dirac distribution function varies for intrinsic and extrinsic semiconductors. Fermi-Dirac distribution function explains the probability distribution of the energies of the quantum states that electrons can exist in at some given temperature. According to the Fermi-Dirac distribution function, at absolute temperature, electrons have the lowest energy and hence no energy states which lie above the Fermi level are occupied by electrons.

Figure 6.6: Schematic shows Fermi-Dirac distribution function for a semiconductor.

The obtained TD $(E_F - E_{F_i})$ values have been validated by comparing the values with previously reported TD Fermi energy values by Nguyen *et. al.*[198] which are found to be consistent and show a similar trend in Fermi energy shift with temperature for both the samples p and n type Si.

Therefore, the major finding of this work is that Raman spectroscopy can be a very simple yet effective tool to calculate the Fermi level and corresponding Fermi level shift with temperature in heavily doped Si. It is important here to mention that the only constraint in this method is that the material should have the Fano interaction because as explained above Fano interaction exhibits the information about the electronic continuum present in the sample.

Table 6.1: Values of $(E_F - E_{F_i})$ calculated using Eq. 6.6 and its comparison with the already reported values as shown in brackets for P⁺⁺ and N⁺⁺ type samples.

$(E_F - E_{F_i})eV$ P++	(E _F -E _{Fi})eV N ⁺⁺		
-0.58 (-0.57)	0.41 (0.42)		
-0.52 (-0.52)	0.37 (0.38)		
-0.44 (-0.47)	0.34 (0.33)		
-0.38 (-0.41)	0.33 (0.31)		
-0.29 (-0.34)	0.32 (0.28)		
-0.22 (-0.28)	0.30 (0.25)		
-0.086 (-0.20)	0.29 (0.18)		
-0.006 (-0.12)	0.27 (0.10)		
	$(E_F - E_{F_i})eV$ P^{++} -0.58 (-0.57) -0.52 (-0.52) -0.44 (-0.47) -0.38 (-0.41) -0.29 (-0.34) -0.22 (-0.28) -0.086 (-0.20) -0.006 (-0.12)		

This method involves the information of Fano and anharmonic parameter from Raman line-shape which makes this method a little bit convoluted. This simple method will be useful for systems other than Si, where these prerequisite parameters are known. Apart from this, this method can be used in other materials also such as MoS₂, Graphene etc. because electronphonon (Fano) interaction has already been widely explored in these materials.

6.4 Summary & Conclusion

Temperature dependent Raman spectromicroscopy gives an additional advantage of estimating the Fermi level position and its thermal Fermi shift simultaneously without performing complicated experiments. In this study, it is demonstrated that Raman spectroscopy can be used as a simpler yet effective tool to determine the Fermi-energy for extrinsic Si by deconvoluting the association between the Fermi energy (the desired quantity) and Fano coupling strength, which is quantified in terms of Raman spectral width (the experimentally measurable quantity). The typical Fano resonance induced broadening, and its atypical temperature dependence, in the Raman spectral width can be exploited for calculating the value of Fermi-energy because the strength of Fano coupling is known to be depending on its relative position to the band edge. This latent information about the Fermi-energy can be obtained using a proposed simple expression obtained by considering different existing established theoretical frameworks. The above formula was found valid for Fermi-energy calculation irrespective of doping type. Moreover, the temperature dependent Fermi shift, with respect to intrinsic level, was found consistent with the reported results to further affirm the utility of Raman spectroscopybased methodology to calculate Fermi-energy. The method can be utilized for any material for which the information about effect of Fano and anharmonic perturbations on Raman line-shape is known.

Chapter 7

Raman Spectroscopic Studies on Low-Dimensional Materials

This chapter deals with the Raman spectroscopic studies of low dimensional TiO₂ (nanorods), amorphous silicon (a-Si) and fractal Si nanowires (SiNWs). For TiO₂ nanorods (rutile phase), the effect of anharmonicity has been studied using TD Raman spectromicroscopy. The degree of anharmonicity has been calculated for the hot phonons by using some theoretical fitting. A theoretical method has been developed to generate the Raman lineshape for the a-Si using the combination of direct matrix method (DMM) and bond polarization model (BPM). The developed method has been validated by fitting some previously reported experimental data for the a-Si. Additionally, Raman spectroscopic study of SiNWs, prepared using metal assisted chemical etching (MACE) technique has been carried out. The reported studies are reported in the following journals[199–201][§].

^{\$}Chanchal Rani et al. Mater. Adv., 3, 3, 1602-1608, (2022)

^{\$}Chanchal Rani *et al.* J. Raman Spectrosc., 52, 12, 2081-2088, (2021)

^{\$}Chanchal Rani *et al.* Can. J. Chem., 100, 7, 500-506, (2022)

7.1 Transition Metal Oxides

Titanium oxide (TiO₂) is one of the widely used metal oxides amongst all transition metal oxides. It is known that the materials which have oxygen are highly sensitive to defects and it will be very difficult to fabricate and store the material in its purest form. The same problem is faced by TiO₂ with respect to its purity hence it is important to take care of the fabrication and storage process. TiO₂ exhibits in three forms, anatase, rutile, and brookite with different band gaps. The Anatase form of TiO₂ is the most stable form and the brookite form is the least stable phase of the TiO₂. Rutile phase of TiO₂ (nanorods) can be obtained by simply using hydrothermal method and at a certain temperature, rutile TiO₂ shows stable nature.

The TD Raman spectra[202–205] from rutile TiO₂ nanorods shows different trend with respect to the known anharmonic trend as discussed in previous chapters. The different Raman modes of the rutile TiO₂ nanorods i.e., $E_g \& A_{1g}$ behaves differently under thermal perturbations which can be observed in terms of spectral parameters such as peak position and the linewidth of the Raman spectra. These TD changes in the spectral parameters arise on the basis of the known anharmonic decay theory of phonons into two and three phonons. To investigate the degree of anharmonicity in the rutile TiO₂ nanorods, a theoretical framework has been studied using already existing theory of anharmonic decay. The same has also been validated using experimental Raman data.

