8.1 Introduction

Due to their versatile capabilities Silicon, Gallium arsenide and Gallium nitride are some of the semiconducting materials, which are used nowadays in the manufacture of variety of electronic gadgets. Interesting phenomena such as persistent photoconductivity, DX centers, room temperature photoluminescence, etc., have been recently observed. Similarly new features are observed, when implanted with hydrogen ions. As mentioned in the motivation of the present thesis, (First chapter), the less explored aspects of the phonon physics of these materials are investigated by experiment, theory and simulation, and also the fabrication of a device. The results of our investigations are summarized in various chapters.

8.2 Chapter 1

The basics of lattice dynamics are brought out in the first chapter. Experimental and theoretical models for phonons, defect modes, Green’s functions and basic ideas on simulations are discussed in detail, and the motivation for the present investigations is clearly brought out.

8.3 Chapter 2

Different doses of $H^+$ with an energy of 30 keV are implanted in silicon doped GaAs wafers A qualitative analysis of the $H^+$ ion induced defects, is
carried out first by Atomic Force Microscopy (AFM). A quantitative study of the damage profiles in n-GaAs at different H\textsuperscript{+} doses is carried out by XRD rocking curves. These experiments are supplemented with Laser Raman and Photoacoustic (PA) measurements. From the PA measurements, various thermal properties are computed.

The strains are determined using a least squares routine show that the out-of-plane strains $\varepsilon_1$ are generally precise to about 2 % for the samples E15 to E17 while it is nearly 13 % for sample E14. Also in-plane strains are much smaller than the out-of-plane strains. Such trends are in agreement with several other reports of strains in implanted layers Servidori [1], Wie [2] and Geeta et al [3]; have found from by XRD only negligible in-plane strain and appreciable perpendicular strain, depending on dose, energy etc, associated with the implantation.

It has not been possible to account for the behaviour of lower dose sample E14, exhibiting all layer peaks consistently on the ‘high’ $\omega$ side of the substrate peak, suggesting ‘lattice contraction’. Such a feature has not been reported in any implantation studies so far, particularly with strain analyses employing XRD.

The analysis suggests that, for doses below amorphization limit, i.e., for E14 and E15 intra-cascade and inter-cascade recombination effects and probable occurrence of different aggregation forms of surviving defects are
responsible for the damage growth. In the E14 sample, the intra-cascade recombination alone takes place, creating vacancies, which leads to the contraction of the implanted surface. Whereas in the case of E15 sample inter-cascade recombination takes place, leaving interstitials in the surface, which allows an expansion of the implanted surface. In the sample E16 the amorphization limit is reached, which could be due to the overlapping of the defect cascades. Then in the sample E17, the surface crystalline region disappears and the amorphous layer appears on the surface. The defects are then annealed out and the recrystallisation of damage-amorphized n-GaAs clusters takes place. The residual damage reaches the saturation, maintaining a balance between damage creation and damage annealing processes. So there can be a possibility of interstitials and vacancies to co-exist in the sample E17.

The type change at $10^{15}$ ions/cm$^2$ dose has made an impact on the system. The change of trend in the strain parameters, when compared with the LOPC and PA signals before and after the type change, clearly explains that all these parameters are type dependant. Also it demonstrates the close relationship of the optical/acoustical characteristics with the damage growth. The variation of thermal diffusivity with the chopping frequency and the wavelength also indicate the presence of the defects and their influence in the diffusion. The thermal parameters evaluated from the PA signals very closely agree with the available reported values [4]. The AFM pictures of the samples
depict the level of damages due to the bombardment of the $H^+$ ions, which agree with the XRD analysis, Raman and PA measurements.

### 8.4 Chapter 3

When hydrogen atoms are substituted into semiconducting systems new localised vibrational modes (LVMs) appear. Infrared absorption on GaAs doped with the isotopes of silicon under hydrogen or deuterium plasma treatment has shown two new localised modes. A simple *lattice dynamical nine-atom molecular model* is presented to compute, the defect modes by assuming the hydrogen or deuterium to be bound in the antibonding position of the substituted Si atom, resulting in a defect complex of $C_{3v}$ symmetry. The two new vibrational modes of the paired Si are found with a small isotope shift, when H is replaced by D. *Group theoretical* methods are employed for the precise identification of the localised modes.

Pajot *et al* [5] have experimentally observed a stretching mode and a doubly degenerate wagging mode in GaAs doped with various isotopes of Si when subjected to hydrogen or deuterium plasma.

