Microstructure, Vacancies and Voids in Hydrogenated Amorphous Silicon

Rajendra Timilsina
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MICROSTRUCTURE, VACANCIES AND VOIDS
IN HYDROGENATED AMORPHOUS SILICON

by

Rajendra Timilsina

Abstract of a Dissertation
Submitted to the Graduate School
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

December 2012
ABSTRACT

MICROSTRUCTURE, VACANCIES AND VOIDS
IN HYDROGENATED AMORPHOUS SILICON

by Rajendra Timilsina

December 2012

This dissertation presents a theoretical and computational study of microstructure, vacancies and voids in hydrogenated amorphous silicon (a-Si:H). The microstructure consists of all possible silicon-hydrogen bonding configurations such as SiH, SiH₂, SiH₃ and SiH₄. However, it is highly dominated (approximately 75% or even more) by monohydride (SiH) configurations. Furthermore, the hydrogen atoms locate in both clustered and diluted phases; as a result, the distribution becomes highly inhomogeneous. Approximately 5% of hydrogen atoms reside in a form of isolated monohydrides at the lower (7 at.%) concentration whereas such configurations do not appear at the higher concentrations (≥14 at.%).

The microstructure is further enriched with different types of vacancies such as mono- and divacancies. At the lower hydrogen content, it consists of split divacancies whereas voids appear in the higher concentrations (≥16 at.%). Structures of the voids are highly irregular and their internal surfaces consist of 6 – 16 hydrogen atoms. The microstructure further shows hydrogen molecules within the voids at the higher (≥16 at.%) concentrations. However, the concentration of the molecules is very low, in a range of 0.9 – 1.4% of the total hydrogen atoms.

In order to investigate the microstructure in further detail, an approximate calculation of the nuclear magnetic resonance (NMR) line spectra is performed. The approximated line spectrum is a superposition of broad (19 – 50 kHz) and narrow line widths (1.7 – 6 kHz) depending on the concentration of hydrogen atoms. These observations are in excellent agreement with infrared (IR), nuclear magnetic resonance (NMR), multiple quantum nuclear magnetic resonance (MQ-NMR) and calorimetry experiments as well as ab initio calculations.
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A Dissertation
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LIST OF ABBREVIATIONS

a-Si - Amorphous Silicon
a-Si:H - Hydrogenated Amorphous Silicon
CRN - Continuous Random Network
NMR - Nuclear Magnetic Resonance
IR - Infrared
PECVD - Plasma Enhanced Chemical Vapor Deposition
DB - Dangling Bond
FB - Floating Bond
MC - Monte Carlo
MD - Molecular Dynamics
DFT - Density Functional Theory
RDF - Radial Distribution Function
PCF - Pair Correlation Function
VDOS - Vibrational Density of States
EDOS - Electronic Density of States
MQ-NMR - Multiple Quantum Nuclear Magnetic Resonance
HW-CVD - Hot Wire Chemical Vapor Deposition
GD - Glow Discharge
LDA - Local Density Approximation
GGA - General Gradient Approximation
ECMR - Experimentally Constrained Molecular Relaxation
SIESTA - Spanish Initiative of Electronic Simulation with Thousands of Atoms
DZP - Double Zeta Polarization
SZ - Single Zeta Polarization
Si - Silicon
H - Hydrogen
SiH - Silicon hydride
FWHM - Full Width at Half Maximum
CVD - Chemical Vapor Deposition
WWW - Wooten, Winer and Weaire
RMS - Root Mean Square
FID - Free Induction Decay
SEM - Scanning Electron Microscopy
Chapter 1

INTRODUCTION

1.1 Amorphous Semiconductor

The semiconductor industry today is a trillion dollar market that accounts for almost 8% of the total global economic activity [1]. Although crystalline semiconductors have dominated the industry, amorphous semiconductors are emerging in these days because of their special properties [2, 3, 4] which make the materials suitable for several technological applications [5, 6]. They are often inexpensive to prepare and their properties can be engineered to suit particular applications. Another attraction of the amorphous semiconductor is in the solar energy industry [7]. The industry uses both crystalline and amorphous silicon in manufacturing of solar cells. Nowadays, 30–40% of the solar cells are thin-film solar cells made from the amorphous silicon [8, 7]. Therefore, more research works are essential on the material to understand its special properties for technological applications.

Amorphous semiconductors are special types of disordered materials that have short-range orders with long range disorders [6, 9]. It is characterized as an irregular arrangement of atoms or molecules in meta-stable (non-equilibrium) states [10, 11]. Its structure varies with nature of bonding schemes of constituent atoms. As a result, the structure becomes a continuous random network (CRN) [6]. Absence of an ordered atomic structure in amorphous materials necessitates a different theoretical approach [9] than the theory of crystalline semiconductors. A description of the amorphous materials is developed instead from chemical bonding between the atoms, with emphasis on the short range bonding iterations rather than the long range order [9].

Structural disorder [10, 12] influences electronic properties [3, 13, 14] in several different ways, and manifest in the form of bonding disorder, structural defects [15, 16] and alternative bonding configurations [6]. The bonding disorder, such as deviations in bond lengths and bond angles, broadens the electron distribution of states and causes electron and hole localization as well as strong scattering of the carriers. One of the structural defects [16], for example, broken bonds have their corresponding electronic states that lie in the band gap, as a result, the energy band gap becomes narrow [14, 17]. Moreover, possible alternating bonding configuration of each atoms leads to a strong interaction between the structural and electronic states that causes meta-stability [11, 18, 19] in the amorphous semiconductor.


1.2 Amorphous Silicon

Amorphous silicon is a glassy form of silicon, one of the most common elements in the Earth’s crust [7]. It is easy to prepare and has some special properties that make it very useful in electronic devices like position-sensitive detectors [20], field effect transistors [21], liquid crystal display [22], solar cells [7, 23] and many more other electronic devices [6]. It can be prepared in several different ways. The most common is to decompose silane gas (SiH₄) by using a radio frequency discharge in a vacuum chamber [9]. Silicon produced in this process may be deposited in very thin films on substrates such as glass, stainless steel or ceramic [7]. This makes amorphous silicon a promising material for large-scale use in thin film solar cells [23]. Although amorphous silicon suffers from lower electronic performance [13] as compared to the crystalline silicon, it is more flexible in its applications. For instance, amorphous silicon layers can be made thinner than the crystalline silicon [8]. Moreover, it can be deposited at very low temperature (as low as 75 degree Celsius) that allows for deposition on not only glass, but also on plastic as well [7]. The amorphous silicon also can be deposited over large area by plasma-enhanced chemical vapor deposition (PECVD) that reduces the production cost of solar cells significantly [5].

Although considerable work has been done over the past 40 years, there are several aspects of the material to be studied thoroughly. We need to find better ways of making it, faster ways of depositing it, and ways of fabricating it into electronic devices. One of the main shortcomings at present is that its properties tend to change under illumination or heating [24, 25] and this can reduce the effectiveness of any device that uses it. Ways need to be found to stabilize the material so that it achieves its full potential.

There are many potential applications of amorphous thin film semiconductors such as the hydrogenated amorphous silicon [5, 7]. However, there are still many materials science problems that must be overcome before amorphous semiconductors achieve their full potential [7]. One possibility is that the amorphous silicon, because of its special attributes of low-cost and ease of preparation, could become the mainstay of the solar cell industry. In the future, we could see huge arrays of solar cells collecting sunlight and converting it into electricity. This is not a science fiction - the costs of doing this are falling rapidly and within a decade, large-scale electricity production from solar cells may be a reality [5]. The hydrogenated amorphous silicon is one of the leading contenders for this role.

1.3 Hydrogenated amorphous silicon

In general, a silicon atom is trahedrally-bonded to four nearest neighbors. If it is bonded with less than four atoms then the silicon atom has dangling bonds (DB). If it is connected with more than four atoms then the silicon atom has floating bonds (FB) [26]. Schematic diagrams of the dangling and the floating bonds are shown in Figure 1.1. The figure (in the left) shows that a
silicon atom is bonding with only three atoms and it has a capacity to bond one more atom. Such configuration is considered as a dangling bond. In right side of the figure, the silicon atom is connected with five atoms and the dashed line is considered as a floating bond. These dangling and floating bonds are considered as defects in the amorphous state and they are responsible for poor quality of technological devices [6].

Amorphous silicon (a-Si) has large number of such dangling bonds [27] with concentration $10^{15} - 10^{20}\ cm^{-3}$ depending on the method of preparation [3] as well as deposition conditions [6]. Those bonds degrade the quality of electronic devices [28]. Hydrogenation is one of the most useful techniques to pacify those dangling bonds so that the performance of the devices improves significantly [29]. Therefore, hydrogenated amorphous silicon (a-Si:H) is used in electronic devices rather than the amorphous silicon itself. Furthermore, hydrogen plays very important role [30] to determine the electronic [14] and optical properties [31] of the material. However, it may cause light-induced degradation which is called Staebler-Wronski effect [32] and several research works have been performed to understand the effect [24, 25, 33, 34, 35]. Therefore, the distribution of hydrogen atoms and their bonding schemes are to be studied thoroughly in the hydrogenated amorphous silicon.

![Figure 1.1: A schematic diagram of a dangling bond (left) and a floating bond (right). Silicon atoms are shown as black circles.](image)

**1.4 What is hydrogen microstructure?**

Hydrogen microstructure refers to the structure of hydrogenated amorphous silicon on a scale of several angstroms that can provide crucial information about bonding mechanisms, distribution of hydrogen atoms and structure of defects such as vacancies and voids in the network. Although several experimental [10, 36, 37, 38, 40] and theoretical works [41, 42, 43, 44, 45] have been devoted on the material in the past four decades, there are very few studies [46, 47, 48, 49] that explicitly focused on the hydrogen microstructure. Disorder in the bond length and bond angle distributions of hydrogen atoms [50, 51, 52] as well as their effects on the quality of electronic devices are not completely understood yet [6]. Thus, the main purpose of this work is to devote on the hydrogen microstructure so that one can understand the material in the further depth.
1.5 Experiments of hydrogenated amorphous silicon

Generally, amorphous materials are prepared via non-equilibrium processes [6], thus, properties of prepared samples depends on the method of preparation. Major preparation methods include rapid quenching from liquid phase, rapid condensation from the gas phase and formation from the solid phase [9]. The first and the second methods are popular for the preparation of glassy and amorphous materials respectively whereas the third method is useful for the ion-implantation [6]. The second method can be further divided into physical vapor deposition and chemical vapor deposition. Sputtering is an example of the physical vapor deposition. On the other hand, plasma-enhanced chemical vapor deposition (PECVD) method is mostly used while preparing the samples of hydrogenated amorphous silicon, which is an example of the chemical vapor deposition method. Once the samples are prepared, x-ray scattering [53] or neutron diffraction [54] methods are used to study the structure of the samples. In addition, nuclear magnetic resonance (NMR) [38, 46] and infrared (IR) experiments [55, 56, 57, 58] are the most used probes that provide crucial information of bonding mechanisms as well as the distribution of clustered and diluted hydrogen atoms respectively.

1.6 Computer simulation of hydrogenated amorphous silicon

Computer simulation for modeling structure of amorphous semiconductors provides an important basis of structural understanding of the material. Experimental investigations that are described in the earlier section for determination of structure are not enough to understand the structure of amorphous semiconductor. One of the reasons behind it is the absence of long-range order. It gives rise to broadening of the diffraction pattern [9]. Therefore, comparison between the results of computer simulations and experiments leads us to a better understanding of the structure. There are two major computer simulation methods: Monte Carlo (MC) and a molecular dynamics (MD).

Monte Carlo simulations are being used for solving physical or mathematical systems by nonderminitic or stochastic methods [59]. However, in this context, it is used for structural determination of disordered materials. Although MC technique is described in detail elsewhere [60, 61], only the relevent parts are presented here. A penalty function is considered and that has to be optimized with respect to experimenatal data by moving particles or atoms in amorphous networks. For example, a radial distribution function or a structure factor is optimized using this technique with respect to experimental data by moving atoms within the network. While doing so there can be several particle congurations which have the radial distribution functions consistent with experimental data. These configurations can later be used for geometrical analysis. Thus, depending on nature of a problem, a suitable penalty function is to be defined in most of MC simulations and then the function is optimized with respect to experimental data (or reference data). Monte Carlo simulation can be performed in many ways depending
on problems. However, one of the useful ways while determining the structure of amorphous material is described below.

Monte Carlo may consist of several algorithms depending on a nature of a problem. However, while modeling the amorphous materials, time evolution of constituent atoms is pursued to a statistical equilibrium at a given temperature [9]. In this method, one starts with a model structure and search for a network with lower energy by changing atomic positions, bond angles and bond length etc. Empirical or semi-empirical potentials such as Keating [62], Stillinger-Weber [63], Tersoff [64] etc. are often used while searching for the minimum energy to get a meta-stable configuration. However, the first-principles or \textit{ab initio} methods [40, 41, 45, 65] are mostly used to get the meta-stable configuration of amorphous silicon by relaxing the final structure. On the other hand, the MD method begins with Newton’s equation of N atoms in which force is derived from potential energy [66]. The potential energy is determined by electronic states of atoms mutually interacting with each other. Therefore, when atomic configurations change, we calculate electronic states for new configurations and then evaluate again the potential energy.

Most of the \textit{ab initio} MD methods [41, 67] treat both atomic and electronic states of the system self-consistently. Car and Parrinello [68] proposed a practical and powerful \textit{ab initio} MD method by combining MD and density function theory (DFT). Their approach not only extends MD beyond usual pair-potential approximations but also allows the simulation of covalently-bonded and metallic systems. However, realistic models of the material are being generated and studied after applying some modifications in the existing methods [42, 61, 69]. It is to be noted that any computer model which is generated from these methods could not represent the real sample exactly because of some approximations made in the methods. However, it can represent those sample within an acceptable range of uncertainties based on the method. The first-principles or \textit{ab initio} and DFT methods are widely accepted in semiconductor research because of their efficacy for providing very close results with experiments [42, 68].

Likewise in experiments, a realistic model (a sample from computer simulation) should be generated before analyzing its structure. For experimental samples, x-ray scattering [70] or neutron diffraction [54] probes are being used to study the structure of the sample. On the other hand, radial distribution functions (RDF) [71] or pair correlation functions (PCF) [6], bond angle distribution functions [42], reducible and irreducible ring statistics [72] etc. are used to study the structural aspects of the realistic models. Electronic density of states (EDOS) and vibrational density of states (VDOS) calculations [15, 73] are used to analyze the electronic [13] and vibrational properties [74, 75] of the models respectively. In addition, calculations of nuclear magnetic resonance line spectra provides several important information [39, 76, 77] regarding the distribution of hydrogen atoms in the amorphous silicon network.