7.2 Synthesis and characterization of Rutile TiO₂ Nanorods

Rutile TiO_2 nanorods (TNRs) have been prepared using hydrothermal method on an FTO substrate using the recipe mentioned earlier (chapter 3, section 3.1.2) and the prepared sample has been characterized by various

techniques. The surface morphology of the rutile TNRs and the size of the nanorods have been estimated using scanning electron microscopy or SEM (Figure 7.1), which confirms that the prepared TNRs are uniform and well-aligned.

Figure 7.1: (A, B) Scanning electron microscope image of rutile TiO₂ nanorods at different magnifications.

To confirm the diameter of the prepared TNRs, imageJ software has been used which also provides the surface profile of the nanorods. Figure 7.2A represents the surface profile of TNRs using one of the SEM images. From surface profile, it can be said that the prepared sample has rod like structure and all the rods are well aligned and have the uniform diameter of all the nanorods. On the other hand, using the surface profile plot, the diameter of the TNRs has been calculated (Figure 7.2B) which is in the range of 220nm.

Figure 7.2: (A) Surface profile of rutile TiO_2 nanorods obtained from imageJ software (B) Plot for the size of the diameter of nanorods.

The obtained SEM images and imageJ calculation of the rutile TNRs confirm that prepared sample is in the range of nanometer and have uniform structure.

The phase and crystallographic studies have been carried out using X-ray diffraction pattern (XRD) and Raman spectroscopy[206]. As mentioned above, TiO_2 is highly sensitive to defects that originated due to the oxygen vacancy in the sample, hence it is necessary to perform the purity check for the prepared sample. Figure 7.3 shows the XRD pattern of the rutile TNRs with corresponding peaks and (hkl) planes.

Figure 7.3: X-ray diffraction pattern of rutile TiO₂ nanorods.

The obtained XRD pattern of the rutile TNRs shows the several diffraction peaks in the pattern at the different diffraction angles. The peaks in the diffraction pattern with corresponding (hkl) planes (Figure 7.3) can be identified as originating from rutile phase of TiO_2 (marked with *) and the

FTO substrate (marked as #). From the XRD pattern, it is observed that no extra peaks are obtained in the patten which means the prepared sample is defect free and in its pure form. Apart from this, the Raman spectroscopy has been performed to confirm the phase of the prepared TNRs (Figure 7.4) which shows four Raman active modes. The Raman peaks appear at 143 cm⁻¹ (B_{1g} mode), 235 cm⁻¹ (originated due to multi-photon process), 447 cm⁻¹ (E_g mode) & 610 cm⁻¹ (A_{1g} mode). The appeared different Raman modes in the spectra represent the different vibrations of the Ti⁺⁴ and O⁻² atoms and confirm that rutile TiO₂ has the tetragonal structure which is also consistent with the XRD results.

Figure 7.4: Raman spectrum of rutile TiO₂ nanorods at room temperature (300K).

The A_{1g} & B_{1g} Raman modes arise due to the motion of O^{-2} ion in the perpendicular to the c-axis with respect to the stationary Ti^{+4} ions. On the other hand, E_g Raman active mode originates when O^{-2} ion moves along to the c-axis. From Figure 7.4, it is clear that the E_g and A_{1g} Raman modes are as usual most intense modes and B_{1g} is the weakest one.

7.3 Temperature-Dependent Raman study of rutile TiO₂ Nanorods

To investigate thermal effect on the rutile TNRs, TD Raman study has been done in the high temperature range i.e., from room temperature, 300K to 800K (Figure 7.5). From Figure 7.5, it can be observed that the E_g Raman active shows a red shift in the Raman peak position with increasing temperature and also shows changes in the spectral width.

Figure 7.5: Raman spectra of rutile TiO_2 nanorods recorded at different temperatures between 300K and 800K.

On the other hand, A_{1g} Raman mode (610 cm⁻¹) does not shows any shift in the peak position of the Raman spectra which is interesting to observed while A_{1g} mode shows change in the spectral width with increasing temperature. Slight changes have been observed in the B_{1g} (147 cm⁻¹) Raman modes but these changes are very small and can be ignored. To see the thermal effect in the peak position of the $E_g \& A_{1g}$ Raman modes, Raman microscopy has been done. Figure 7.6 shows the thermal Raman image of the rutile TNRs which shows the change in the Raman peak position with temperature by showing intensity profile.

Figure 7.6: Thermal Raman image obtained by using Raman microscopy of rutile TiO₂ nanorods.

Figure 7.6 also shows that the E_g mode shows significant shift in the Raman peak position with increasing temperature but A_{1g} mode does not show any shift in Raman peak position which means A_{1g} Raman mode is immune to the thermal effects. The thermal immunity of the A_{1g} Raman mode has been explained by the Samara and Pearcy *et. al.*[78] They reported that the thermal immunity of the B_{1g} and A_{1g} modes is caused by the fact that the shifts due to thermal expansion and higher order anharmonicities are complementary to each other to compensate each other. On the other hand, position and spectral linewidth with increasing temperature which undergoes the anharmonic effect. Hence to investigate the anharmonic effect and degree of anharmonicity in the E_g mode, the Raman parameters have been calculated from the experimental Raman data (Figure 7.5) and a theoretical framework has been used.