The present lattice dynamical model in the harmonic framework is not only simple but also successful in explaining the observed defect modes. The identification of the stretching and wagging modes are carried out by group theory, which helps to obtain the modes of various symmetry species of the entire defect complex. The modes of the molecule include besides the
stretching and wagging modes, a defect lattice mode, a LVM of GaAs:Si, three acoustical modes and the modes of the molecule in the static lattice of GaAs with frequencies less than \( \omega_{LO}(I) \), \( I \) being the zone center.

The present results on the defect modes thus explain the experimental results. The localised mode at 1718.5 cm\(^{-1}\) \((^{28}\text{Si,H})\), 1717.0 cm\(^{-1}\) \((^{29}\text{Si,H})\), 1715.2 cm\(^{-1}\) \((^{30}\text{Si,H})\), 1248.1 cm\(^{-1}\) \((^{28}\text{Si,D})\) and 1247.0 cm\(^{-1}\) \((^{29}\text{Si,D})\) under \( A_1 \) representation (stretching mode) are both IR and Raman active. The modes at 77 and 30 cm\(^{-1}\) are IR and Raman inactive. The modes at 896.5 cm\(^{-1}\) or 895.9 cm\(^{-1}\) or 895.6 cm\(^{-1}\) due to hydrogen and 639.6 cm\(^{-1}\) or 638.8 cm\(^{-1}\) due to deuterium under the \( E \) representation, are identified as the bending or wagging modes from the displacement pattern of the H atom in the Si-H bond.

The small isotope shift in the stretch modes indicates that the H or D is paired with the \( \text{Si}_{\text{Ga}} \) atom. This silicon isotope splitting in the stretch modes demonstrates that it must originate from a hydrogen atom bonded to a silicon atom, substituted either at the Ga site or As site. The available evidence indicates that the two modes – the stretching and the wagging – are always observed with the same ratio of strengths and it is inferred that they arise from a common defect [5].

The LVM absorption (384 cm\(^{-1}\)) from isolated \( \text{Si}_{\text{Ga}} \) atoms has almost been removed, due to the neutralization of the \( \text{Si}_{\text{Ga}} \) donors by the hydrogen atoms, as observed by Pajot et al [5] but another new perturbed \( \text{Si}_{\text{Ga}} \) mode \( \approx 590 \) cm\(^{-1}\) is obtained under \( A_1 \) representation. Thus a simple lattice
dynamical model explains satisfactorily the observed defect modes, without resorting to a broken bond or other approximations.

8.5 Chapter 4

Infrared absorption on hydrogen passivated and magnesium doped GaN has shown the localised mode at $3125 \text{ cm}^{-1}$. LDA calculations predict LVM’s at 3277 (stretch) and 1311 (wag) cm$^{-1}$ for a configuration with H antibonding to the nitrogen atom. The simple nine-atom molecular model is extended to compute the defect modes assuming all the possible orientations with hydrogen bound in the antibonding position of the nitrogen (AB$_N$), the bond center (BC) or the antibonding position of the substituted Mg atom (AB$_{Mg}$), resulting in a defect complex of $C_3v$ symmetry. Group theoretical methods are employed for the precise identification of the localised modes in all the three possible configurations. The present results not only satisfactorily explain the experimental LVMs but also predict the presence of new wagging modes at 1502 cm$^{-1}$ for the BC and 910 cm$^{-1}$ for the AB$_{Mg}$ configurations, which have not been reported anywhere.

Torres et al [6] have used an *ab initio* local density functional method on a large H- terminated cluster, [7] employing norm-conserving pseudopotentials [8] for this GaN system. However their results do not agree with the experimental observations.
CHAPTER-8 SUMMARY

In the present approach using the molecular model for lattice vibrations, all the modes related to the hydrogen vibrations are obtained in a realistic fashion. The observed localised modes at 3124 cm$^{-1}$ (AB$_N$), 3643 cm$^{-1}$ (BC) and 2138 cm$^{-1}$ (AB$_{Mg}$), under $A_1$ representation (stretching mode) are both IR and Raman active. The modes at 188 and 46 cm$^{-1}$ are IR and Raman inactive. The modes at 1323 cm$^{-1}$ (AB$_N$), 1502 cm$^{-1}$ (BC) and 910 cm$^{-1}$ (AB$_{Mg}$) under the $E$ representation, are identified as the bending modes from the displacement pattern of the H atom in the Mg-H bond.