The plan of the dissertation is as follows. In Chapter 2, we briefly discuss the literature which have been devoted on hydrogenated amorphous silicon followed by Density Functional Theory
(DFT) and related first-principles methods. Chapter 3 belongs to the hydrogen microstructure whereas we discuss the structure of vacancies in chapter 4. We present an information-based inverse method, that uses simultaneously the nuclear magnetic resonance (NMR) moments and hydrogen cluster information, as an input of the method while generating some realistic models of the hydrogenated amorphous silicon. We present procedure of the method and results in the fifth chapter, followed by voids with molecular hydrogen in chapter 6. Finally, we summarize the entire work in chapter 7.
Chapter 2

BACKGROUND

2.1 A brief literature survey

Hydrogenated amorphous silicon (a-Si:H) was first produced by Chittick et al in late 1960s via glow discharge deposition technique [78]. However, an essential role of the hydrogen in a-Si:H was only recognized by Paul et al in 1974 [6]. They studied the high defect density of amorphous silicon prevented the material, from being useful for electronic devices, by introducing hydrogen to lower the defects significantly into the sputtering system. Although the device research on a-Si:H was started by Carlson and Wronski in 1976 with the development of photo-voltaic devices [23] at RCA laboratories, research on large area electronic arrays of a-Si:H devices was started a few years later after the first field effect transistors were reported by Snell et al in 1981 [22]. In the past three decades, several experimental [37, 38, 46, 79, 80] and theoretical [40, 41, 60, 48, 49, 81, 82] studies have been conducted on the material because of its wide range of application in technological devices.

Nuclear magnetic resonance (NMR) [39, 38, 46] and infrared (IR) spectroscopy [37, 55, 83] are two widely used techniques to address the hydrogen micro-structure in amorphous silicon. NMR data reveal the nature of the hydrogen distribution via dipolar interactions [77, 84, 85] between the hydrogen atoms. On the other hand, the IR experiments identify the presence of various silicon-hydrogen bonding configurations by probing the bonding environment of hydrogen atoms [19, 57]. A highly inhomogeneous distribution of hydrogen atoms in amorphous silicon was observed for the first time by Reimer et al [38] via a proton magnetic resonance study on plasma-deposited samples. Their research shows that the hydrogen atoms can reside both in clustered and diluted environments as a result the hydrogen distribution becomes highly inhomogeneous.

While NMR studies can not provide directly a description of the hydrogen distribution in the network [86], it is possible to infer useful information about the size of hydrogen clusters and the nature of the distribution (either sparse or dense) of hydrogen atoms in the samples by analyzing the shape and the width of an NMR spectrum. A typical NMR spectrum of a device-quality sample shows the presence of both narrow and broad line widths, which can be approximated as a convolution of a truncated Lorentzian and a Gaussian distribution [77]. An analysis of the NMR spectra of amorphous silicon samples with $8 - 32$ at.% H by Reimer et al [38] reported that the broad line width of the spectrum lie in the range $22 - 27$ kHz, whereas the narrow line width was of the order of $3 - 5$ kHz. Similar observation was also reported in
the NMR experiments by Carlos et al [39], who also noted a variation of the line width of up to 20% depending on the nature of amorphous samples used in the measurements.

Although several studies were performed as mentioned earlier, Baum et al [87] presented a definitive picture about the micro-structure from multiple- quantum nuclear magnetic resonance (MQ-NMR) experiments. These experiments confirmed that for device-quality samples a characteristic feature of the micro-structure was the presence of small clusters (of size $4 - 7$ H atoms), and with increasing concentration of hydrogen these clusters merged into large clusters. Furthermore, these experimental data suggest that the distribution is inhomogeneous and the micro-structure mainly consists of small (hydrogen) clusters and a dilute distribution of hydrogen atoms dispersed in the silicon matrix at the low hydrogen concentration. However, a study by Wu et al [88] on hot wire chemically vapor deposited (HW-CVD) samples shows that a new hydrogen distribution with broad line widths of about $34 - 39$ kHz for the glow discharge (GD) samples of concentration $8 - 10\%$, and about $47 - 53$ kHz for the hot wire (HW) samples of concentration $2 - 3\%$. In these both samples, the narrow line width lies in the order of $3 - 6$ kHz. It means even at very low concentration, it is possible to have large clusters of hydrogen in the samples that can produce a line width as broad as 50.0 kHz. Therefore, the micro-structure can vary significantly depending on the preparation conditions, method of deposition and substrate temperature, and not just on the concentration of hydrogen in the samples.

Infrared (IR) spectroscopy [37, 55, 83] on the other hand, detects the presence of different hydride configurations by measuring the vibrational frequencies of hydrogen in various hydrogen bonding environments [41, 89, 90]. The results from the IR studies by Ouwens et al [47] reported that for device-quality samples, $3 - 4\%$ of total hydrogen atoms reside in the network as isolated or distributed mono-hydrides (SiH). This observation is consistent with the MQ-NMR study of Baum et al [87] on the device-quality samples of hydrogenated amorphous silicon. Furthermore, the IR experiments by Manfredotti et al [55] and Lucovsky et al [37], and the MQ-NMR study by Baum et al [87] provided evidence of the presence of various hydride configurations such as SiH, SiH$_2$ and SiH$_3$ in device- quality samples. They also observed that at high concentration the amorphous silicon networks consist of open chains of (SiH$_2$)$_n$.

The hydrogen micro-structure is further enriched by the presence of vacancies [79, 91, 92], voids [53, 93, 94] and molecular hydrogen [80, 95, 96] in the networks. The Mössbauer spectroscopic studies by Hoven et al [79] showed the presence of vacancies in hydrogenated amorphous silicon. Similarly, Smets et al [97] observed that the micro-structure is dominated by mono- and divacancy at low concentration of up to 14 at. % H, and micro-voids or voids at high concentration beyond 14 at. % H. These results were obtained from the samples by means of infrared absorption spectroscopy prepared via an expanding thermal plasma techniques. The presence of molecular hydrogen in the amorphous silicon network has been studied extensively by several groups using NMR [39, 53, 80], infrared-absorption [55] and calorimetry experiments.
These experiments show that approximately 1% of total hydrogen can reside in the network in the molecular (H₂) state [80, 96, 98].

As compared to the experimental studies, there are very few theoretical studies that explicitly focus on the hydrogen micro-structure of amorphous silicon [41, 48, 49, 60, 81, 82, 99]. For instance, Drabold et al [81], Jarolimek et al [40] and Ranber et al [72] etc., have focused on the hydrogen micro-structure. In addition, the theoretical studies by Kim et al [91] focused on the calculation of electronic structure of hydrogenated amorphous silicon and some properties of vacancy configurations, such as the changes in the volume of a vacancy upon relaxation of the network. Zhang et al [100] studied the creation of higher order vacancies and their stability by relaxing the network from first-principles calculations. Their observations show that any higher order vacancy had the tendency to evolve into a lower order vacancy including a mono-vacancy and a stable divacancy.

A unsatisfactory feature of these theoretical studies [81, 82, 91, 100] as mentioned above, was that the vacancies or defect configurations were created artificially or by hand, which were then relaxed locally or globally in order to obtain a stable vacancy configuration. These approaches are correct in principle and a prolonged first-principles molecular dynamics simulation can indeed find the minimum energy (stable) configuration of the defects. However, a short local or global relaxation may not be sufficient to eliminate the initial bias associated with the defect creation (by hand) in an over-constrained network. Here we have generated the models in which the vacancies [60], voids and molecular hydrogen manifested themselves while relaxing the hydrogenated amorphous silicon network from the first-principles method [101].

At the end of literature review, we would like to mention that to our knowledge no theoretical work has been devoted to calculated nuclear magnetic resonance line spectra of hydrogenated amorphous silicon other than just calculating the first few moments, broad and narrow line widths [39, 87]. Therefore, we have calculated a theoretical NMR line spectra of different models and compared with the experimental line spectra [102]. The calculated line shapes are very close with the NMR experiments [39]. Details of the line spectra calculations has discussed in the fifth chapter.

2.2 Density Functional Theory

Material properties are related to microscopic processes which rely on quantities that are not assessable by experiments but they can be extracted from atomistic simulations. The first-principles or ab initio calculations solve the Schrödinger equation of the electrons for a given atomic configuration without any fitting parameters [67, 103, 104, 66]. Density Functional Theory (DFT) is the first-principles method that deals with many-body densities rather than the many-body wavefunctions. It is a quantum mechanical modeling method to investigate the electronic structure mainly the ground state properties [68, 105, 106, 101]. In other words, the method reformulates the energy of an atomic system as a functional of the ground state electron
density rather than the electron wavefunction [106]. Although the DFT has a conceptual root in the Thomas-Fermi model, it was put on a firm theoretical footing by two very important theorems called Hohenberg-Kohn theorems [107]. The first theorem demonstrates that the ground state properties of a many electron system can be uniquely determined by an electron density. It can reduce the many-body problem of N electrons with 3N spatial coordinates to 3 spatial coordinates. The second theorem defines an energy functional in which the correct ground state electron density minimizes that energy functional [107]. However, another foundation to construct the DFT without the Hohenberg-Kohn theorems is getting popular that uses a Legendre transformation from external potential to electron density [108].

The DFT is further extended by Kohn and Sham [109] by introducing an effective potential. This concept corresponds to a mean-field approach in which the wavefunction is decomposed into a product of single electron orbitals [106, 101]. However, it neglects correlations; as a result, a functional $E_{xc}[\rho(r)]$ must be introduced to capture exchange and correlations interac-

$Figure 2.1$: A flow chart of the self consistent loop (SCF) in DFT.
tions in the Hamiltonian. The following equation, so called Kohn-Sham equation, is a single particle Schrödinger equation, and it is derived from the modified Hamiltonian after applying the variation principle [109]. Furthermore, it includes an effective potential \( v_{\text{eff}}(r) \) which incorporates the exchange and correlation interactions.

\[
\left( -\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r)
\]  

(2.1)

The terms \( \psi_i \) and \( \varepsilon_i \) are electron orbitals and the corresponding eigen values. The effective potential, \( v_{\text{eff}}(r) \), can be written as

\[
v_{\text{eff}}(r) = V_{\text{ext}}(r) + \int \frac{\rho_o(r')}{|r-r'|} dr' + \frac{\delta E_{\text{xc}}[\rho_o(r)]}{\delta \rho(r)}
\]  

(2.2)

where \( v_{\text{ext}}(r) \), \( \rho_o(r') \) and \( \rho_o(r) \) are external potential, ground state electron density and electron density respectively. Furthermore, the second and third term in the right side of the equation represent electron-electron interaction, \( V_{\text{ee}}(r) \), and exchange-correlation interactions, \( V_{\text{xc}}(r) \), respectively.

In order to describe essential steps of a DFT calculation, flow chart of a self-consistent loop [105, 106] is presented in Figure 2.1. First, an initial guess of the electron density \( \rho_i(r) \) is used to calculate the effective potential, \( v_{\text{eff}}(r) \). The Kohn-Sham equation (see Equation 2.1) is solved and a current electron density, \( \rho_f(r) \), is calculated along with the total energy, \( E_{\text{tot}}[\rho_f(r)] \). If the loop acheived convergence then output quantities are calculated, otherwise a new density is calculated by mixing initial and the current electron densities as shown in the flow chat. The numerical procedure is continued as long as the convergence criterion is not fulfilled with the new electron density, \( \rho_{\text{new}}(r) \), instead of the initial guess, \( \rho_i(r) \). The electronic part of the system is solved only when the self-consistency is achieved as shown in the flow chart [106]. The total force is calculated from the electronic and ionic forces.

### 2.3 Simulation process

In this dissertation, simulations are performed using the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) [106, 101]. SIESTA is an \textit{ab-initio} density functional calculation based on numerically- truncated local orbitals [106]. The code performs according to the self-consistent loop as described in the earlier section. The code can perform total energy calculations, structural relaxations, as well as force constant calculations to determine phonon dispersions and also electronic transport calculations [101]. Furthermore, it is a self-consistent density functional method that uses standard norm-conserving pseudo-potentials [106, 110, 111]. The code also includes a flexible numerical linear combination of atomic orbitals basis set as well as multiple-zeta and polarization orbitals. In this code, exchange and correlation are treated with the local spin density or generalized gradient approximations [109, 106].
In order to calculate the Hartree and exchange-correlation potentials and matrix elements, the electron density and the basis functions are projected on a real space grid with a number of operations that may scale linearly with the size of the system (number of atoms) [106]. However, it may not be true for all materials. SIESTA uses a modified energy functional, whose minimization produces orthogonal wave functions and the same energy and density as the Kohn-Sham energy functional, without the need for an explicit orthogonalization [109]. Furthermore, it uses localized Wannier-like electron wave functions that allows the computation time and memory required to minimize the energy to also scale linearly (not always) with the size of the system [101]. The code also calculates forces and stresses efficiently and accurately that permits structural relaxation and molecular dynamics simulations [106]. In this work, we use the code mostly in relaxing the structure of the realistic models as well as calculating their electronic density of states (EDOS).
Chapter 3

HYDROGEN MICROSTRUCTURE

3.1 Introduction

We study the hydrogen micro-structure that provides crucial information about silicon-hydrogen bonding mechanisms [55], distribution of hydrogen atoms [38] and coordination defects [16] in realistic models of hydrogenated amorphous silicon. We first describe how the models were generated [61] followed by the results and discussion. In this section, we also present theoretical calculations of nuclear magnetic resonance (NMR) line widths [77] that can describe further the hydrogen micro-structure.

3.2 Models of hydrogenated amorphous silicon

We study two realistic models of a-Si:H at 7 at.% (number of hydrogen atoms/total number of atoms) and 22 at.% of hydrogen concentrations generated by Experimentally Constrained Molecular Relaxation (ECMR) method [61]. The method has been applied to model a number of complex glassy systems in recent years [60, 112]. It has the ability to combine the power of a first-principles force field [67] with the available experimental information of the material. Furthermore, the method constructs a series of guesses of the solution that are consistent with the available experimental data and an appropriate force field. Then, these approximate solutions are refined in an augmented solution space, which is a direct product of the configuration space of a potential (either empirical or first-principles) and that of the solution space feasible to the input experimental data. The details of the method are described in Ref [61, 60]. However, we briefly present the characteristic features of the method in the following paragraph.

The ECMR is a two-step process that involves Monte Carlo method [61] followed by first-principle relaxations. It consists of packing silicon atoms randomly into a cubic super cell with a constraint that no two atoms are closer than 2.0 Å to each other. The density of the super cell is adjusted by applying periodic boundary conditions to match with the experimental density of amorphous silicon. Then, a quadratic penalty function is introduced to incorporate experimental pair correlation data along with a set of constraints that describe the chemical and geometrical properties of the networks. Then, the penalty function is optimized to provide a set of amorphous silicon co-ordinates which is used to hydrogenate the network in the next step. The method uses similar but not identical hydrogenation process used by Holender, Morgan and Jones [99]. Then, the hydrogenated networks are relaxed several times using SIESTA [106] during the second step to ensure that the total force on the atoms is less than 0.007 eV$^{-1}$. While
relaxing the networks, silicon atoms are treated using a minimal single \( \zeta (sz) \) basis, whereas a double \( \zeta \) with polarization (DZP) orbitals is employed to represent the correct bonding behavior and hydrogen interaction accurately [60]. We choose the size of the model in the order of 500 atoms, because it is found to be sufficiently large to show no finite size effect. However, the size is small enough to relax by the first-principles density functional code SIESTA [106, 101].