From the TD Raman spectra (Figure 7.5), the E_g Raman mode shows redshift in the Raman peak position in the temperature range 300K to 800K which is mainly due to the thermal expansion induced by temperature, resulting in a decrease the vibrational frequency. Apart from this, the spectral linewidth of the E_g Raman mode increases with the increasing temperature. The increment in the spectral linewidth means that the energy of the phonons increases due to which the lifetime of the phonons decreases with the temperature. To explain this, the Balkanski's anharmonic decay theory has been used. According to Balkanski's theory, an optical phonon decays into two (three phonon scattering) or three (four phonon scattering) lower energy phonons due to temperature. The decay of an optical phonon into two or three phonons is represented mathematically as cubic or quartic anharmonicities. Hence according to anharmonic decay theory, the TD Raman peak position can be given as Eq 7.1 & Eq 7.2:

$$\omega(T) = \omega_0 + \Delta \Omega(T), \tag{7.1}$$

$$\Delta\Omega(T) = A \left[1 + \frac{2}{e^{x} - 1} \right] + B \left[1 + \frac{3}{e^{y} - 1} + \frac{3}{(e^{y} - 1)^{2}} \right],$$
(7.2)

where, ω_0 (= 447 cm⁻¹) Raman peak position of rutile TNRs at room temperature (taken as reference), x = $\hbar\omega/2kT$ and y = $\hbar\omega/3kT$. The term $\Delta\Omega(T)$ is the anharmonicity Raman shift, arises due to thermal effects, A & B are the anharmonic parameters which show the degree of anharmonicity in the sample.

On the other hand, the TD spectral linewidth can be written as Eq 7.3 & Eq 7.4:

$$\Gamma(T) = \Gamma_0 + \Delta \Gamma(T), \tag{7.3}$$

$$\Delta\Gamma(T) = C \left[1 + \frac{2}{e^{x} - 1} \right] + D \left[1 + \frac{3}{e^{y} - 1} + \frac{3}{(e^{y} - 1)^{2}} \right],$$
(7.4)

where, Γ_0 (= 35 cm⁻¹) is the spectral linewidth of rutile TNRs respectively at 300K. Here the term $\Delta\Gamma(T)$ is the thermally induced linewidth in the Raman spectra. And C & D are the anharmonic parameters.

Eq 7.2 & 7.4 have been used to fit the experimentally observed Raman spectral parameters i.e., shift in the Raman peak position and change in the spectral linewidth, respectively and the anharmonic parameters have been calculated. The experimentally observed and theoretically calculated Raman spectral parameters have been shown in Figure 7.7 in which solid lines shows the theoretically generated curve and scattered curve shows the experimentally observed parameters from the TD Raman spectra of the rutile TNRs. The solid line in Figure 7.6A has been obtained by using A & B as the fitting parameters which shows best fit with the experimental data (scattered curve) when a value of A = -0.50 cm⁻¹ & B= -0.85 cm⁻¹ was used.

Figure 7.7: The TD variation of (A) Raman peak position & (B) Raman spectral linewidth, discrete points show the experimentally observed data whereas solid lines show the theoretical curve (Eq. 7.1 and 7.3).

In this study the role of confinement effect has not been considered because its effect on the mode vibrational energy and thus Raman peak position for rutile phase is not significant enough, as reported by T. Mazza *et al.* In other words, the total Raman peak shift in E_g mode is solely because of anharmonic effect. Apart from this, Similar theoretical analysis has also been done for the Raman spectral width (Figure 7.7B) using Eq. 7.3 & Eq. 7.4. The best fit between the experimental data (discrete points, Figure 7.7B) and theoretical values (solid line, Figure 7.7B) are obtained for the values of C= 2.3 cm⁻¹ & D= 0.42 cm⁻¹ (anharmonic parameters).

Figure 7.8: The TD variation of (A) FWHM and (B) phonon lifetime for $A_{1g} \& E_g$ modes.

As explained above, the A_{1g} Raman mode shows immunity against the thermal effects which indicate that the thermal expansion is small enough to keep the corresponding mode to vibrate in the harmonic regime. The important thing is the spectral linewidth of the A_{1g} Raman mode shows increment with the increasing temperature which has been shown in Figure 7.8. The increment in the spectral linewidth means that though the vibrations remain harmonic it still suffers phonon decay thus decreasing the phonon lifetime with increasing temperature.

7.4 Quantification of Short-Range Order in Amorphous Silicon using Raman spectroscopy

Amorphous materials are said to have a "short range order" up to which they show some extent of crystallinity. Amorphous materials [207-211] such as semiconductors (Si, Ge, GaAs etc.) show unique properties in comparison to the nano part or the crystalline form due to no periodicity present in the material. Nanomaterials also show different properties than their crystalline counterparts which are of the interest of scientists to manufacture different electronic devices. At microscopic level, nanomaterials still retain their crystalline nature within nanometer-sized boundaries within which lattice momentum and thus associate wave vectors can be defined. While, amorphous materials, lack this crystallinity nature, thus it is difficult to define a wave vector unlike (nano-)crystalline materials due to nonexistence of long-range order. Due to this reason, it is very difficult to understand the physics of amorphous materials or to give any theoretical phenomena. There are various theoretical studies present in the literature to define nanomaterials or to generate theoretical lineshape for the materials in the nanometer range, but all the models fail when comes into the very short range or in amorphous range. Therefore, in this study, a model has been developed to generate the theoretical Raman lineshape for the amorphous silicon (a-Si).

7.5 Developing a Generalized function to represent Raman lineshape of a-Si

The Raman spectra for the nanocrystalline Si is usually obtained in the range of 515 cm⁻¹ to 505 cm⁻¹ depending upon the size of the nano Si whereas for a-Si the Raman speak position appears in the range of 480 cm⁻¹ to 500 cm⁻¹. It is well known that Richter and Campbell[212] gave a

model i.e., phonon confinement model (PCM) to generate the Raman lineshape for the nanomaterials and that model takes care of the confinement effect in the material. To generate the first order Raman lineshape an intensity Eq given by given by Richter and Campbell (PCM model) can be given as Eq. 7.5:

$$I(\omega) = \int_0^1 \frac{\exp\left(-\frac{q^2 L^2}{4a^2}\right)k^m}{(\omega - \omega(q))^2 + (\frac{Y}{2})^2} dq,$$
(7.5)