8.6 Chapter 5

In continuation to our damage (ion implantation) study in the case of H$^+$ ion implanted $n$-GaAs, a study on chemically etched Si crystals is performed and the fabrication of a solar cell using gold coated porous silicon (PS) is also carried out.

The PS [9] behaves as a direct band gap semiconductor (similar to GaAs and GaP) with a large quantum efficiency. When porous silicon is coated with a thin film of gold, a solar cell is formed and the photoluminescent [10] and photovoltaic measurements give a clear idea, that this porous silicon can be used for the fabrication of optoelectronic devices [11]. But there are some difficulties in fabricating a high efficient device under the laboratory conditions.
In the present study, photoluminescence (PL) is observed at room temperature. Similarly, the excitation and emission PL spectra are also observed. Thus, a device by coating gold over the porous layer of the material could be successfully fabricated and its electrical characteristics are studied.

8.7 Chapter 6

The diffusion in silicon is studied employing simulation by Chandrasekhar hopping. The method of Chandrasekhar on astronomical bodies is applied to study of self and impurity diffusion in silicon. The Fokker-Planck form of the Fick’s law and a smooth continuous position probability density for the diffusing particle \( \omega(r,t) \), which represents the position of the diffusing particle at any time \( t \), is used for the evaluation of the diffusion constant. The results agree reasonably well with the available experimental and theoretically reported values.

Self and impurity diffusion studies in Si and Ge, by experiment and theory are reported in literature and of late by simulation techniques have been proposed. Even though many of the investigations employ either Monte Carlo or Molecular Dynamics simulation, in the present study a relatively new approach for diffusion is carried out. Collins \textit{et al} [12] have worked out a one dimensional diffusion problem, to demonstrate the Chandrasekhar hopping. This model is extended to study the self and impurity diffusion in a real three
dimensional Si crystal, with suitable modifications. The results obtained from the present simulation agree with the experimental results and the previously reported theoretical values [13].

Thus, the *Chandrasekhar-hopping*, though developed originally for astronomical objects, can be extended to *microscopic* level such as crystalline systems. Various Ising models, including Monte Carlo and Molecular dynamics simulations can be refined according to *Chandrasekhar-hopping*, to simplify the problem.

The exact mechanism of diffusion is, however, not determined, but could be demonstrated from the Arrhenius plot (where different slopes are observed in different temperature regions), that there is a change in diffusion mechanism above and below certain temperature. This is an important result from the present simulation work and explains why no two diffusion experiments on the same system could give identical results.

8.8 Chapter 7

In view of the fact that, diffusion studies are always made at high temperatures of the order of 700 - 1000°C, a study on thermal expansion and hence the anharmonicity becomes necessary to work out a suitable model in the lattice dynamical environment on systems like CdTe, ZnTe, HgTe, GaAs, InP, etc.
Anharmonicity in crystals is viewed generally through the Grüneisen parameter. Several independent investigations on low and high temperature anharmonicity have been reported but, there is no attempt to present a unified approach to workout the Grüneisen parameter for any system and for any temperature. Batana et al [14] have implemented the above prospects in their program. However, their program could handle only the systems with $s > 1$ (greater anisotropy). But for systems with $s < 1$ (lower anisotropy) their program is unsuitable. A generalized program incorporating suitable modifications on the program of Batana et al [14] with extensions to other types of systems is developed. This becomes essential as the role of anharmonicity in different systems are different and once such a software is available, it will be simpler to study a particular system for anharmonicity, immediately and proceed further with all computations.

This modified program computes the $\gamma$ values for different temperatures from $\sim 0$ K to any high temperature (1000 K). The low and high temperatures are determined from the Debye temperatures of the systems. The results of the modified program are compared with the available experimental results reported by Born et al [15], Sheard [16], and those reported recently by Chuan–Hui Nie [17]. Appreciable agreement is observed between the calculated and the experimental results.

The evaluation of thermal expansion or Grüneisen parameter for ZnTe, CdTe, etc., systems with the anisotropy and the anharmonicity are not very
high could not be carried out with the program of Batana et al [14], or the modified program of Batana et al [14]. Another program has been developed for the evaluation of $\gamma$ for such systems for different temperatures. The results computed using this software package for systems with $s < 1$, give a very satisfying result compared to the available experimental values reported by Soma et al [18] and Talwar et al [19]. This technique can evaluate the negative values of $\gamma$ also.
8.9 References