These two models were previously validated thoroughly by comparing their structural, electronic and vibrational properties to the experimental data [60]. In this work, we focus on micro-structure, vacancies, and theoretical calculations of nuclear magnetic resonance line width of the hydrogenated amorphous silicon. The model at low concentration (7 at.% H) consists of 540 atoms with 2.9% defect concentration (including both dangling and floating bonds). The average co-ordination number of the model is 3.98. However, the model at high concentration (22 at.% H) has only a defect (a two-fold Si atom). It is to be noted that both the models have clean electronic band gaps and the correct vibrational density of states [60].

### 3.3 Results and Discussion

#### 3.3.1 Bonding schemes in a-Si:H

Silicon and hydrogen have different bonding properties [83]. Silicon forms a rigid non-equilibrium structure whereas the hydrogen has more mobile equilibrium structure [6]. In addition, hydrogen can partially penetrate the silicon network [113]. However, stable SiH and unstrained Si-Si bonds are very strong so that the hydrogen can not break those bonds. On the other hand, it can break strained Si-Si bonds either into stable SiH or unstrained Si-Si bonds because the highly strained Si-Si bonds have energies close enough to the chemical potential of hydrogen [6].

At low hydrogen concentration (7 at.% H) model, approximately 75% of total hydrogen atoms form mono-hydrides (SiH) and the remaining hydrogen atoms are found in dihydrides (SiH\(_2\)) configurations. Approximately 5% of bonded hydrogen are observed in a form of isolated mono-hydrides (not more than one hydrogen atom within a radius of at least 6 Å). One of such configurations is shown in Figure 3.1. The figure shows a three-dimensional complex that consists of only one hydrogen atom at the center surrounded by several silicon atoms. In the figure, all large (green) spheres represent silicon and the small (yellow) sphere represents hydrogen atom respectively. These observations are consistent with the infrared experimental work by Ouwens et al [47] in which authors were reported that approximately 3 – 4 % hydrogen atoms form isolated mono-hydrides (SiH) in the device quality sample. On the other hand, 95% of bonded hydrogen reside in a form of small or big clusters (4-7 hydrogen atoms). Figure 3.2 is a representative complex of 6 Å radius in a three dimensional space at 7 at.% hydrogen concentration. It should be noted that unless it is mentioned, the big (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively throughout the work.
Figure 3.1: An isolated mono-hydride at low concentration (7 at.% hydrogen) in a silicon complex of radius 6.0 Å. Silicon and hydrogen atoms are shown in green (big) and yellow (small) respectively.

Bonding configurations such as SiH and SiH$_2$ are visible in the figure.

Figure 3.6 is a three-dimensional (3D) complex of 6 Å radius at 22 at.% hydrogen concentration. In this model also the hydrogen atoms form either mono-hydrides or dihydrides except a few SiH$_4$ bonding configurations as shown in Figure 3.6. Likewise in the lower concentration model, the micro-structure is dominated by SiH bonds (approximately 73% hydrogen atoms) at this concentration. The SiH, SiH$_2$ and SiH$_4$ configurations are visible in the figure. These results are in very good agreement with infrared experiments by Lucovsky et al [37] and Manfredotti et al [55]. However, no SiH$_3$ bonds and H$_2$ molecules are observed in both models. Our studies further show that the bond lengths in the both models lie in a range of 2.0-2.8 Å in Si-Si and 1.45-1.65 Å in Si-H configurations respectively. It is to be noted that these local Si-H bonding configurations generate further structural inhomogeneities in the amorphous silicon.

This observation is consistent with Touir et al [114] in which the authors were studied how the local Si-H bonding configurations create structural inhomogeneity in the amorphous silicon. Scharff et al [90] also reported the similar results by observing the dynamics of Si-H bonds in the hydrogenated amorphous silicon. Before addressing the distribution of hydrogen atoms, we should mention an important aspect of the hydrogen micro-structure at high concentration (22 at.% H). Some mono-hydrides can form an open chain-like structure, that consists of 4 to 6
Figure 3.2: A sparse distribution of hydrogen atoms at low concentration (7 at.% hydrogen) showing six H atoms in a complex of radius of 6.0 Å.

mono-hydrides (SiH) and a few dihydrides. Examples of such chain-like structures are shown in Figures 3.8 and 3.9. Figure 3.8 consists of six SiH that are connected to each other via Si-Si bonding, whereas the structure in Figure 3.9 has four mono-hydrides and a dihydride. Notably, such chain configurations are not observed at low concentration (7 at.%) of hydrogen. Similar results were reported experimentally by Lucovsky et al [37], Manfredotti et al [55], and Baum et al [87]. Furthermore, a research by Tsu et al [102] shows an evidence of heterogeneity in hydrogenated silicon by showing intermediately ordered chain like structures which are similar to our results.

3.3.2 Distribution of hydrogen atoms

Several nuclear magnetic resonance (NMR) experiments [39, 38, 46, 88] have reported that the distribution of hydrogen atoms in a-Si:H network is highly inhomogeneous [115], however, each distribution has a different nature. In other words, hydrogen atoms locate in clusters of different sizes as well as in a diluted phase. However, there are no sufficient statistics that can provide what percentage of hydrogen atoms reside in the clustered or diluted phases as well as what is the degree of inhomogeneity of the hydrogen distribution. Therefore, providing the further details of these issues is one of our goals.

At the low hydrogen content (7 at. %) model, a few clusters of 4-7 H atoms are observed and
Figure 3.3: Overall hydrogen distribution in the network at 7 at.% hydrogen concentration is shown in the figure. Only those silicon atoms which are bonded with hydrogen are presented after leaving the silicon matrix in the background. Green (big) spheres represent silicon atoms whereas yellow (small) spheres are hydrogen atoms. Two small clusters are encircled in the figure.

one of the clusters is shown in Figure 3.5. It is a complex of 6 Å radius in a three dimensional space. Approximately 40% of total hydrogen atoms are found in the cluster phase whereas the remaining hydrogen are in the diluted phase. An example of the isolated mono-hydride is shown in Figure 3.1. The nature of hydrogen distribution can be studied by plotting the overall structure as shown in figure 3.3. Since we are focused in the distribution of hydrogen atoms, all hydrogen atoms and only those silicon atoms which are connected to hydrogen are shown in the figure. Two clusters of size 3 and 4 hydrogen atoms are encircled in the figure. It is very clear that the hydrogen distribution is highly inhomogeneous at this concentration.

Now we want to discuss the hydrogen distribution at the high concentration (22 at.% hydrogen). The model consists of some small clusters of 4 – 7 H atoms likewise at low concentration, and a few large cluster up to 20 H atoms. An example of a big cluster is shown in Figure 3.6. The complex consist of total 16 H atoms in which 12 H atoms made a dense cluster. The distances among them lie in a range of 1.6 – 2.3 Å. On the other hand, the model does not consist of isolated mono-hydrides as in the low concentration model, however, it has a pair of lone mono-hydrides as shown in Figure 3.5. It is obvious that at higher concentration
Figure 3.4: Overall hydrogen distribution in the network at 22 at.% hydrogen concentration is shown in the figure. Only those silicon atoms which are bonded with hydrogen are presented after leaving the silicon matrix at the background. Green (big) spheres represent silicon atoms whereas yellow (small) spheres are hydrogen atoms. Two clusters of hydrogen atoms (6–8 H) are encircled in the figure.

the probability of having hydrogen in a cluster phase is very high as compared to the lower concentration. The overall distribution of hydrogen atoms is shown in Figure 3.4 without showing the silicon atoms which are not connected to the hydrogen atoms. Two clusters of 6 and 7 hydrogen atoms are encircled in the figure. Various types of clusters are observed at this concentration and the hydrogen distribution is found highly inhomogeneous. Furthermore, the nature of clusters can be observed via H-H distance distribution as shown in Figure 3.7. It is a local hydrogen distribution up to 3.5 Å distance from each hydrogen atoms. The first peaks at 1.8 Å is the H-H distance among Si-H H-Si configurations. The maximum peak at approximately 2.1 Å is the distance between H atoms in SiH\textsubscript{2} and SiH\textsubscript{4} bonds. Furthermore, the peaks in a range of 1.8 – 2.35 Å provide the evidence of big clusters in the model. All these observations show that the hydrogen distribution is highly inhomogeneous which is consistent not only with NMR experiments [46, 88] but also with the small-angle neutron scattering experiment by Williamson et al [115].
3.3.3 NMR line widths calculation

A theoretical NMR line width calculation can provide quantitative information about the distribution of hydrogen atoms in the amorphous silicon network. From the position of hydrogen atoms in the network, one can calculate the first few moments such as the zeroth, second and the fourth moments. However, odd moments cancel out because of symmetry. Once these NMR moments are available, an approximate shape and the width of the resonance curve can be estimated [77] and compared to experimental NMR data [39, 76]. It is to be noted that one-dimensional NMR spectrum cannot fully represent every aspect of the three-dimensional hydrogen distribution or the hydrogen micro-structure of the network. Nonetheless, the moments of an NMR spectrum provide valuable information such as the presence of hydrogen in isolated, sparse and in the clustered environment [77, 85]. In the lowest order approximation, a typical NMR line spectrum can be expressed as a combination of a Gaussian and a truncated Lorentzian distributions [38] in which the contribution of the higher moments generally comes from the wings of the distribution that is rarely observed in experiments. Therefore, the first two or three non-zero moments should suffice to capture the characteristic features such as the shape and the width of the resonance curve [77, 84].

A schematic diagram, shown in Figure 3.10, illustrates how the hydrogen distribution is

Figure 3.5: A pair of lone mono-hydrides realized in a dilute environment at high hydrogen concentration (22 at.\% H). The complex has a radius of 6.0 Å. The large (green) and the small (yellow) spheres represents silicon and hydrogen atoms respectively.
Figure 3.6: A silicon complex of 19 H atoms in a radius of 6.0 Å at high hydrogen concentration (22 at.% H). A dense cluster of 12 H atoms is visible at the center of the complex. Silicon and hydrogen atoms are indicated in green (big) and yellow (small) respectively. The bonding configuration (SiH$_4$) is also shown in the figure.

correlated to the corresponding NMR line spectra. If the hydrogen atoms form clusters then according to the Central Limit theorem, the hydrogen distribution can be approximated as a Gaussian distribution. On the other hand, the diluted distribution of hydrogen atoms follows the Cauchy’s distribution and it can be approximated by a truncated Lorentzian distribution. In the schematic diagram, the black circles represent hydrogen atoms and their distributions determine the shape of the line spectra.

Table 3.1: Van Fleck moments and the overall line widths for the models from the Gaussian approximation

<table>
<thead>
<tr>
<th>Conc (at.% H)</th>
<th>Directions</th>
<th>$\mu_2(\gamma^4h^4)$</th>
<th>$\mu_4(\gamma^8h^8)$</th>
<th>$\Gamma$</th>
<th>$\sigma_q$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>100</td>
<td>$3.95 \times 10^{-3}$</td>
<td>$6.71 \times 10^{-3}$</td>
<td>4.30</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>$3.15 \times 10^{-3}$</td>
<td>$5.30 \times 10^{-5}$</td>
<td>5.34</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>$4.15 \times 10^{-3}$</td>
<td>$9.68 \times 10^{-5}$</td>
<td>5.64</td>
<td>18.2</td>
</tr>
<tr>
<td>22</td>
<td>100</td>
<td>$3.12 \times 10^{-2}$</td>
<td>$2.98 \times 10^{-3}$</td>
<td>3.07</td>
<td>49.9</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>$3.19 \times 10^{-2}$</td>
<td>$3.04 \times 10^{-3}$</td>
<td>2.99</td>
<td>50.5</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>$3.26 \times 10^{-2}$</td>
<td>$3.18 \times 10^{-3}$</td>
<td>2.99</td>
<td>51.1</td>
</tr>
</tbody>
</table>

In this section, we calculate NMR moments and line widths of the models. The details of
Figure 3.7: The distribution of H-H distances in a model of a-Si:H with 22 at.% H atoms. A cut-off of 3.5 Å is used to obtain the distribution. The peak at 1.8 Å is found to originate from the small clustered environment, whereas the peaks at 2.1 Å and 2.35 Å are from geometrical consideration of SiH$_2$ and SiH$_4$ configurations.

Table 3.2: Deconvoluted line widths for the model with 7 at.% H for the diluted and clustered regions

<table>
<thead>
<tr>
<th>Conc (at.% H)</th>
<th>Directions</th>
<th>$\sigma_u$ (kHz)</th>
<th>$\sigma_g$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cluster</td>
<td>100</td>
<td>25.1</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>22.6</td>
<td>25.4</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>19.2</td>
<td>21.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_L$ (kHz)</th>
<th>$\sigma_{narrow}$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute</td>
<td>100</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>4.9</td>
</tr>
</tbody>
</table>

NMR moments, line widths and line spectra has been discussed in Chapter 5. However, we would like to describe the important equations which are used in the calculations. The second and the fourth moments of the spectrum is calculated using Equations 5.1 and 5.2 respectively. The full width at half maxima (FWHM) is then calculated from Equation 5.4 using the Gaussian approximation. In Table 3.1, we have listed the values of the Van Vleck moments and the overall line widths of the models in the Gaussian approximation. The values of $\Gamma$ (i.e. $\mu_4/\mu_2^2$) for the model with high concentration (22 at.%) suggest that the NMR spectrum can be well
Figure 3.8: An open chain-like structure via Si-Si bonding at high concentration (22 at.% H). The structure is comprised of six mono-hydrides connected via silicon atoms to form an open chain. Silicon and hydrogen atoms are represented by green (big) and yellow (small) spheres respectively.

Table 3.3: Deconvoluted line widths for the model with 22 at.% H for the diluted and clustered regions

<table>
<thead>
<tr>
<th>Conc (at.% H)</th>
<th>Directions</th>
<th>$\sigma_u$ (kHz)</th>
<th>$\sigma_g$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cluster</td>
<td>100</td>
<td>33.8</td>
<td>40.6</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>47.3</td>
<td>46.8</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>44.3</td>
<td>46.4</td>
</tr>
<tr>
<td>Dilute</td>
<td>100</td>
<td>5.9</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>6.9</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>5.9</td>
<td>6.4</td>
</tr>
</tbody>
</table>

approximated by a Gaussian line shape. In addition, the higher values of the broad line widths ($\sigma_g$) show that the hydrogen atoms are densely distributed in clusters with small proton-proton separation. The H-H distances lie within the range of 1.6 – 2.4 Å in the dense clusters. This
Figure 3.9: A chain-like structure at high concentration (22 at.% H). The structure shows four mono-hydrides and a dihydrides. The big (green) and small (yellow) spheres represent silicon and hydrogen atoms.