where, L & a are the size of the Si and lattice constant of the Si, γ represents the width of the Raman lineshape and m define the degree of confinement. In this model 'm' can take the values 0, 1, or 2 for one-, two-, or threedimensional confinement and taken as 1 in the present case. The term $\omega(q)$ in Eq 7.5 represents the phonon dispersion relation function for Si and can be defined as $\omega^2(q) = 171,400 + 100,000 \cos(\pi q/2)$. It is important here to understand that the PCM takes care of the fact that in nanomaterials, phonons away from the zone-centered ones are also allowed to participate in the Raman scattering which were not allowed in the c-Si. Such a relaxation is possible due to uncertainty in identifying the exact zone center which has a spread in its momentum proportional to the inverse of the size. All the phonons lying within this spread can participate in Raman scattering to generate the asymmetric Raman line shape. In Equation 1, the factor $exp(-q^2L^2/4a^2)$, the confinement function takes care of the relative contribution of individual phonon taking part in the scattering. The PCM model depends upon the size and wavevector (q) of the material. Hence the constraint with the PCM model is that it can only define the Raman lineshape within the size limited up to the wavevector can be defined. But for amorphous material (a-Si, here) where wavevector is not defined, this model does not work. Therefore, for short range order materials, a model, combination of direct matrix method and bond polarization model (DMM-BPM) has been reported by Koniakhin et. al. [213], for the diamond material

by changing the weighing function used in PCM model. Hence the proposed DMM-BPM model can be written as Eq 7.6:

$$I(\omega) = L^3 \int_0^1 \frac{\frac{q^2 F(q) \Gamma}{2}}{(\omega - \omega(q))^2 + (\frac{\Gamma}{2})^2} dq,$$
(7.6)

In Eq 7.6, F(q) is the new weighing function defined by Koniakhin *et al.*, which can be written as $F(q) = \frac{\delta(q-q_L)}{q_L^2} + C_2 N(q) \theta(q-q_L)$ with the δ function used as the Lorentzian function with the small width. $N(q) = (q^2 - q_L^2)^{-3/2}$ is the average scattering intensity in the momentum domain, and $\theta(q-q_L)$ is defined as the Heaviside function and $C_2 = 0.2$ is a constant. In Eq 7.6, $\Gamma = \gamma . \lambda$ is the fitting parameter which gives the information about the factor λ .

Figure 7.9: (A) Weighing function of DMM-BPM model, inset shows the weighing function of PCM model, (B) Raman lineshape generated using DMM-BPM model for the different sizes.

Figure 7.9A shows the variation of weighing function F(q) with respect to the wavevector q introduced in the DMM-BPM model for two different sizes 1.8 nm and 2nm. Along with the one used in the PCM (inset). The F(q) shows a symmetric peak for both the sizes because DMM-BPM model has been taken as Lorentzian instead of Gaussian function (Figure 7.9A) because of the assumption of the hard boundaries of crystallites. On the other hand, the inset of Figure 7.9A shows the weighing function of the PCM which uses a size-dependent slowly varying function of q. In DMM-BPM approach, weighing function depends upon the average scattering intensity of phonons while in the PCM approach, the confinement function F(q) is assumed to be a direct consequence of the proportionality of phonon amplitude $|\psi|^2 \propto W^2(r)$, where W(r) is Gaussian confinement function.

Lorentzian-shaped weighing function is more appropriate rather than a Gaussian one because Gaussian profile apparently works well for the solid where all the atoms are arranged in a regular manner, but at short range, this arrangement of atoms vanishes due to the quantum confinement effect. To see the effect of size (the distance up to which the short-range order is intact), on the Raman spectra, Raman line shapes from a-Si have been generated using the DMM-BPM model (Eq 7.6) for three different representative sizes of 10, 15, and 20 Å and a given value of $\Gamma = 500$ cm⁻¹ (Figure 7.8B). The generated Raman line shapes (Figure 7.9B) clearly show a size-dependent shift in peak position with little effect on the width which is consistent with the available reports.

Apart from this, the Raman lineshape for a 2nm sized a-Si has been generated theoretically using both the models i.e., PCM and DMM-BPM (Figure 7.10). From Figure 7.10 it is clear that the obtained Raman lineshape from PCM model (black curve) gives a random curve while the Raman lineshape obtained from DMM-BPM model gives a asymmetric broad peak at 490 cm⁻¹. Therefore, it can be observed from Figure 7.9 that DMM-BPM method can generate the theoretical Raman lineshape for the amorphous materials by simply changing the value of known parameters (depending upon material) used in the Eq 7.6.

Figure 7.10: Theoretically generated Raman line shape using both models i.e., PCM model (black curve) and DMM-BPM model (red curve).

To verify whether the theoretical model obtained using the new DMM-BPM is suitable and more appropriate to generate the theoretical Raman line shape at very short range, three sets of experimental Raman scattering data of a-Si have been used for validation. All the three sets of experimental Raman data of a-Si have been taken from published reports with permission and named as samples AS1, AS2, and AS3 (table 7.1 below). These experimental data correspond to a-Si prepared by three different techniques but are of amorphous nature. These experimental data have been fitted using Eq 7.6 by using L and Γ as the fitting parameters to estimate the value of L which also is the cluster size in the a-Si sample. The values of fitting parameters corresponding to the obtained best fit of Raman spectra (solid line, Figure 7.11) have been summarized in Table 7.1 below which also lists the parameters reported in the previous work along with observed Raman peak positions.

Figure 7.11: Raman spectra of a-Si of three different samples AS1, AS2 and AS3.

Table 7.1: Raman parameters estimated by fitting of Raman spectra (Figure7.11) using Eq 7.6

Sample	Peak Position (cm ⁻ 1)	Short range order (Å) from Yogi <i>et al.</i>	Short range order L (Å) estimated Figure 7.9	Fitting Parameter $\lambda = \Gamma / \gamma$
AS1	472.5	8.3	9.8	225
AS2	477.5	8.8	11.2	175
AS3	482.0	9.3	12.6	125

The above discussion discusses an elaborate method to represent Raman line-shape from a-Si. An empirical relation can also be proposed to estimate the size dependent Raman peak position in the amorphous materials using BPM model proposed by Zi *et al.*, which can be given as Eq 7.7:

$$\Delta\omega = -\xi (\frac{a}{L})^{\kappa},\tag{7.7}$$

In Eq 7.7, *a* & *L* represent the lattice constants and size of the a-Si, respectively. $\Delta\omega$ shows the deviation in the Raman peak position of a-Si with respect to the c-Si ($\Delta\omega = \omega - 520.5$) cm⁻¹. Here, ζ (=117 cm⁻¹) represents the allowed wavenumber values of all the phonons spread across the phonon dispersion curve. The experimentally observed size-dependent variation ($\Delta\omega$ vs. L) in Figure 7.12 can be fitted using Eq 7.7 by taking $\kappa = 1.4$ which predicts the short-range order sizes of 9.8, 11.2, and 12.6 Å for samples AS1, AS2, and AS3, respectively, which has been shown in the Figure 7.12A.

Figure 7.12: (A) Variation of Raman peak position with the size of the samples (orange curve). Brown curve represents the already reported data for the same variation. (B) Same variation in the large range using proposed empirical relation.

Figure 7.12B shows size dependent Raman peak position variation in the large range order which can be used to estimate the short-range order present in any *a-Si* sample. From Figure 7.12B it is clear that, at larger sizes where momentum conservation law participates in the Raman scattering and only zone center phonons take part in the scattering phenomena. The Raman peak position appears at 520.5 cm⁻¹ (c-Si) but as smaller sizes where momentum conservation law does not follow the Raman peak position shows deviation.

7.6 Fabrication of Si NSs and Raman spectroscopic study

As mentioned above, the field of nanoscience and nanotechnology[214-220] is very fascinating due to their applications. There are various techniques which are used to fabricate the nanowires, a special kind of nanostructure, of the Si such as electron beam lithography, ion implantation, laser induced etching, electrochemical etching. Metal assisted chemical etching (MACE), also known as metal induced etching (MIE) is one of the easier and economic techniques to fabricate various porous-silicon (p-Si) NSs owing to many advantages such as simplicity, compatibility with existing industrial applications. MACE process is a two-step process in which, first step is to deposit the metal nanoparticles such as (Ag, Au etc.) on the Si wafer and the second process is the etching process. The deposited metal nanoparticles work as a catalyst to increase the etching process in the chemical process. In etching process, an oxidizing agent has been used to etch the Si wafer with the mixing of HF acid in appropriate amount. A detailed discussion about the MACE process has been given in chapter 3 (section 5.3.1).

As various oxidizing agents are available in the market but to fabricate SiNWs, the oxidizing agent choose on the basis of their electrochemical potential. Basically, for SiNWs, H_2O_2 is used because its electrochemical potential is very high, and it gives a well-aligned wire like structure of the SiNWs. But here in this study, a new oxidizing agent has been introduced which also has advantages over H_2O_2 . There is no fundamental constraint about not using other oxidizing agents hence a new oxidizing agent has been used here to fabricate SiNWs and its effect on porosity has been studied as discussed below.

7.7 Potassium Per Manganate as Oxidizing Agent for

Porosification Using Metal Induced Etching

In MACE process, etching mechanism (second step) is important to fabricate the SiNWs and as explained above an oxidizing agent has been used to etch the Si wafer and prepare nanostructures of the Si such as nanowires, nanodots etc. The oxidizing agent used in the etching process decides the etching rate of the wafer which depends upon the ability of the oxidizing agent to inject holes into the valance band of the Si. Typically, H_2O_2 is used because its electrochemical potential is sufficiently high to directly inject holes in the valance band of Si. Figure 7.13 represents the electrochemical potential scale for the two different oxidizing agents $H_2O_2/KMnO_4$. Figure 7.13 summarizes following observations:

- The electrochemical potential of H₂O₂ (1.71 V) is much higher than the valance band of Si thus making it a good choice for making the etching solution.
- H₂O₂ can easily inject holes into the valance band of Si to initiate the etching process.
- Similarly, KMnO₄ also can be chosen instead of H_2O_2 due to its favorable electrochemical potential (1.51 V) as shown in Figure 7.13.

Figure 7.13: Electrochemical potential scale for the different oxidizing agents. E_c and E_v show the electrochemical potential of valance and conduction band edge of Si.

It is clear from the above points that both the oxidizing agents, H_2O_2 and KMnO₄, can be used to etch the Si wafer but due to the difference in redox potential, the etching rate, or the surface morphology of SiNWs may be different. The surface morphology of the prepared SiNWs (using the recipe mentioned in chapter 3) can be seen by using scanning electron microscopy (SEM). Figure 7.14 shows the SEM images of the SiNWs prepared by using H_2O_2 as an oxidizing agent. Figure 7.14A shows the top surface of the SiNWs which shows a porous surface which is expected as a result of continuous removal of Si atoms consequent to repeated etching process. During MACE process, the etching proceeds along the depth of the wafer and pores are formed at locations where metal nanoparticles are present whereas the portion not covered by the metal nanoparticles remains unetched. These unetched portions remain on the sample and appear as wire

like structures and the length of these wires depends on the etching time. The long parallel wires have been obtained by etching in H₂O₂/HF solution as can be seen in the cross-sectional SEM image (Figure 7.14B). Figure 7.14 also reveals an average pore-depth or wire-length of \sim 80 µm.

Figure 7.14: SEM images of SiNWs prepared by metal assisted chemical etching using H_2O_2 as oxidizing agent, (A) shows the top surface and, (B) shows the cross-sectional view.

On the other hand, the etching of the Si wafer has also been done by the KMnO₄. From Figure 7.14 it has been observed that, on using H_2O_2 the fine wire like structure can be obtained with high aspect ratio which have many applications but it H_2O_2 gives more vertical etching than the horizontal etching which leads to the less surface area or porosity of the SiNWs. Therefore, H_2O_2/HF has been replaced by KMnO₄/HF to be used as the etching solution to prepare the next set of samples. KMnO₄ can be a good option to replace H_2O_2 because of its advantage in procurement, storage, and non-hazardous nature. Hence to know the morphologies' difference by using different oxidizing agent, SEM study has been done as shown in Figure 7.15. Figure 7.15A shows the surface morphology of the SiNWs. The top view SEM images (Figures 7.15) shows porous structures by using KMnO₄ and similar to the one obtained using H_2O_2/HF solution (Figure 7.14).