Figure 3.10: A schematic diagram of hydrogen distribution and the corresponding nuclear magnetic resonance line spectra. The black circles in the figures are hydrogen atoms.

produces a broad resonance via dipolar interaction that can be approximated by a Gaussian
Table 3.4: Summary of the theoretical and experimental line widths

<table>
<thead>
<tr>
<th>Theory</th>
<th>(at.% H)</th>
<th>$\sigma_u$ (kHz)</th>
<th>$\sigma_g$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>540-atom model</td>
<td>7</td>
<td>19.0 – 25.0</td>
<td>2.8 – 5.3</td>
</tr>
<tr>
<td>611-atom model</td>
<td>22</td>
<td>33.8 – 47.3</td>
<td>5.9 – 6.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiments</th>
<th>(at.% H)</th>
<th>$\sigma_{broad}$ (kHz)</th>
<th>$\sigma_{narrow}$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reimer et al[38]</td>
<td>8.0 – 32.0</td>
<td>22.0 – 27.0</td>
<td>3.0 – 5.0</td>
</tr>
<tr>
<td>Gleason et al[46]</td>
<td>8.0 – 15.0</td>
<td>25.0 – 30.0</td>
<td>...</td>
</tr>
<tr>
<td>Wu et al[88]</td>
<td>8.0 – 10.0</td>
<td>34.0 – 39.0</td>
<td>4.0 – 6.0</td>
</tr>
<tr>
<td>Wu et al[88]</td>
<td>2.0 – 3.0</td>
<td>47.0 – 53.0</td>
<td>3.0 – 6.0</td>
</tr>
</tbody>
</table>

line shape. For the model with low concentration of hydrogen, the ratio $\Gamma$ is somewhat larger than the ideal Gaussian value ($\Gamma = 3$), which is a very good evidence of a narrower spectrum than a Gaussian. The contribution from the wings of the spectrum to the higher moments is not negligible in this case, and a direct application of the Gaussian approximation may not provide a correct estimate of the width.

Further difficulties can arise in characterizing the micro-structure of model networks via the NMR width in the presence of strong inhomogeneity. The calculation of the narrow width of the resonance curve at high concentration via Equation 5.5 can be misleading in the presence of a large hydrogen clusters. If the contribution from the few large clusters dominates the moment summations, the effect of the dilute environment on the width can be missed out. Similarly, the presence of a large cluster in a diluted environment (at low concentration) may not be reflected in the calculated value of the narrow line width from model networks. It is, therefore, more appropriate to partition the overall micro-structure into regions of clustered and diluted phases and to use the corresponding moments in Equations 5.4 and 5.5 for the calculation of width from the broad and the narrow part of the spectrum. This partition of the spins into clustered and diluted regions can be viewed as analogous to the deconvolution of one dimensional NMR spectrum into a broad and narrow spectrum. In the following, we discuss our results for two different concentrations by partitioning the micro-structure into three-dimensional regions of diluted and clustered environments. As mentioned earlier, we can expect to see that the broad line width mainly originates from the clustered environment, where as the diluted environment accounts for the narrow part of the spectrum.

The results for the broad and narrow line widths from the clustered and dilute environment for each of the model configurations are listed in Tables 3.2 and 3.3. In addition to the Gaussian line width ($\sigma_g$) for the broad spectrum, we have also included the universal line width ($\sigma_u$) obtained from Equation 5.7 via the Gaussian memory function approximation [77]. The narrow line width of the spectrum is calculated assuming a truncated Lorentzian shape, and it is indicated in the tables as $\sigma_L$. We have also included the value of the narrow line width estimated from the density of hydrogen atoms ($n$) in the diluted region [77] using Equation 5.6. Since the equation is often used by experimentalists to get an approximated value of the narrow line
width $\sigma_{\text{narrow}}$, this provides a simple way to compare our results to the experimental data.

In Table 3.4, we have summarized the experimental values of the line widths obtained by different authors with the theoretical results from the models. The experiments of Riemer et al [38] and Gleason et al [46] have indicated that the broad line width typically ranges from 22 to 30 kHz for samples with 8 to 15% hydrogen atoms. This is comparable to the values of 19.0 to 25.0 kHz obtained from the models with 7 at. % hydrogen. The calculated value of the broad line width from the model with 22 at.% hydrogen is somewhat larger than the experimental value. However, this can be understood by taking into account the presence of a large cluster (see Figure 3.6) in the model. The presence of such large clusters is not surprising and have been reported by Wu et al [88], who have observed a broad line width of approximately 50 kHz in hot-filament-assisted CVD deposited films.

### 3.4 Conclusion

The micro-structure is studied at low and high concentration (of hydrogen) starting from two realistic models of the hydrogenated amorphous silicon. The hydrogen atoms are found to be distributed in a dilute or sparse and a dense or clustered environment in the silicon matrix. At low concentration, the micro-structure is characterized by the presence of a few small clusters ($4 - 7$ H atoms) in the background of a sparse distribution of hydrogen. On the other hand, several small clusters and a few large clusters up to 20 H atoms are observed in the high concentration model. In the dense clusters, the hydrogen atoms reside in a range of $1.6 - 2.4 \text{ Å}$. These observations show that the hydrogen distributions in both models are highly inhomogeneous. Another important aspects of the hydrogen micro-structure is the bonding schemes. The low concentration model consists of SiH and SiH$_2$ whereas a few SiH$_4$ configurations are also observed in the high concentration model. The SiH configurations dominate both the models, however, SiH$_3$ bonds and H$_2$ molecules are not observed. In addition, the micro-structure consists of some open-like and closed-like chain structures at the high concentration model.

The widths of the NMR spectra of the model networks are calculated from a knowledge of the distribution of hydrogen in the network using the Van Vleck moments. The narrow and the broad line widths of the spectra for the low concentration model are found to be in the range of $3 - 6 \text{ kHz}$ and $19 - 25 \text{ kHz}$, whereas the corresponding values for the high concentration model lie between $5.9 - 6.4 \text{ kHz}$ and $34.0 - 48.0 \text{ kHz}$, respectively. From this work, we strongly recommend that the broad and narrow line widths calculations should be done only by partitioning clustered and diluted hydrogen atoms if the hydrogen distribution is highly inhomogeneous. Otherwise, neither a Gaussian nor a truncated Lorentzian functions can provide the correct line widths of the overall hydrogen distribution. Our results are in excellent agreement with experimental data obtained from the NMR and the multiple- quantum NMR studies.
Chapter 4

STRUCTURE OF VACANCIES

4.1 Introduction

It is difficult to define or identify vacancies in the amorphous materials because of their structural disorder \([6, 9]\) as compared to the crystalline materials. However, depending on a number of missing atoms in the amorphous network, one can define a vacancy. For example, if a structure shows missing of one or two atoms then it is considered as a mono-vacancy or a divacancy \([97]\) respectively. If the structure show missing of several atoms then it is considered as a void or a micro-void \([53]\) depending on how many atoms are missing in the structure. It can be further clarified by visualizing the structures. A schematic diagram of the mono-vacancy that consists of four mono-hydrides (SiH) is shown in Figure 4.1. If an \(a\)-Si:H model consists of a region of four such mono-hydrides and that can accommodate a silicon atom in the absence of those four hydrogen atoms then the structure is known as a mono-vacancy. Similarly, if the model consists of six mono-hydrides as shown in Figure 4.2 and two silicon atoms can be accommodated after removing the hydrogen atoms then the region is considered as a divacancy. Those two silicon atoms are called missing silicon atoms. Based on the distances between those two missing atoms, a divacancy can be a split or a stable divacancy. If the distance lies within the range of Si-Si bond length \((\leq 2.8 \text{ Å or so})\) then the divacancy is stable. Similarly, If it is greater than the maximum bond length \((<2.8 \text{ Å up to the second nearest neighbors or so})\) then it is considered as a split divacancy. It is to be noted that such split divancancies have always a tendency to split into monovacanies or converted to stable divacancies \([100]\). In this section, we study their existence and the stability of such types of vacancies in our \(a\)-Si:H models.

Infrared (IR) \([56, 57, 58]\) or Raman \([10, 83]\) spectroscopy, x-ray diffraction \([70]\), calorimetry \([116]\) etc., are being used to study the physical properties of the pure amorphous silicon. However, an experiment using Mössbauer spectroscopy by Hoven et al \([79]\) provided the evidence of vacancies in the amorphous silicon for the first time. Later on, Smets et al \([97]\) provided much more details about the vacancies and voids from the samples prepared by expanding thermal plasma technique and infrared spectroscopy. They reported that the micro-structure in hydrogenated amorphous silicon samples can be characterized by the presence of vacancies and voids that largely depends on the amount of hydrogen present in the samples. The key result of their research \([97]\) can be written as the micro-structure is dominated by mono-and divacancy at low concentration up to 14 at.\%, whereas micro-voids or voids appear at high concentration (above 16 at.% or so).
There are some theoretical studies regarding the vacancies in the past few years [100, 92, 82]. For example, a study by Zhang et al [100] shows the presence of mono- and divacancy on prolonged relaxation of the network. It is to be noted that in these theoretical studies [82, 92, 100], the vacancies were explicitly introduced by hand, and the stability of the (vacancy) configurations were studied by relaxing the network using an appropriate \textit{ab initio} [106] or tight-binding energy functional [104].

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{monovacancy.png}
\caption{A schematic diagram of a mono-vacancy. The big and the small spheres represent silicon and hydrogen atoms respectively. A dashed circle in the figure shows that a silicon atom can adjust itself in the structure after removing the four hydrogen atoms.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{divacancy.png}
\caption{A schematic diagram of a divacancy is shown in the figure. The big and the small spheres represent silicon and hydrogen atoms respectively. Two dashed circles in the figure show that two silicon atoms can adjust themselves within the structure after removing those six hydrogen atoms.}
\end{figure}

Motivated by the results of Smets et al [97], we decided to study whether the micro-structure of our models consist of mono and divacancies or not. Interestingly, our real-space analysis of the ECMR networks indeed confirms that both mono- and divacancies exist in the models. This observation is remarkable because both the mono and divacancies were evolved while generating and relaxing the model networks. In other words, those vacancies are inherent features of the micro-structure which are completely different than those earlier studies as mentioned above. We present various structure of the vacancies in detail in the following section.
4.2 Results and Discussion

We have taken the same two $\alpha$-Si:H models of 7 at. % and 22 at. % hydrogen concentrations as discussed in the previous chapter. Mono-vacancies, split and stable divacancies of the models are presented in this section.

4.2.1 Mono-vacancies in $\alpha$-Si:H

Figure 4.3 shows a structure of a mono-vacancy at 7 at.% hydrogen concentration. As mentioned earlier, at least four SiH configurations are required to form a mono-vacancy. The big (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively in the figure. The structure of mono-vacancy can be further clarified by introducing a silicon atom in the network as shown in Figure 4.4, which we called a missing silicon atom (cyan). We removed those four hydrogen atoms that were contributed to form a mono-vacancy and introduced one silicon atom in the figure. The purpose of doing this is very clear because if a silicon atom can adjust itself within the region then only it is considered as a monovacancy otherwise not. Another important thing to be noted is the missing silicon atom should adjust itself not only physically but also it should have minimum energy for its stability. Therefore, we relax the network even after introducing the missing silicon atom in absence of those four hydrogen atoms. Finally, the first-principles relaxation using SIESTA [101] shows that the missing silicon atom which is bonded with other four neighboring silicon atoms in the network, and it has the minimum strain as well. Similar process is applied to the model with 22 at.% hydrogen content. Figure 4.5 is a region of mono-vacancy at 22 at.% model including four hydrogen atoms (contributed to form a mono-vacancy) and Figure 4.6 is the relaxed structure with minimum strain after introducing a missing silicon atom (cyan) and removing those four hydrogen atoms. These plots clearly show that the micro-structures consist of mono vacancies in both the models.

4.2.2 Divacancies in $\alpha$-Si:H

Having discussed of mono-vacancies we would like to study whether the models have divacancies or not. Our studies show that there are two types of divacancies, one is stable and the other is split. The stable divacancy is found in the high concentration model (22 at.% H) whereas the split divacancy has realized at the low concentration (7 at.% H) model. Notably, the two missing silicon atoms in the split divacancy are not nearest neighbor but they are in close proximity of each other typically within a distance of next nearest neighbor or so. Such split divacancies were observed by Zhang et al [100], and they have reported that the split divacancy has a tendency to break into a stable divacancy or two mono-vacancies. Figure 4.7 shows the region that consists of a cluster of mono-hydrides at low concentration (7 at.%). Likewise described in the mono-vacancy earlier, the position of the two missing silicon atoms (cyan) are shown in Figure 4.8. The exact location is obtained by removing six hydrogen atoms and
introducing two silicon atoms, and relaxing the resulting network via SIESTA as before. The missing silicon atoms are separated by a distance approximately 6.1 Å, and it is an evidence of a split divacancy (see Figure 4.8) at low hydrogen concentration. Furthermore, the origin of the split divacancy can be understood in view of the low concentration of hydrogen in the network, where the micro-structure is dominated by a sparse distribution of hydrogen atoms.

At the high hydrogen concentration model, we found stable divacancies rather than the split divacancies. The reason behind it is simple because the presence of more hydrogen atoms at high concentration reduces the average (hydrogen) cluster-cluster separation, and thereby it facilitates the formation of a stable divacancy. One such stable divacancies is presented in Figure 4.9. We have also shown two missing silicon atoms (cyan) in Figure 4.10. Those two missing atoms are separated by 2.6 Å, which is very less as compared to that of split divacancies, and they are nearest neighbor to each other.

4.3 Conclusion

We studied two realistic models of hydrogenated amorphous silicon at 7 at.% and 22 at.% consist of mono and divacancies. We introduced missing silicon atoms in the corresponding vacancies and relax the network. While doing so the missing atoms not only accommodate themselves
Figure 4.4: The reconstructed network showing the hypothetical missing silicon atom (in cyan), and its bonding to the neighboring Si atoms. Silicon and hydrogen atoms are shown in green (big) and yellow (small) spheres respectively.

within the structure but also they have the minimum strain (for equilibrium). In addition, the micro-structure consists of split divacancies in the lower concentration (7 at. divacancies at the higher concentration (22 at. two missing silicon atoms at 7 at. to twice of the Si-Si bond length. However, it is 2.6 Å at the higher concentration model because of having the stable divacancies. Notably, these structures of the vacancies were evolved themselves while relaxing the networks via the first-principles method density functional method. These remarkable observations are also consistent with the experiments by Smets et al [97] and Hoven et al [79].
**Figure 4.5:** A mono-vacancy at high concentration (22 at.\% H) in a region of several mono-hydrides (SiH). The large (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively.
Figure 4.6: The reconstructed network shows the missing silicon atom (in cyan) at 22 at.% hydrogen concentration. The large (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively.
Figure 4.7: A split divacancy with six mono-hydrides (SiH) at low hydrogen concentration (7 at.%). The large (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively.
**Figure 4.8:** The origin of the divacancy is illustrated by showing the hypothetically missing two silicon atoms (in cyan) in the network at 7 at.% hydrogen concentration. The large (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively. The distance between two missing silicon atoms is 6.1 Å.
Figure 4.9: A stable divacancy at high concentration (22 at.%) is shown in the figure. The large (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively.
Figure 4.10: The reconstruction of two missing silicon atoms (cyan) in the region of divacancy at 22 at.% hydrogen concentration. The large (green) and the small (yellow) spheres represent silicon and hydrogen atoms respectively. The distance between two missing silicon atoms is 2.6 Å.
Chapter 5

NUCLEAR MAGNETIC RESONANCE LINE SPECTRA

5.1 Introduction

The first-principles methods are very successful in designing complex materials and predicting their properties at a quantitative level [40, 41, 44, 45, 65, 67, 103, 104]. However, the direct force field based approaches have limitations while determining structure and properties of bulk non-crystalline materials. One of the distinct routes for structure determination of non-crystalline materials is considered as an inverse problem. The inverse approach uses all available information of about a material, for example, experimental, topological and geometric, etc., while designing a realistic model [61]. In addition, the approach critically depends on availability of sufficient experimental data as well as feasibility of the data sets. One of our goals in this chapter, is to demonstrate the efficacy of an information-based inverse approach to understand the hydrogen micro-structure from the knowledge of nuclear magnetic resonance data.