Figure 7.15: The SEM images of SiNWs prepared by metal assisted chemical etching using $KMnO_4$ as oxidizing agent, (A) shows the top surface and, (B) shows the cross-sectional view.

From Figure 7.15, it is evident that the Si wafer has been etched in all the three dimensions and shows a cheese like structure and makes a highly porous sample. Figure 7.15B shows the cross-sectional view of the SiNWs which confirms that prepared samples are highly porous.

7.8 Effect of Oxidizing Agent on the Porosity

To check the highly porous or surface area of the prepared SiNWs, porosity analysis has been done by simply using Origin 9.0 software. Therefore, to calculate the porosity a sample relation has been used which can be given

as Eq 7.8: Porosity (%) =
$$\frac{Volume \ of \ pore \ (V_{pore})}{Volume \ of \ solid \ (V_{solid})} \times 100,$$
 (7.8)

Table 7.2. Porosity analysis of top surface of Si wafer etched by $KMnO_4$ and H_2O_2 .

Parameter	For	KMnO ₄	etched	For	H_2O_2	etched
	wafer (Figure 7.15A)		wafer (Figure 7.14A)			
Porosity	0.70	37		0.559	9	
Porosity (%)	70.3	7%		55.68	%	

From table 7.2, it is clear that the porosity of KMnO₄ etched wafer is more than the porosity of H_2O_2 etched wafer and the morphology of sample prepared using KMnO₄ looks cheese-like structure whereas that prepared using H_2O_2 looks wire like. The high porosity of the KMnO₄ etched wafer confirms that the etching takes part in all the three dimensions of the wafer. The highly poroused SiNWs are useful in the solar cell and many other fields where high surface area is required. On the other hand, H_2O_2 etched wafers are less poroused and provide a well-aligned wire-like structure and as explained before, these structures have advantages in many fields such as field emission area.

7.9 Raman Study of the SiNWs prepared by using KMnO₄

Now to confirm the size of the KMnO₄ etched SiNWs, Raman spectroscopy analysis has been done (Figure 7.16). The obtained Raman spectra from the KMnO₄ etched wafer (black scattered curve) shows asymmetry, broadening and shift in the Raman peak position in comparison with the Raman spectra of the c-Si which confirms that the prepared sample is in the nonorange. Therefore, to know the size of the prepared sample, a theoretical analysis has been done using PCM model (red solid curve) discussed in section 7.5 (Eq 7.5) and the experimentally observed Raman spectra has been fitted.

The inset of Figure 7.16 shows the observed Raman spectral parameters of the experimentally observed Raman spectra.

Figure 7.16: Fitting of the Raman spectra obtained using KMnO₄ to fabricate SiNWs, solid line and scattered curve represent the theoretically generated Raman lineshape and experimentally observed Raman spectra, respectively.

The peak position of the Raman spectra is centered at 518.5 cm⁻¹ which is redshifted in comparison with the c-Si (520.5 cm⁻¹) counterpart and the spectral linewidth of the Raman spectral is obtained to be 9 cm⁻¹ meaning a broadened spectrum in comparison with the c-Si (4 cm⁻¹). Hence by using these Raman parameters, a fitting of the observed Raman spectra has been done by using Eq 7.5. From fitting the size of the SiNWs is observed approximately 8nm. Therefore, it can be said that SiNWs of size ~8 nm is present at the microscopic level in porous Si prepared using KMnO₄ which are found to be more porous as compared to those prepared using H₂O₂.

7.10 Summary and Conclusion

In this chapter, Raman study of low dimensional materials i.e., nanomaterials and amorphous materials as well, has been done. First of all, TD Raman spectromicroscopy has been used to investigate the anharmonic effect on the rutile TNRs. From the TD Raman spectra of the rutile TNRs, it has been observed that all the Raman active modes that appear in the spectra behave differently with temperature. The E_g Raman mode is affected by the temperature and follows the Balkanski's anharmonic theory of phonon decay, and a theoretical analysis has been done to calculate the degree of anharmonicity in E_g mode. On the contrary, $B_{1g} \& A_{1g}$ Raman modes seems to be immune against thermal effects which is also interesting to observe.

Apart from this, a theoretical analysis has been proposed to predict the Raman lineshape for a very short-range order materials by giving an example of amorphous Si. A new model, DMM-BPM has been developed which is free from the various fitting parameters and gives a lineshape for the a-Si and has also been compared with the already existing PCM model. The PCM model is suitable to generate the Raman lineshape for the nanomaterials and which have the size upto 3nm and this model depends upon the various fitting parameters i.e., wavevector q, size of the sample, linewidth of the Raman spectra due to which this model has many limitations. On the other hand, an empirical relation has been proposed for the size dependent Raman peak position in the a-Si and validated by comparing previously reported data.

Additionally, a Raman spectroscopic study on the SiNWs fabricated using MACE process was also carried out. The effect of different oxidizing agents namely KMnO₄ and H_2O_2 has also been studied. The obtained etched wafers using KMnO₄ result in a cheese like structure while wire like structures is obtained by using H_2O_2 . On the other hand, KMnO₄ etched wafers are highly porous and have a larger surface area in comparison to the H_2O_2 due to the multi-dimensional etching using KMnO₄. Also, the Raman spectroscopic study has been done to estimate the size of the KMnO₄ etched wafer where the well-established PCM model has been used to fit the obtained Raman spectra and the size of the KMnO₄ etched wafers has been

calculated which was found to be approximately 8 nm showing moderate confinement.

Chapter 8

Conclusion and Future Scope

The major findings of the current study are being summarized in this chapter and the scope for extending it further has also been discussed here.

8.1 New Scientific Findings in the Present Thesis Work:

- Thermally tuned Fano interaction or nonlinear Fano interaction in the heavily doped p-type silicon has been discovered by temperature dependent Raman spectroscopy.
- The reported nonlinear Fano interaction in heavily doped p-type silicon has been established by calculating phonon-self energy perturbed by both the perturbations i.e., temperature and doping concentration.
- Direct evidence of dispersive nature of Fano interaction has been provided through excitation wavelength dependent thermally tuned Fano interaction in heavily doped p-type Si using Raman spectromicroscopy.
- The inverse relation of the excitation wavelength and temperature to Fano interaction in heavily doped p-type Si has been discovered.
- The presence of two different quasi-micro phases in the heavily doped p-type Si has been reported and is being validated by the study of thermal hysteresis.

- Developed Raman spectromicroscopy as a tool to estimate temperature dependent Fermi energy and Fermi level position in heavily doped p-type and n-type silicon.
- Anharmonic effect has been investigated in rutile TiO₂ nanorods using Raman spectromicroscopy.
- A theoretical model has been developed to predict the Raman lineshape for very short range ordered materials i.e., for amorphous silicon.

8.2 Conclusions

The major conclusions of the work reported in the current thesis are discussed below:

- The nonlinear Fano interaction can be observed in a single system by providing temperature as an external perturbation.
- There exist different pathways for phonon decay which are intermediated through phonon annihilation by interferons.
- A TD Raman spectromicroscopic study reveals that p-type Si with very high doping (resistivity 0.001 Ω-cm) shows anomalous behavior with temperature and deviates from the conventional anharmonic theory of phonon decay.
- The linewidth of the Raman spectra from heavily doped p-type Si shows parabolic nature with increasing temperature. This parabolic nature of the spectral linewidth of heavily doped p-type Si is due to the inherently present Fano interaction due to the high doping.
- At lower temperatures, the phonon decay in heavily doped p-type Si is dominated by the Fano interaction and all the phonons behaves as interferons.

Due to the interaction between electron-phonon i.e., interferon, initially spectral linewidth decreases with temperature at lower temperatures. This interaction gets weaker with the increasing temperature and at a certain temperature (transition temperature, 475K) all the interferons converted into phonons. After 475K, heavily doped p-type Si, the phonons adopt the process of anharmonic decay and spectral linewidth increases with increasing temperature.

- > To validate the above, TD Raman spectroscopy has also been performed on control samples of moderately doped and very lightly doped p-type Si of resistivities 0.01 and $10^3 \Omega$ -cm, respectively. The moderately doped and lightly doped samples follow Balkanski's anharmonic decay theory for the phonon annihilation.
- The effect of excitation wavelength on the nonlinear Fano interaction has been studied using three different excitation wavelengths 532nm, 633nm, and 785nm of Raman spectrometer to reveal that the observed nonlinear Fano interaction is energy dispersive in nature.
- The strength of the Fano interaction present in the heavily doped ptype Si, is directly proportional to the excitation wavelength.
- While using 785nm excitation laser, the phonon to interferon transition temperature of interferons is very high, approximately near to 700K (extrapolated) where all the interferons get converted into the phonons. And the Raman spectra is broad at lower temperatures.
- The strength of the bound state of electron-phonons i.e., interferons have different energies and require different temperatures (thermal energy) to dissociate.
- An empirical relation has been proposed to calculate the interferon dissociation energy corresponds to the given thermal energy.

Heavily doped p-type Si consists of two micro phases in the different temperature range. In the low temperature range, the system remains in the interferonic rich state and in the high temperature region, the system remains in the phononic rich state.
- To confirm the different phases in the heavily doped p-type Si, theoretical calculation has been done and TD Fano coupling parameter (q) has been calculated and also proposed a new relation for the TD Fano coupling parameter.
- At high temperatures little Fano interaction is present, and the system does not contain any interferon.
- To check the stability of the different phases, present in the heavily doped p-type Si, thermal hysteresis in Raman spectral parameter from low to high temperature (heating) and high to low temperature (cooling) has been performed. Lack of thermal hysteresis confirms that both the phases are equally stable in the system and requires 41.2 meV energy for transition.
- Raman spectromicroscopy can be used to effectively estimate the position and temperature dependent shift in Fermi energy in heavily doped n- and p-type Si by using TD Raman spectro & microscopy.
- It has been concluded in this study that if any material exhibit Fano interaction, then Fermi energy can be calculated by simply using TD Raman spectroscopy.
- Raman spectra from a-Si can be represented using a theoretical lineshape function generated using DMM-BPM which can be used to estimate the short-range order in amorphous materials.
- The comparison between DMM-BPM and phonon confinement model reveals that PCM model cannot be used if the wavevector is not defined in any material while DMM-BPM method can generate the Raman lineshape for such materials.
- An empirical relation based on the BPM model has been proposed to calculate the size dependent Raman peak position and validated.
- It is established that oxidizing agent plays a role in metal assisted chemical etching of semiconductors.

- It is concluded that KMnO₄ etched wafers are highly porous and have larger surface area in comparison to the H₂O₂ etched wafers due to the multi-dimensional etching.
- Raman study reveals that 8nm sized nanostructure are present in the fractal type porous Si synthesized using MACE.

8.3 Future Scope

As mentioned above, the current work focuses on the TD Raman spectromicroscopic study of semiconductor i.e., Si and transition metal oxide (TiO₂ nanorods) and the nanowires of the Si. This study mainly focuses on the thermally induced Fano interaction in Si which can be further studied in the various materials. The work can be extended for:

- The study of nonlinear Fano effect in different materials such as 2D materials like graphene, MoS₂, and complex materials which have inherent electron-phonon interaction present in the sample.
- The study of low energy phonons i.e., acoustical phonons and their behavior against temperature in Si and in other materials as well.
- Ultra-low temperature (up to liquid helium) study of heavily doped Si using TD Raman spectroscopy to investigate the behavior of interferons in ultracool range.
- TD Raman study of other materials such as Maxene, MOF/COF, and other new materials.