Before describing the details of the inverse approach, we would like to address the significance of the approach. As we described in the earlier sections, our models at 7 at. % and 22 at. % concentrations do not show the bonding configurations such as SiH$_3$ and H$_2$ molecules. In addition, even at the higher concentration model, a clear picture of voids does not appear. These observations motivated us to develop a new method from which we can generate a model of $a$-Si:H that can incorporate all possible silicon hydrogen bonding configurations, vacancies and voids with molecular hydrogen.

In order to develop the inverse approach, we briefly recall the key experimental facts of micro-structure in a-Si:H, from NMR [39, 38], neutron diffraction [36], and infrared spectroscopy [37, 55]. These experiments suggest that the hydrogen distribution in a-Si:H is highly inhomogeneous because the material consists of clustered as well as diluted hydrogen atoms. However, the number of clustered hydrogen atoms lies in a range of 4 – 7 in the device quality (8-14% H) samples [39, 46, 87]. Their results also suggest that the hydrogen prefers to be distributed sparsely with occasional clustering at low concentration. However, depending on the preparation conditions, hydrogen concentration, history of sample treatment, etc., the micro-structure can be highly inhomogeneous and it may consists of several large clusters [88], vacancies [79], void [91, 97] and molecular hydrogen [39, 76, 80] at high concentration. Our theoretical studies mentioned in the earlier sections [48, 49] also confirm these observations. Furthermore, the NMR experiments [39, 46] also provide the nature of hydrogen distribution by calculating NMR line spectra, which is a combination of a Gaussian and a truncated Lorentzian functions. The
line spectra can be approximated by considering the dipolar interaction between the hydrogen atoms [77, 85] in which the broad line width is attributed to a dense or clustered environment of hydrogen whereas isolated and sparsely-distributed hydrogen are most likely to cause a narrow Lorentzian-like line shape.

From the knowledge of these earlier works [39, 37, 41, 87, 97], we want to use their results in our model generating approach as an input information. The input information is divided into two parts. The first part is a cluster information that provides a number and size of hydrogen clusters based on the hydrogen concentration. The second provides moment information in which experimental moments are extracted from the nuclear magnetic resonance line spectra [39]. A detail of the method is presented in the following section.

5.2 Model generation

![Flow diagram of the inverse approach implemented in this work.](image)

**Figure 5.1:** A flow diagram of the inverse approach implemented in this work.

The starting point of our approach is to generate a set of trial hydrogen distributions using experimental NMR data for a given concentration. Hydrogen atoms are chosen randomly in a cubic box of length 26.75 Å that corresponds to the experimental density of a-Si:H for a model of 1000 Si atoms. The initial positions of the hydrogen atoms are generated in such a way that the resulting H distribution has several small clusters (4-7 atoms), and a few large clusters (10-16 atoms at high concentration) in the background of a sparsely-distributed H atoms. Since a unique hydrogen distribution cannot be determined from these limited data, we construct
several such hydrogen distributions each of which is different from the other but is characterized by the presence of clusters.

Once the trial hydrogen distributions are available, a three-step procedure is followed:

1. The NMR moments of a trial hydrogen distribution is matched to that of the experimental line spectrum by optimizing a penalty function via simulated annealing,

2. The optimized hydrogen distribution is then embedded in a previously-built 1000-atom silicon network, and the superfluous silicon atoms within a distance closer than the silicon-hydrogen bond length are purged.

3. Finally, the resulting network is relaxed using a first-principles energy functional to obtain a stable, low energy conformation within the Harris functional approximation [45, 105, 106].

The method can be further described as below. In the first step, we take an experimental NMR line spectrum of a particular hydrogen content. Then, we calculate the first few order moments (i.e. zeroth, second, fourth etc.) from the line spectrum. The moments are denoted by \( \mu_{\text{exp}} \). Once we have the experimental NMR moments, we generate a trial hydrogen distribution within a cubical box having the same dimensions of a previously-built amorphous silicon model. We calculate the Van Vleck’s moments of the trail distribution and they are denoted by \( \mu_{\text{th}} \). Then, by moving the position of hydrogen atoms randomly we optimize the moments \( \mu_{\text{th}} \).

In the second step, the trial configuration whose moments are optimized, are merged into the previously-made amorphous silicon configuration. While doing so, some hydrogen atoms may overlap with the silicon atoms or they may be very close to some of the silicon atoms. In that case, we set a rule in which if a silicon atom is overlapped or it lies within a distance of the minimum Si-H bond length (1.4 Å) then the silicon atom should be removed so that the optimized hydrogen distribution will not be affected. The merged final network becomes a starting configuration of hydrogenated amorphous silicon and it must be relaxed using a proper method.

In the third step, one can use any \textit{ab initio} or semi-empirical potential methods to relax the model networks, however, we use the density functional code (SIESTA) [101]. The hydrogen atoms are found to be minimally disturbed during the relaxation, which maintains the moment information intact via a self-consistent loop between the relaxation and the optimization. Once the self-consistency is achieved, the final conformation is accepted. Otherwise, the procedure is repeated with a new hydrogen distribution going back to step 1. The various intermediate steps are depicted in the flow diagram in fig.5.1.
5.3 Nuclear magnetic resonance line widths and line spectra

To approximate nuclear magnetic resonance line widths and line spectra, one should calculate the first few NMR moments of hydrogen distribution. As we mentioned earlier, the dipolar interaction between hydrogen atoms provides a route of moment calculations. According to Van Vleck research [84], the second and fourth moments of a system of $N$ particles (of spin 1/2) can be written as:

\begin{equation}
\frac{\mu_2}{\gamma^4 h^2} = \frac{1}{2N} \sum_{j<k}^N B_{jk}^2
\end{equation}

\begin{equation}
\frac{\mu_4}{\gamma^8 h^4} = \frac{3}{16N} \sum_{<jkl>}^N B_{jk}^2 B_{jl}^2 - \frac{1}{36N} \sum_{<jkl>}^N B_{jk}^2 (B_{jl} - B_{kl})^2 + \frac{1}{72N} \sum_{<jkl>}^N B_{jk} B_{kl} (B_{jl} - B_{jk}) (B_{jl} - B_{kl}) + \frac{1}{8N} \sum_{J<k}^N B_{jk}^4 \tag{5.2}
\end{equation}

where

\begin{equation}
B_{jk} = \frac{3}{2} \frac{(1 - 3\cos^2 \theta_{ij})}{r_{ij}^3}
\end{equation}

and the symbol $<jkl>$ stands for no two indices being equal in the triple summation. It should be noted that Equations 5.1 and 5.2 above are independent of the symmetry of the system, and can be applied to both crystalline lattices and amorphous networks [49]. The shape of the resonance curve can be interpreted in terms of the second and the fourth moments. For an identical Gaussian, $\Gamma = \mu_4/\mu_2^2 = 3$, and a low value of $\Gamma$ indicates a bi-modal behavior or two separated peaks in the spectrum. For a Gaussian Line shape, the full width at half maximum (FWHM) is given by [77],

\begin{equation}
\sigma_g = \sqrt{8 \mu_2 ln 2} \tag{5.4}
\end{equation}

It is to be noted that at low hydrogen content with diluted hydrogen distribution the ratio $(\mu_4/\mu_2^2)$ can be large ($>> 3$) and the Gaussian broad line width calculation does not represent the distribution correctly. Therefore, one should use the following expression that provides the correct narrow line width of the distribution.

\begin{equation}
\sigma_L = \sqrt{\frac{\pi^2 \mu_2}{3 \Gamma}} \tag{5.5}
\end{equation}

However, most of the experimentalist use the following equation [39, 77] for calculating the narrow line width which is based on the density of sparse or distributed hydrogen atoms.

\begin{equation}
\sigma_{narrow} = \frac{4\pi}{3\sqrt{3}} \gamma^2 n h \tag{5.6}
\end{equation}

The experimental NMR spectra deviate significantly from an ideal Gaussian or a truncated Lorentzian behavior depending on hydrogen concentration, preparation conditions, and the
degree of inhomogeneity present in the micro-structure. Therefore, Equations 5.4 and 5.5, provide only approximate values of this widths originating from the clustered and the diluted environments. For a small deviation from the ideal Gaussian distribution, one often uses the Gaussian memory function approximation and that express the universal line width as: [85]

\[ \sigma_u = \sqrt{\frac{2\pi \mu_2}{\Gamma - 2}} \quad \text{for} \quad \Gamma > 3 \] (5.7)

If we separate the hydrogen distribution as clustered and diluted phases then Equations 5.4 and 5.7 provide similar results. Once the second and the fourth moments are available we can calculate the NMR line spectrum by taking a penalty function which is a combination of a Gaussian and a truncated Lorentzian function. The penalty function is defined as below:

\[ f = Af(G) + Bf(L) \] (5.8)

where A and B are the weight factors associated with the distributions. They are calculated based on percentage of hydrogen atoms in clustered and diluted phases respectively. Similarly, f(G) and f(L) are Gaussian and truncated Lorentzian functions. It is to be noted that the penalty function (from Equation 5.8), can be optimized with respect to an experimental line spectrum of the material by choosing any optimization technique.

5.4 Results and Discussion

In this section, we first analyze the structural and electronic aspects of the models for the purpose of validation. Then, we discuss about the hydrogen micro-structure, distribution of hydrogen atoms, structure of vacancies and voids, and nuclear magnetic resonance line widths and line spectra of the representative models.

5.4.1 Hydrogen micro-structure

In order to demonstrate the efficacy of our approach, we generate a number of a-Si:H conformations with a concentration between 10 at.% to 23 at.% hydrogen. We choose three model conformations at 10 at.% H, 14 at.% H and 23 at.% H, and study their structural and electronic properties, and the micro-structure via experimental NMR and IR data. It should be noted that while the hydrogen distribution in all these conformations is consistent with experimental NMR results, this does not necessarily imply that the structural and other properties would be reproduced correctly. An independent check, therefore, is needed for verification of the structure of these models.

We begin with the Si-H and H-H pair correlation functions (PCF) followed by the bond-angle distribution in the networks. Since a previously-built amorphous (silicon) matrix is employed in this work, we refrain ourselves from addressing the Si-Si pair correlation. In Figure 5.2, we have presented the results for the pair correlation function of Si-H pair at 10 at.% hydrogen.
Figure 5.2: A pair correlation plot of Si-H configurations as a function of radial distance (in Å) at 10 at.% hydrogen concentration. The first peak lies in a range of 1.54–1.68 Å whereas the second peak locates in the order of 2.9–3.5 Å.

Figure 5.3: A pair correlation plot of Si-H configurations as a function of radial distance (in Å) at 14 at.% hydrogen concentration. The first peak lies in a range of 1.54–1.68 Å whereas the second peak locates in the order of 2.9–3.5 Å.
Figure 5.4: A pair correlation plot of Si-H configurations as a function of radial distance (in Å) at 23 at.% hydrogen concentration. The first peak lies in a range of 1.54–1.68 Å whereas the second peak locates in the order of 3–3.6 Å.

Figure 5.5: Bond angle distribution for 10 at.% hydrogen concentration. The distribution has an average bond angle of 108.7° with 13.5° root mean square deviation.

concentration. Similarly, Figures 5.3 and 5.4 are the pair correlation functions at 14 at.% and 23 at.% hydrogen contents respectively. The positions of the first and the second peaks lie
Figure 5.6: Bond angle distribution for 14 at.% hydrogen concentration. The distribution has an average bond angle of 108.8° with 13.7° root mean square deviation.

Figure 5.7: Bond angle distribution at for at.% hydrogen concentration. The distribution has an average bond angle of 108.8° with 13.9° root mean square deviation.

in a range of 1.54 – 1.68 Å and 2.9 – 3.6 Å, respectively in the all three figures. The first peaks which correspond to the first neighbors are sharp in the all figures. However, the second and third peaks corresponding to the second and third nearest neighbors are broader. These
Figure 5.8: Hydrogen-hydrogen distribution for 10 at.% hydrogen concentration. The maximum peak lies at approximately 2.1 Å whereas most of the H-H pairs lie in a range of 1.6–2.5 Å.

Figure 5.9: Hydrogen-hydrogen distribution for 14 at.% hydrogen concentration. The maximum peak lies at approximately 2.1 Å whereas most of the H-H pairs lie in a range of 1.6–2.5 Å.

Observations are in agreement with the \textit{ab initio} results [41] as well as the experimental data [36].

Another important aspect of the model validation is PCF of H-H distribution or local
Figure 5.10: Hydrogen-hydrogen distribution for 23 at.% hydrogen concentration. The maximum peak lies at approximately 2.1 Å whereas most of the H-H pairs lie in a range of 1.6—2.5 Å.

Figure 5.11: Density of electronic states/eV for the model with 10 at.% H is shown in the figure. The Fermi level is at 0.0 eV.

distributions of hydrogen atoms. The distributions at 10 at.%, 14 at.% and 23 at.% hydrogen concentrations are shown in Figures 5.8, 5.9 and 5.10 respectively. The maximum peaks in
Figure 5.12: Density of electronic states/eV for the model with 14 at.% H is shown in the figure. The Fermi level is at 0.0 eV.

Figure 5.13: Density of electronic states/eV for the model with 23 at.% H is shown in the figure. The Fermi level is at 0.0 eV.

The all three plots lie in a range of 1.6 – 3.0 Å which are broader enough as compared to the first peaks of Si-H PCFs. The first peaks in the range of 1.6 – 3.0 Å provide an evidence of the nonexistence of molecular hydrogen (bond length ≈ 1.0 Å) in all the models. The H-H distances
in the range of 1.8 – 2.3 Å belong to the SiH₂, SiH₃ and SiH₄ (if available) configurations respectively whereas the distances ≤ 1.8 Å and ≥ 2.3 Å belongs to those hydrogen atoms which are connected to the different silicon atoms but close to each other. Furthermore, the first clear peaks in the local hydrogen distributions ensure the existence of clustered hydrogen atoms in the all three models. These results are consistent with the neutron diffraction data reported by Bellissent [36]. It indeed suggests that as far as two-body correlation functions are concerned, the inverse method produces the correct structure of a-Si:H.

A further characterization of the structure can be obtained from the bond-angle distribution that provides information about the three-body correlation. The results for the bond-angle distributions for all three concentrations are presented in Figures 5.5, 5.6 and 5.7. A pure amorphous silicon model having no coordination defect at all (i.e. known as the WWW model) has an average bond angle (Si-Si-Si) of 108.57° with RMS deviation of 11.19° [42]. In hydrogenated amorphous silicon, the introduced hydrogen atoms to pacify the dangling bonds create vacancies and voids because of the nature of hydrogen clusters. That does eventually affect on the bond angle distribution. However, the average bond angle and the RMS deviations should not be much deviated from the pure amorphous silicon model. In our all three models, the average bond angle is found to be around 108.8°, with a root mean square (RMS) deviation between 13.5° to 13.9°. These observations are very clear from Figures 5.4, 5.5 and 5.6 as well as they are in excellent agreement with the WWW model [42].

Having discussed of the pair correlations and the bond angle distribution, we would like to address an important aspect of hydrogen micro-structure that describes various hydrogen-bonding configurations. Such configurations can be studied via infrared experiments by measuring the vibrational frequencies of variously bonded hydrogen atoms. We present such bonding configurations of hydrogen in Table 5.2. There are only SiH (86% of total hydrogen) and SiH₂ (14% of total hydrogen) configurations at 10 at.% hydrogen content. Similarly, at 14 at.% hydrogen concentration, 81% of the total hydrogen atoms are found as SiH, 14% as SiH₂ and only 2% as SiH₃ configurations. At 23 at.% hydrogen concentration model, there are 75% SiH, 24% SiH₂ and 1% SiH₃ configurations. These results show that the SiH bonds are dominant bonding configurations in the hydrogenated amorphous silicon network. Furthermore, 14 – 24 % dihydrides (SiH₂) configurations are observed which are visible in the table. Notably, with increasing hydrogen concentrations the dihydride configurations are also increased. In contrast, the mono-hydrides (SiH) configurations decrease with increasing hydrogen contents. Interestingly, the trihydrides (SiH₃) are not observed at 10 at.% likewise in our ECMR models. However, a few (approximately 1 – 2% of the total hydrogen atoms) such configurations appear at 14 at.% and 23 at.% hydrogen concentrations. It is noteworthy that these results are in good agreement with the IR spectroscopy data reported by Manfredotti et al [55], and Lucovsky et al [37].

At the end of structural properties, we would like to present the coordination of silicon
atoms with their neighbors in Table 5.1. The table shows that up to 97% of all the silicon atoms are four-fold coordinated along with a few three-fold dangling bonds (≤ 1.62%), and five-fold floating bonds (≤ 2.25%). These results ensure that the models have tetrahedral bonding nature. A statistics of clustered and diluted hydrogen atoms are presented in Table 5.3. With increasing the hydrogen contents a number of clustered hydrogen increases. That make sense because when the concentration increases more and more hydrogen atoms are available to form a cluster. Then, small clusters merge into a large cluster as a result a number of diluted hydrogen atoms decreases (see the Table 5.3). The overall results of structural properties of hydrogenated amorphous silicon are consistent with ab initio results [40, 41], and the experimental results by Bellisent et al [36] and Lucovsky et al [37].

<table>
<thead>
<tr>
<th>Conc (%H)</th>
<th>3-fold(%)</th>
<th>4-fold(%)</th>
<th>5-fold(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.95</td>
<td>96.80</td>
<td>2.25</td>
</tr>
<tr>
<td>14</td>
<td>1.30</td>
<td>96.86</td>
<td>1.84</td>
</tr>
<tr>
<td>23</td>
<td>1.62</td>
<td>97.10</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Table 5.2: Statistics of hydride configurations with H concentration

<table>
<thead>
<tr>
<th>Conc (%H)</th>
<th>SiH(%H)</th>
<th>SiH₂(%H)</th>
<th>SiH₃(%H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>86</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>81</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>23</td>
<td>75</td>
<td>24</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 5.3: Statistics of clustered and diluted H atoms

<table>
<thead>
<tr>
<th>Conc (%H)</th>
<th>Clustered(%H)</th>
<th>Diluted(%H)</th>
<th>H atoms in a cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>40</td>
<td>60</td>
<td>4-7</td>
</tr>
<tr>
<td>14</td>
<td>60</td>
<td>40</td>
<td>4-8</td>
</tr>
<tr>
<td>23</td>
<td>75</td>
<td>25</td>
<td>4-16</td>
</tr>
</tbody>
</table>

Having discussed the structural aspect of the models, we now focus on the electronic properties in the networks. It is obvious that the presence of even a very minute defect can significantly affect the electronic density of states. In particular, the band gap region is very sensitive to structural disorder, especially the presence of floating and dangling bonds. It is therefore necessary to establish that the models can produce an accurate electronic density of states (EDOS) with a correct band gap. We have used a first-principles density functional code, SIESTA, [106, 101] and the result of EDOS calculations are presented in Figures 5.11, 5.12 and 5.13 for 10 at.%, 14 at.% and 23 at.% respectively. The overall shape of the EDOS is almost identical in all the models except near the band gap. The models with a lower concentration of hydrogen tend to show a cleaner gap in the electronic spectrum. The shape of the band tails near the gap region in the figures is exponential. Such exponential behavior of band tail
states has also been shown by Jarolimek et al [40], Buda et al [41] and other several theoretical
[44, 66, 69, 104] and experimental [13, 15] works. This is a universal feature of amorphous
semiconductors which is caused by short range order and the long range disorder.

5.4.2 Vacancies and voids in a-Si:H models

Infrared experiments [97] and theoretical [49] studies both show that the hydrogen micro-
structure consists of built-in mono- and divacancies. Therefore, we want to focus on whether the
models generated via the inverse method consist of the vacancies or not. A real space analysis
shows that the models at 10 at.% and 14 at.% hydrogen concentrations consist of both the stable
mono- and divacancies whereas the model at 23 at.% H concentration shows empty cavities also,
which we called micro-voids, surrounded by hydrogen atoms in the inner surface of the cavity.
However, no hydrogen molecule is observed within the cavities. We present a representative
mono-vacancy of 10% and a divacancy of 14% hydrogen concentrations in Figure 5.14. The sub
plots (a) and (c) depict the mono- and divacancies at 10 at.% and 14 at.% respectively. We can
further understand these structure of vacancies by introducing new silicon atoms after removing
four hydrogen atoms for mono and six hydrogen atoms for divacancies as shown in sub plots
(c) and (d) respectively. The small (yellow) and big (green) atoms are hydrogen and silicon
atoms whereas the big (white) atoms are introduced silicon atoms, which are considered as
the missing silicon atoms in the both cases. It should be noted that the missing silicon atoms
can adjust themselves with neighboring silicon atoms even after relaxing the network via the
first-principles method (i.e. SIESTA).

Having discussed with vacancies in the lower concentration models (≤ 14), we would like
to discuss about voids at the high concentration (23 at.% H) model. It is observed from the
experiment that at the high concentration model the hydrogen micro-structure shows voids
rather than the vacancies [97]. In our high concentration model, an empty cavity or micro-void
is observed and it is depicted in Figure 5.15. We have shown the same complex with and without
applying a molecular surface [117]. The micro-void is visible in the Figure 5.15 (left), however,
to make it further clear we apply molecular surface and present it to the right side of the figure.
The cavity consists of 16 hydrogen atoms in the inner surface, however, no molecular hydrogen
is observed within it. These observations are remarkable because the vacancies and micro-voids
are evolved themselves while relaxing the model networks. Furthermore, these results are
consistent with IR experiments by Smets et al [97] in which the authors were reported that the
hydrogen micro-structure consists of mono- and divacancies at low (< 14%) and micro-voids
or voids at high (> 14%) hydrogen concentrations.

5.4.3 Calculation of NMR line spectra

Nuclear magnetic resonance experiment is one of the best probe to characterize clustered and
diluted phases of hydrogen atoms in the micro-structure [6, 9]. These experiments provide one
Figure 5.14: (a) A stable mono-vacancy with a cluster of six hydrogen atoms, (b) the same complex after removing four hydrogen atoms and introducing a missing silicon atom for the purpose of clarity at 10% hydrogen concentration. Similarly, (c) a stable divacancy with a cluster of seven hydrogen atoms, (d) the same complex after removing the six hydrogen atoms and introducing two missing silicon atoms at 14% hydrogen concentrations. All big (green) and small (yellow) atoms are silicon and hydrogen atoms whereas the big (white) atoms are the missing silicon atoms. The distance between two missing silicon atoms is approximately 2.5 Å.

dimensional line spectrum via the Fourier transform of a free induction decay (FID) of three dimensional distribution of hydrogen atoms in bulk materials [76]. The line spectrum consists of two components: a Gaussian line originated from clustered and a truncated Lorentzian line from diluted environments. Therefore, the NMR line spectrum is a combination of the both and it can be constructed from the knowledge of dipolar interactions among the hydrogen nuclei [77]. To the best of our knowledge, no theoretical study has reported yet the calculation of NMR line spectrum of hydrogenated amorphous silicon. Therefore, we focus on providing an approximated calculation of the line spectra at different hydrogen concentrations.

In order to calculate the NMR line spectra, we first separate the overall hydrogen distribution
Figure 5.15: (Left) A big cluster up to 16 H atoms and the same complex (right) by applying molecular surface to provide a clear picture of the micro-void at 23% hydrogen concentration are shown in the figure.

into a clustered phase and a diluted phase of the hydrogen atoms. The second and fourth moments were calculated from Equations 5.1 and 5.2 respectively. Once the moments are available, we construct a Gaussian function, \( f(G) \), from the moments of the clustered hydrogen atoms and a truncated Lorentzian function, \( f(L) \), from the diluted hydrogen atoms. Then, the line spectrum is approximated by using Equation 5.8. The constants, \( A \) and \( B \) in the equation, are taken based on the contribution of hydrogen atoms in the clustered and diluted phases respectively. The NMR line spectra at 10 at.\%, 14 at.\% and 23 at.\% are shown in Figure 5.16. The corresponding line widths are also presented in Table 5.4.

<table>
<thead>
<tr>
<th>%H</th>
<th>( \sigma_G ) (kHz)</th>
<th>( \sigma_L ) (kHz)</th>
<th>( \sigma_n ) (kHz)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20.23</td>
<td>3.38</td>
<td>22.0</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>*NRL[39]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>26.21</td>
<td>2.73</td>
<td>26.0</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>*RCA[39]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>27.29</td>
<td>1.79</td>
<td>25-30</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>*Gleason[46]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Hydrogen concentration of samples is 10-15 %.

In Figure 5.16, NMR line spectra of 10 at.\%, 14 at.\% and 23 at.\% are represented by blue, red and black colors. The line spectra in the figure clearly show a highly inhomogeneous nature of the hydrogen distributions because none of them are neither a Gaussian nor a truncated Lorentzian shape. These spectra further indicate that with increasing hydrogen concentration the broad line widths increases and vice versa for the narrow line widths. The results from our models and the experimental works are presented in the Table 5.4. The broad and narrow line widths at 10 at.% hydrogen concentrations are 20.23 kHz and 3.38 kHz respectively. Similarly, in 14 at.% hydrogen content, the broad and narrow line widths are 26.21 kHz and 2.73 kHz respectively. These observations are very close with NRL and RCA data [39]. Furthermore,
Figure 5.16: NMR spectra of the 10% (blue), 14% (red) and 23% (black) hydrogen concentrations respectively. The broad line widths increases with increasing hydrogen concentrations whereas the narrow line widths decreases.

Figure 5.17: NMR spectrum for the 10% H model. The experimental data (NRL) corresponds to 10-15% H, and are taken from Ref. [39]. the y-axis of 10% H concentration is scaled with respect to NRL data for the purpose of comparison.

the broad and narrow line widths of 27.29 kHz and 1.79 kHz are observed at 23 at.% hydrogen concentration. The over all values of line widths at different hydrogen concentration regimes are in excellent agreement with NMR experiments [39, 46].

Finally, for the purpose of comparison, we have rescaled the data of 10% and 14% hydrogen concentrations with respect to NRL data  [39] as shown in Figures (5.17) and (5.18). The
Figure 5.18: NMR spectrum for the 14% H model. The experimental data (NRL) corresponds to 10-15% H, and are taken from Ref. [39]. The y-axis of 14% H concentration is scaled with respect to NRL data for the purpose of comparison.

nature of the plots at 10 at.% and 14 at.% are similar to the experimental NRL line spectra. However, a number of clustered hydrogen atoms is slightly less than that of NRL sample at 10 at.% hydrogen concentration. Similarly, they are slightly greater than NRL sample at 14 at.% concentration. On the other hand, there are more diluted hydrogen atoms at 10 at.% and less hydrogen atoms at 14 at.% with respect to NRL sample. These observations can be made by analyzing the Gaussian and Lorentzian parts of the spectra. From all these results, we came in a conclusion that the models, which were generated via the information-based inverse method, provide not only the correct NMR line spectra but also satisfy structural and electronic properties of the hydrogenated amorphous silicon. Therefore, this result is one of the remarkable outcome of our research to understand the hydrogen micro-structure in further detail.

5.5 Conclusion

We have developed a new method which is based on the inverse approach that uses experimental cluster and moment information as its input and generates the models of hydrogenated amorphous silicon. The method is very simple and it can produce the correct hydrogen micro-structure. We have presented three representative models of 10 at.%, 14 at.% and 23 at.% hydrogen contents. The models not only provide the correct pair correlation functions but also the bond angle distribution. The electronic density of states (EDOS) calculations show that there is a very clean energy band gap between the valence and the conduction bands. All the models have more than 97% four-fold coordinated silicon atoms having less than 3% three-fold and five-fold defects. Furthermore, the micro structures have all possible hydride configurations
such as SiH, SiH$_2$ and SiH$_3$. However, it is dominated by mono-hydrides (SiH) configurations. The lower concentration models (10 at.% and 14 at.%) consist of mono and stable divacancies whereas the higher concentration (23 at.%) model shows the existence of the voids surrounded by several hydrogen atoms in the internal surface of the voids. However, no H$_2$ molecule is observed within the void even at the high concentration. The NMR line spectrum of all three models are calculated using Van Vleck’s moments. The calculated line spectra are very consistent with the experimental samples provided by the NRL and RCA laboratories. Thus, the method is very efficient to generate the models of the hydrogenated amorphous silicon in all concentration regimes.
Chapter 6

VOIDS AND MOLECULAR HYDROGEN

6.1 Introduction

Based on our knowledge, a characterization of micro-voids in a device quality sample of the hydrogenated amorphous silicon was made by Mahan et al [53] by small-angle x-ray scattering and infrared measurement. However, multiple-quantum nuclear magnetic resonance (MQ-NMR) [87], scanning electron microscopy (SEM) [118], small-angle scattering [119] etc. demonstrate the existence of micro-voids in non device-quality samples of the hydrogenated amorphous silicon. The calorimetry experiment by Graebner et al [98] directly suggested the micro-voids having diameter in a range of $10 - 40$ Å. Later on, Smets et al [97] reported the evidence of micro-voids or voids at greater than 14 at.% hydrogen concentrations. Most of these studies suggest that inner surface of the voids contain $4 - 9$ hydrogen atoms [53] depending on the samples.