Appendices

Appendix 1

Silicon elemental facts

Classification:	Si is a metalloid
Atomic weight:	28.0855 g/mol
Density @ 20 °C:	2.33 g/cm ³
Atomic Volume:	12.1 cm ³ /mol

States

Solid
1687 K (1414 °C)
3538 К (3265°С)

Energies

Specific Heat Capacity:	0.71 J g ⁻¹ K ⁻¹
Heat of Fusion:	50.21 kJ mol ⁻¹
1 st Ionization Energy:	786.4 kJ mol ⁻¹
2 nd Ionization Energy:	1577 kJ mol ⁻¹
3 rd Ionization Energy:	3231.4 kJ mol ⁻¹
Heat of Atomization:	456 kJ mol ⁻¹
Heat of Vaporization:	359 kJ mol ⁻¹
Electron Affinity:	133.6 kJ mol ⁻¹

Oxidation & Electrons

Shells:	2,8,4
Min. Oxidation Number:	-4
Min. Common Oxidation No.:	-4
Electronegativity (Pauling Scale):	1.9
Electron Configuration:	1s ² , 2s ² , 2p ⁶ , 3s ² , 3p ²
Max. Oxidation No .:	4
Max. Common Oxidation No.:	4
Polarizability Volume:	5.4 Å ³

Appearances & Characteristics

Structure:	Diamond Structure
Hardness:	11.9 GPa
Color:	Silvery

Reactions & Compounds:

Reaction with Air:	None
Reaction with 15M HNO ₃ :	None
Oxide(s):	SiO ₂
Hydride(s):	SiH_4 (Silane), Si_2H_6 + more
Reaction with 6M HCl:	None
Reaction with 6M NaOH:	Mild (Silicates)
Chloride:	$SiCl_4$, Si_2Cl_6 + more

Conductivity

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

Abundance & Isotopes:

Abundance Earth's Crust:	28% by weight, 21% ppm by moles
Abundance Solar System:	900 ppm by weight, 40ppm

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 its crystalline form is very brittle with a marked metallic luster. Si occurs mainly in nature as 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.

Appendix 2

Energies

TiO₂ Elemental facts

Phases:	4, Akaogiite, Anatase, Rutile, and
	Brookite
Molecular Weight:	79.87 g/mol
Dielectric constant:	10 - 85
Density @ 20°C (rutile):	4.23 g/cm3
Density @ 20°C (anatase):	3.78 g/cm3
Atomic Volume:	18.84 cm ³ /mol
Refractive index (anatase):	2.488 (anatase)
Refractive index (brookite)): 2.583
Refractive index (rutile):	2.609

States		
State:	White Solid	
Odor:	Odorless	
Boiling Point:	3245 K (2972 °C)	
Melting Point:	2116 K (1843 °C)	

Bandgap (Anatase):	3.2 eV
Bandgap (Rutile):	3 eV

Bandgap (Brookite): bandgap semiconductor)	1.92 eV (indirect
Specific Heat Capacity (Anatase):	100.46 J.mol-1 K-1
Specific Heat Capacity (rutile):	67.3 J.mol-1 K-1

Oxidation & Electrons

Min. Oxidation Number:	+2
Min. Common Oxidation No.:	+2
Electron Configuration (Ti):	1s ² , 2s ² , 2p ² , 3s ² , 3p ⁶
Electron Configuration (O):	$1s^2$, $2s^2$, $2p^4$
Max. Oxidation No.:	4
Max. Common Oxidation No.:	4

Appearances & Characteristics

Crystal Structure (Akaogiite):	Monoclinic
Crystal Structure (Anatase):	Tetragonal
Crystal Structure (Brookite):	Orthorhombic
Crystal Structure (Rutile):	Tetragonal
Color:	White

Reactions & Compounds:	
Solubility:	Insoluble in water, dilute acids
	and base
Reaction with Air:	None
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Reaction with conc. H ₂ SO ₄ :	$Ti(SO_4)_2$, and $TiOSO_4$
Oxide(s):	TiO, TiO ₂ , and Ti ₂ O ₃
Hydride(s):	TiH
Reaction with 6M HCl:	TiCl ₄
Reaction with 6M NaOH:	Na ₄ TiO ₄
Chloride:	TiCl ₄ , TiCl ₃ , TiCl ₆ + more

Conductivity		
Thermal Conductivity:	$11.8 \text{ W m}^{-1} \text{ K}^{-1}$	
Electrical Conductivity:	70 S cm ⁻¹	

Harmful Effects

 TiO_2 is not known to be toxic, but if breathed in as dust it may cause eye damage, skin burns, and respiratory irritations. TiO_2 is suspected to causing cancers.

Appendix 3

Symbol and Description of Vibrational Bands

- v: Stretching
- δ: Bending
- w: Wagging
- r: Rocking
- t: Twisting
- *σ*: Out of plane
- as: Antisymmetric
- s: Symmetric
- d: Degenerate

Stretching Vibrations



Bending Vibrations



Figure A3.1: Types of vibrations

Symbol and Description of Mulliken Symbol of Symmetry Species

A:	Symmetric with respect to principal axis of symmetry
B:	Antisymmetric with respect to principal axis of symmetry
E:	Doubly degenerate, two-dimensional irreducible representation
Т:	Triply degenerate, three-dimensional irreducible representation
g:	Symmetric with respect to a center of symmetry
u:	Antisymmetric with respect to a center of symmetry
1 (subscript)	Symmetric with respect to a C2 axis that is perpendicular to the principal axis. Where there is no such axis the subscript indicates that reflection in a v plane of symmetry is symmetric.
2 (subscript)	Antisymmetric with respect to a C2 axis that is perpendicular to the principal axis. Where there is no such axis the subscript indicates that reflection in a v plane of symmetry is antisymmetric.

(prime):	Symmetric with respect to reflection in a
	horizontal plane of symmetry
"(double prime):	Antisymmetric with respect to reflection in a
	horizontal plane of symmetry

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ANNEXURE 1

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