In addition to the voids, a small number of hydrogen molecules were observed within the voids by Conradi et al [120], Carlos et al [39] and Leopold et al [121]. However, a direct experimental evidence of the molecular hydrogen in $\alpha$-Si:H was reported by Löhneysen et al [96] in samples prepared by the glow discharge technique. Similarly, Chabal et al [95] reported the first observation of gaseous molecular $H_2$ via the infrared absorption spectroscopy in 1984. Then, Boyce et al [80] and Su et al [76] observed the similar results by NMR experiments. Motivated from these experiments, we are interested in generating a model that can incorporate micro-voids with molecular hydrogen in the device-quality sample (7-20 at.% hydrogen atoms) of hydrogenated amorphous silicon.

We made significant progress by generating models of hydrogenated amorphous silicon between 10-16 at.% hydrogen concentration as described in the earlier section. Although the model shows an evidence of the voids having several hydrogen atoms in its internal surface, we do not have a theoretical evidence of molecular hydrogen within the voids. That motivate us finding a better way of model generation that can prove the micro-structure consists of voids and hydrogen molecules within it. In addition, our interest involves generating models with less than 20 at.% hydrogen concentration (range of a device-quality sample).

Before describing the model generating technique, we would like to start from a schematic diagram of a void which is shown in Figure 6.1. The big and small spheres are silicon and hydrogen atoms respectively. An empty space, considered as a micro-void, that can accommodate at least four silicon atoms in absence of those hydrogen atoms in the figure. It is
to be noted that hydrogen molecules may or may not reside within the voids. Some experiments [80, 96], for instance, Löhneysen et al [96] showed the hydrogen molecules lie within the voids whereas Mahan et al [53] reported the non-existence of hydrogen molecules within the voids. However, it is generally accepted that the micro-structure consists of voids at higher concentrations (> 14 at.%) and it depends on several factors such as deposition conditions, preparation methods and quality of the samples.

Figure 6.1: Schematic diagram of a void structure. The big and the small circles represent silicon and hydrogen atoms respectively. The empty cavity in the figure is considered as a micro-void.

We have developed several models of the hydrogenated amorphous silicon at the higher hydrogen contents (>15 at.%). The micro-structure of the models consist of voids with molecular hydrogen. One of the very important results of this work is an evolution of H$_2$ molecules within the voids while relaxing the network. It is remarkable because no theoretical work is reported yet with an evidence of the molecular hydrogen. However, some theoretical works [82] have created a void in the beginning, and relaxed the network globally or locally after keeping some hydrogen atoms within the voids or nearby. While doing so they have observed some H$_2$ molecules within the voids. Our approach is completely different from them and a detail of the work is presented in the following sections.

6.2 Model Generation

We use the same algorithm (an information-based inverse approach) described in Chapter 5 for the purpose of model generation. However, we have chosen a bigger box size (approximately 36 Å) at this time. Several samples in a range of 10-20 at.% hydrogen contents are generated to study whether the models consist of molecular hydrogen or not within the voids. The samples having the hydrogen contents of ≤ 15 at.% do not show presence of micro-voids and H$_2$ molecules in their structures. It is in good agreement with the results of Smets et al [97] in which they had reported that the micro-structure incorporates vacancies rather than voids at these concentration regimes, and the H$_2$ molecules reside mostly within the voids [80]. Therefore, we considered the samples in a range of 16 – 20 at.% hydrogen concentration. However, we
have presented the results of only two representative samples at 16 at.% and 18 at.% hydrogen concentrations. Now onward, we refer the sample at 16 at.% hydrogen as 'Sample A', and at 18 at.% hydrogen concentration as 'Sample B' respectively.

Sample A consists of 2560 atoms within a cubic box of linear dimension 35.7 Å including 417 hydrogen and the remaining silicon atoms. Similarly, in sample B, there are 460 hydrogen out of 2625 atoms within the same cubic box. The size of the box is calculated based on experimental density of hydrogenated amorphous silicon [6]. Both samples have several small clusters of 4 – 7 and a few large clusters of 14 – 22 hydrogen atoms. It is to be noted that the input NMR moments information at these concentrations are not available directly from experiments. Therefore, we calculate the first, second and the fourth NMR moments from the experimental NMR line spectra of the NRL and RCA samples [39]. These experimental samples consist of 10 – 15 at.% hydrogen contents. However, the NRL sample shows more diluted and the RCA sample illustrates more clustered environment of hydrogen atoms. Such observations can be easily made from their line spectra because the RCA sample has broader line width as compared to that of the NRL sample.

Once the models are generated, their validity should be checked. Pair correlation function and bond angle distribution are two important structural measures of a valid model. The first provides an information about two-body correlation whereas the second provides three body correlation in the amorphous network. Figures 6.2 and 6.3 are the pair correlation functions between silicon and hydrogen atoms of the samples A and B respectively. In other words, correlation between Si and H atoms only are presented in the figures. The first peaks in the both figures lie in a range of 1.45 Å – 1.7 Å. Those sharp peaks are measures of SiH bond lengths as well as the first nearest neighbors of silicon atoms. The second peaks locate in a range of 2.5 Å – 3.5 Å as shown in the figures. They are broader as compared to the first peaks. These observations are very consistent with earlier experimental [38, 42] and theoretical works [40, 41].

Bond angle distribution is another structural measure to validate the model. Figures 6.6 and 6.7 are the bond angle distributions of samples A and B respectively. The average bond angle is 108.65° with RMS deviation of 13.7° in sample A. Similarly, they are 108.55° with 13.78° respectively in sample B. These results show that the models have correct two body (i.e. pair correlation) and three body correlations (i.e. bond angle distribution). Once the structural aspects are satisfied by the models then electronic density of states (EDOS) should be checked. A semiconductor must have a very clean energy band gap between valence and conduction bands. An EDOS calculation provides whether the network has a clean energy band gap or not. Figures 6.8 and 6.9 clearly show that there is a clean gap between the valence and the conduction bands in the both models. If a model has defects then they reflect in the band gap. Hence the gap becomes thinner or even it may disappear, as a result, the material may show anomalous electronic properties. Therefore, the energy band gap should be clean for the device
Figure 6.2: Si-H pair correlation in sample A (16 at.% H concentration model). The first peak lies in a range of 1.45 Å – 1.7 Å whereas the second peak locates in an order of 2.5 Å – 3.5 Å.

Figure 6.3: Si-H pair correlation in sample B (18 at.% H concentration model) is shown in the figure. The first peak lies in a range of 1.45 Å – 1.7 Å whereas the second peak locates in an order of 2.5 Å – 3.5 Å.

quality model. In both the figures, the gap is not wider as compared to the experiment (≈ 1.7 eV) because in density functional theory calculation, the band gap is under estimated, as a result,
Figure 6.4: Distribution of hydrogen atoms in sample A (16 at.% H concentration model). The first peak lies in a range of 0.7 Å – 1.0 Å that indicates the existence of H₂ molecules in the model. The maximum peak lies in a range of 1.8 Å – 2.6 Å that represents the H-H distance of SiH₂ and SiH₃ configurations.

the gap become thinner as compared to the experiment [36]. Similar observations were reported by Jarolimek et al [40].

6.3 Results and Discussion

Having discussed with the major aspects of model validation, we would like to focus on results of the hydrogen micro-structure, voids and molecular hydrogen of the models.

6.3.1 Hydrogen Microstructure

Table 6.1 provides various silicon-hydride configurations of sample A. The model consists of 74.5% SiH, 21.2% SiH₂, 2.9% SiH₃ and 1.4% of the total hydrogen as H₂ molecules. Similarly, in sample B, there are 76% SiH, 19% SiH₂, 3.2% SiH₃, 0.9% SiH₄ and 0.9% of the total hydrogen as H₂ molecules. The micro structures are highly dominated by SiH configurations in both models which is in very good agreement with IR experiments [83] as well as our previous theoretical models [48, 49]. Only one SiH₄ configuration is observed in sample B, which is considered as a defect because no experimental work has reported yet the existence of SiH₄. However, sample A has no such configuration. Furthermore, a few hydrogen molecules are observed in both models which is reported by some experimental works [76, 80, 96]. The models show all possible silicon-hydrogen bonding configurations such as SiH, SiH₂, SiH₃ etc.,
Figure 6.5: Distribution of hydrogen atoms in sample B (18 at.% H concentration model). The first peak lies in a range of 0.7 Å – 1.0 Å that indicates the existence of H2 molecules in the model. The maximum peak lies in a range of 1.8 Å – 2.6 Å that represents the H-H distance of SiH2 and SiH3 configurations.

Figure 6.6: The bond angle distribution for sample A (16 at.% H concentration model). An average bond angle of the distribution is 108.65° with root mean square deviation of 13.7°.
Figure 6.7: The bond angle distribution for sample B (18 at.% H concentration model). An average bond angle of the distribution is $108.55^\circ$ with root mean square deviation of $13.78^\circ$.

Figure 6.8: Electronic density of states (EDOS) in sample A (16 at.% H concentration model) is shown in the figure. A clean gap between the valence and the conduction bands is visible. Thus, it is one of the remarkable observations.

Another important aspect of the hydrogen micro structure is coordination schemes of silicon atoms with their nearest neighbors. Table 6.2 suggests that more than 97% of silicon atoms
Figure 6.9: Electronic density of states (EDOS) in sample B (18 at.% H concentration model) is shown in the figure. A clean gap between the valence and the conduction bands is visible.

Table 6.1: Statistics of hydride configurations with H concentration

<table>
<thead>
<tr>
<th>Conc (%H)</th>
<th>SiH(%H)</th>
<th>SiH₂(%H)</th>
<th>SiH₃(%H)</th>
<th>SiH₄(%H)</th>
<th>H₂(%H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>74.5</td>
<td>21.2</td>
<td>2.9</td>
<td>0.0</td>
<td>1.4</td>
</tr>
<tr>
<td>18</td>
<td>76.0</td>
<td>19.0</td>
<td>3.2</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

have four-fold bonds in both models. The defects in the models are very low (≤2.7%) including ≤ 0.8% three-fold and ≤ 1.9% five-fold bonds in both models. Furthermore, the coordination number of 4.01 in both the models preserves the tetrahedral nature of amorphous silicon. However, the coordination number is slightly greater than four because the both models have more five-fold floating bonds as compared to a total of two-fold and three-fold dangling bonds.

Table 6.2: Statistics of Silicon hydrogen bonding configurations with H concentration

<table>
<thead>
<tr>
<th>Conc (%H)</th>
<th>3-fold(%)</th>
<th>4-fold(%)</th>
<th>5-fold(%)</th>
<th>coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.70</td>
<td>97.60</td>
<td>1.7</td>
<td>4.01</td>
</tr>
<tr>
<td>18</td>
<td>0.80</td>
<td>97.30</td>
<td>1.9</td>
<td>4.01</td>
</tr>
</tbody>
</table>

In order to investigate a hydrogen distribution in the models, we have separated the distribution into clustered and diluted hydrogen atoms. Table 6.3 shows how the atoms are distributed in the silicon network. More than 75% hydrogen atoms reside in the clustered phase including several small clusters of 4 – 7 and a few large clusters of 14 – 22 hydrogen atoms. It can be further characterized by a local distribution of hydrogen atoms. Figures 6.4 and 6.5 are the local hydrogen distributions of samples A and B respectively. The first peaks in a range of 0.7 Å–
1.0 Å in both the figures elucidate the presence of H₂ molecules in the networks. The distance between hydrogen atoms in SiH₂, SiH₃ and SiHHSi configurations are reflected in the range of 1.8 Å–2.6 Å. These observations are consistent with the NMR experiments by Su et al [76] and a theoretical work by Drabold et al [81].

<table>
<thead>
<tr>
<th>Table 6.3: Statistics of clustered and diluted H atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc (%H)</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>18</td>
</tr>
</tbody>
</table>

6.3.2 NMR line spectra

We have already presented a detail procedure of NMR line spectra calculations in Chapter 5. Therefore, we just want to present the results in this section. Likewise in the previous sections, the second and fourth moments were calculated using Equations 5.1 and 5.2 respectively. Table 6.4 provides the second and fourth moments as well as Γ of overall, diluted and clustered phases of the hydrogen distribution. The moments were presented after taking an average of 1000 random directions of applied magnetic field. The values of Γ lie in a range of $3.15 - 7.34$. They are very close to 3 ($\Gamma_G = 3$) in the clustered phase and significantly deviated from 3 ($\Gamma_L >> 3$) in the diluted phase. However, they are similar in the overall calculations. These observations recommend to separate clustered and diluted hydrogen atoms while calculating the line widths rather than using the overall distribution.

In Table 6.5, we have listed the broad line widths ($\sigma_g$) using the Gaussian approximation and the narrow line widths via the truncated Lorentzian ($\sigma_L$) and the density approximation ($\sigma_{narrow}$). The broad line widths lie in a range of $30.33 - 35.00$ kHz in the clustered phase whereas they are in an order of $28.0 - 31.0$ kHz in the overall calculations. Their values decrease in the overall calculations as compared to the clustered phase due to a contribution of the diluted hydrogen atoms. On the other hand, $\sigma_L$ and $\sigma_{narrow}$ lie in a range of $3.25 - 4.70$ kHz and $4.47 - 5.37$ kHz respectively in the diluted phase. However, their larger values, $11.0 - 12.7$ kHz and $8.22 - 9.0$ kHz respectively in the overall calculations, include a contribution of the clustered hydrogen atoms as well. Thus, the overall calculations of NMR moments and line widths mislead the information of any highly inhomogeneous hydrogen distribution. Hence, it is again recommended that those calculations should be performed only after separating the overall hydrogen distribution into clustered and diluted phases.

Table 6.6 is a comparison of theoretical models with some experimental works. The broad line widths ($\sigma_g$) and narrow line widths ($\sigma_L$) are $30.33$ kHz and $3.25 - 4.47$ kHZ respectively in sample A whereas they are $35.0$ kHz and $4.7 - 5.37$ kHz respectively in sample B. On the other hand, the experimental broad and narrow line widths lie in a range of $22.0 - 39.0$ kHz and $2.7 - 6.0$ kHz respectively other than HW sample in the table.
Figure 6.10: An NMR line spectrum in sample A (16 at.% H concentration model) is shown in the figure. The spectrum shows a broad line width of 30.33 kHz and a narrow line width of 3.25 kHz.

Figure 6.11: An NMR line spectrum in sample B (18 at.% H concentration model) is shown in the figure. The spectrum shows a broad line width of 35 kHz and a narrow line width of 4.7 kHz.
Table 6.4: Van Vleck moments of overall, clustered and diluted phases of hydrogen atoms

<table>
<thead>
<tr>
<th>Conc (at. % H)</th>
<th>Phase</th>
<th>$\mu_2(\gamma^4\hbar^2)$</th>
<th>$\mu_4(\gamma^8\hbar^4)$</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Overall</td>
<td>$9.94 \times 10^{-5}$</td>
<td>$3.64 \times 10^{-4}$</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
<td>Cluster</td>
<td>$1.15 \times 10^{-2}$</td>
<td>$4.26 \times 10^{-4}$</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td>Dilute</td>
<td>$1.64 \times 10^{-3}$</td>
<td>$1.97 \times 10^{-5}$</td>
<td>7.34</td>
</tr>
<tr>
<td>18</td>
<td>Overall</td>
<td>$1.25 \times 10^{-2}$</td>
<td>$5.81 \times 10^{-4}$</td>
<td>3.69</td>
</tr>
<tr>
<td></td>
<td>Cluster</td>
<td>$1.54 \times 10^{-2}$</td>
<td>$7.45 \times 10^{-4}$</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td>Dilute</td>
<td>$2.68 \times 10^{-3}$</td>
<td>$4.14 \times 10^{-5}$</td>
<td>7.34</td>
</tr>
</tbody>
</table>

Table 6.5: Line widths of overall, clustered and diluted phases of hydrogen

<table>
<thead>
<tr>
<th>Conc (at. % H)</th>
<th>Phase</th>
<th>$\sigma_g$ (kHz)</th>
<th>$\sigma_L$ (kHz)</th>
<th>$\sigma_{narrow}$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Overall</td>
<td>28.0</td>
<td>11.0</td>
<td>8.22</td>
</tr>
<tr>
<td></td>
<td>Cluster</td>
<td>30.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dilute</td>
<td>3.25</td>
<td>4.47</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Overall</td>
<td>31.0</td>
<td>12.7</td>
<td>9.00</td>
</tr>
<tr>
<td></td>
<td>Cluster</td>
<td>35.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dilute</td>
<td>4.70</td>
<td>5.37</td>
<td></td>
</tr>
</tbody>
</table>

Once we have the correct NMR moments and line widths, we would like to calculate theoretical NMR line spectra of the models. We calculate NMR line shapes after separating the clustered and diluted moments as shown in Figures 6.10 and 6.11 for the samples A and B respectively. The line spectra of both the samples are similar to the RCA data [39]. However, the exact clustered and diluted hydrogen information of those models are unavailable for the purpose of comparison. Both plots show the dominant character of clustered hydrogen because the line spectra are more Gaussian than the truncated Lorentzian. From these observations, one can conclude that the models generated via the inverse approach, are in excellent agreement with the device quality samples.

6.3.3 Structure of voids and molecular hydrogen

We have already discussed about the existence of the voids and molecular hydrogen from several experimental works. The void structures of the sample A and B are presented in Figures 6.12 and 6.14 respectively. In the both figures, the large (green) atoms and small (white) atoms are silicon and hydrogen respectively. A hydrogen molecule (two connected white spheres) in the center of the voids are visible in both figures. It is to be noted that the structures of the voids are highly irregular in a three dimensional space. Therefore, it is a nontrivial task to visualize them from the bulk network. For the purpose of clarity, we apply Gaussian surface to depict the void structures in both Figures 6.13 and 6.15. Once again, the white (small) and big (green) spheres are hydrogen and silicon atoms respectively. Figure 6.13 is the same complex as in Figure 6.12 after applying the Gaussian surface. Figure 6.15 is presented in a similar fashion from Figure 6.13. The shapes of the voids are quite irregular. The diameter of the space (voids) varies in a
Table 6.6: Summary of the theoretical and experimental line widths

<table>
<thead>
<tr>
<th>Theory (at.% H)</th>
<th>$\sigma_g$ (kHz)</th>
<th>$\sigma_L$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>30.33</td>
<td>3.25 - 4.47</td>
</tr>
<tr>
<td>18</td>
<td>35.0</td>
<td>4.7 - 5.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiments (at.% H)</th>
<th>$\sigma_{broad}$ (kHz)</th>
<th>$\sigma_{narrow}$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reimer \textit{et al}</td>
<td>8.0 - 32.0</td>
<td>22.0 - 27.0</td>
</tr>
<tr>
<td>Gleason \textit{et al}</td>
<td>8.0 - 15.0</td>
<td>25.0 - 30.0</td>
</tr>
<tr>
<td>Wu \textit{et al} (GD sample)</td>
<td>8.0 - 10.0</td>
<td>34.0 - 39.0</td>
</tr>
<tr>
<td>Wu \textit{et al} (HW sample)</td>
<td>2.0 - 3.0</td>
<td>47.0 - 53.0</td>
</tr>
<tr>
<td>NRL</td>
<td>10 - 15</td>
<td>22.0</td>
</tr>
<tr>
<td>RCA</td>
<td>10 - 15</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Figure 6.12: A complex having at least seven hydrogen atoms in the inner surface of the void with a hydrogen molecule is shown in the figure at 16 at.% hydrogen concentration. The large (green) and small (white) spheres represent silicon and hydrogen atoms respectively.

range of 5 – 16 Å in both the models which are comparable with calorimetry experiments by Graebner \textit{et al} [98]. Similar observations were observed by Mahan \textit{et al} [53], Chabal \textit{et al} [95] and Boyce \textit{et al} [80].

Another important aspect of the voids is a decoration of its internal surface by hydrogen atoms. In sample A, at least 6 hydrogen atoms are visible in the inner surface of the void as shown in Figures 6.12 and 6.14. All the hydrogen atoms are located forming the mono hydride (SiH) configurations. Because of the difficulty while visualizing the inner surface, we have presented only a few silicon atoms. However, no silicon atoms in the surface has the dangling bonds. It is one of the most important results that describes a stable nature of the void. Similarly, there are at least nine hydrogen atoms in the surface of the void in sample B (see Figures 6.13 and 6.15). Likewise in sample A, all hydrogen atoms form mono hydrides (SiH). No other
Figure 6.13: The same complex of Figure 6.12 after applying the molecular surface is shown in the figure. The irregular inner shape of the void is visible in the figure. The large (green) and small (white) spheres represent silicon and hydrogen atoms respectively.

Figure 6.14: A complex having at least nine hydrogen atoms in the inner surface of the void with a hydrogen molecule is shown in the figure at 18 at.% hydrogen concentration. The large (green) and small (white) spheres represent silicon and hydrogen atoms respectively.

configurations such as SiH$_2$ and SiH$_3$ are observed in the surface of the voids.

Finally, we would like to complete our discussion by mentioning the existence of hydrogen molecules in the models. As we discussed earlier, the probability of having H$_2$ molecules in the micro-structure is very low. The earlier studies [80, 96] reported that the concentration of hydrogen molecules is approximately 1% of the total hydrogen. In sample A (16 at.% hydrogen
concentration), 1.4 % of the total hydrogen are found as hydrogen molecules. One of a such configurations is shown in Figure 6.13. The distance between two hydrogen in the H$_2$ molecules lie in a range of 0.7 – 0.98 Å. Similarly, approximately 0.9% of total hydrogen are in molecular hydrogen state in sample B. The H-H distance of the H$_2$ molecules have the same range as in sample A. We relax the network several times via the first-principles density function code (SIESTA) to remove the strain in hydrogen molecules. Therefore, these H$_2$ molecules are stable configurations and all the molecules reside within the voids only. These observations imply that the micro-structure consists of the voids and hydrogen molecules in the samples of hydrogenated amorphous silicon.

6.4 Conclusion

We study several models of hydrogenated amorphous silicon in a range of 10 – 20 Å, which were generated by the information-based inverse approach. The models have not only the correct structural and electronic properties but also they satisfy IR and NMR properties independently. Furthermore, the models, having concentration ≤ 15 at.% hydrogen, do not show any evidence of micro-voids and hydrogen molecules. However, the models at ≥ 15 at.% consist of micro-voids and H$_2$ molecules inside the micro-voids. The microstructure consists of very few H$_2$ molecules which is in a range of 0.9 – 1.4% of total hydrogen. These are very good theoretical results which are consistent with the NMR, IR and calorimetry experiments.
Chapter 7

SUMMARY

We would like to summarize the work in four parts. In the first part, we study the hydrogen micro-structure from the models which were generated via the ECMR method at 7 at.% (low concentration) and 22 at. % (high concentration) of hydrogen atoms. These models show that the micro-structure mostly consists of SiH and SiH$_2$ bonding configurations at both concentrations. However, it is highly dominated ($\geq 75\%$ of total hydrogen) by mono-hydrides (SiH). The hydrogen distributions in both model are highly inhomogeneous as it is reported by earlier several experimental works. The micro-structure consists of a small cluster of $4-7$ hydrogen atoms at the low and $10-20$ at the high concentrations. Furthermore, the micro-structure is enriched by open-chain like structures of mono and dihydride configurations at the high concentration. These observations are further confirmed by calculating NMR line widths of the models. The broad line widths lie in a range of $19-25$ kHz whereas the narrow line width belongs to $2.8-5.3$ kHz at the low concentration. Similarly, their values are $33.8-47.3$ kHz and $5.9-6.4$ kHz respectively at the high concentration. From this study, we recommend that the NMR line widths should be calculated by separating the clustered and diluted hydrogen atoms from the overall hydrogen distribution. While doing so, the highly inhomogeneous hydrogen distribution can be represented correctly.

In the second part, we mainly focused on the defects beyond the dangling and floating bonds, such as vacancies and voids of the hydrogenated amorphous silicon. The low hydrogen concentration model has mono and split divacancies whereas there are mono and stable divacancies at the high concentration model. However, no voids were observed even at the high hydrogen concentration. These observations are remarkable because the vacancies were evolved by themselves while relaxing the network via the first-principles density functional method.

From the ECMR models, we were able to address the various important aspects of the hydrogen micro-structure. However, we could not provide any results regarding SiH$_3$ and H$_2$ configurations as well as voids in the micro-structure. Therefore, we develop a new method of model generation that is able to address the shortcomings of the earlier models. The method not only provides correct structural properties including all possible hydride configurations but also address the defects such as vacancies and voids in the micro-structure. Moreover, approximate calculations of NMR line spectra are very close to the experiments. These remarks were made only after performing a detail study on several models of the hydrogenated amorphous silicon at 7-23 at.% concentration regimes. Despite having the correct structural and electronic properties of the micro-structure, the existence of H$_2$ molecules within the voids at the higher
concentrations is not recognized from the models. That motivates us to develop the model that can also show an evidence of H\textsubscript{2} molecules in the micro-structure.

Finally, we were able to construct the models at 15 – 20 at.% hydrogen concentrations, which gave the evidence of H\textsubscript{2} molecules within the voids. The structure of the voids are highly irregular in a three dimensional shape having 6 – 9 mono-hydrides (SiH) in their inner surface. The voids consists of 0.9-1.4% of total hydrogen as the hydrogen molecules. The models have correct structural, electronic, vibrational and nuclear magnetic resonance properties. These results are consistent with IR, NMR, MQ-NMR and calorimetry experiments as well as the first-principles or \textit{ab initio} calculations.
Appendix A

SIESTA INPUT AND OUTPUT FILES

An example of the input file is presented below.

```
# this is the input file for siesta
SystemName SiH
SystemLabel sih

NumberOfAtoms 2573
NumberOfSpecies 2

%block ChemicalSpeciesLabel
  1 14 Si
  2 1 H
%endblock ChemicalSpeciesLabel

PAO.BasisSize SZ
PAO.EnergyShift 300 meV

LatticeConstant 35.72 Ang
%block LatticeVectors
  1.000 0.000 0.000
  0.000 1.000 0.000
  0.000 0.000 1.000
%endblock LatticeVectors

MaxSCFIterations 50
DM.MixingWeight 0.3
DM.NumberPulay 3
DM.Tolerance 5.d-4
UseSaveData T
MeshCutoff 100.0 Ry

SolutionMethod diagon
ElectronicTemperature 25 meV
Harris_functional .true.

XC.functional LDA
XC.authors CA

MD.TypeOfRun CG
MD.NumCGsteps 2000
MD.LengthTimeStep 2.5 fs
MD.MaxForceTol 0.01 eV/Ang

WarningMinimumAtomicDistance 1.0 Ang
AtomicCoordinatesFormat NotScaledCartesianAng
%block AtomicCoordinatesAndAtomicSpecies
  14.18000 4.06000 3.03000 1 # si 1
  8.03000 10.61000 11.45000 1 # si 2
  15.92000 4.43000 8.39000 1 # si 3
  13.30000 6.81000 15.72000 1 # si 4
  11.28000 2.01000 10.26000 1 # si 5
```
An example of output file is presented below.

#FDF: Opened INPUT_TMP.1532554149 for input. Unit: 12

fdf-debug 0  # Default value
SystemName SiH
SystemLabel sih
WriteXML T  # Default value
alloc_report_level 0  # Default value
xc.functional LDA
xc.authors CA

%endblock AtomicCoordinatesAndAtomicSpecies
user-basis F # Default value
user-basis-netcdf F # Default value
PAO.BasisSize SZ
PAO.BasisType split # Default value
Number_of_species 2

%block ChemicalSpeciesLabel
  1 14 Si
  2 1 H
%endblock ChemicalSpeciesLabel

PAO.EnergyShift 0.2204939653E-01 Ry
# Above item originally: PAO.EnergyShift 300.0000000 meV
PAO.SplitNorm 0.1500000000 # Default value
PAO.SplitNorm 0.1500000000 # Default value
PAO.EnergyShift 0.2204939653E-01 Ry
# Above item originally: PAO.EnergyShift 300.0000000 meV
PAO.SplitNorm 0.1500000000 # Default value
PAO.SplitNorm 0.1500000000 # Default value
PAO.BasisType split # Default value
Atom-Setup-Only F # Default value
MD.UseStructFile F # Default value
LatticeConstant 67.50104407 Bohr
# Above item originally: LatticeConstant 35.72000000 Ang

%block LatticeVectors
  1.000 0.000 0.000
  0.000 1.000 0.000
  0.000 0.000 1.000
%endblock LatticeVectors

%block LatticeVectors
  1.000 0.000 0.000
  0.000 1.000 0.000
  0.000 0.000 1.000
%endblock LatticeVectors

AtomicCoordinatesFormat NotScaledCartesianAng
NumberOfAtoms 2573
ZM.UnitsLength Bohr # Default value
ZM.UnitsAngle rad # Default value
ZM.ForceTolLength 0.1555740000E-02 Ry/Bohr # Default value
ZM.ForceTolAngle 0.3565490000E-02 Ry/rad # Default value
ZM.MaxDisplLength 0.2000000000 Bohr # Default value
ZM.MaxDisplAngle 0.3000000000E-02 rad # Default value
ZM.CalcAllForces F # Default value

%block AtomicCoordinatesAndAtomicSpecies
  14.18000  4.06000  3.03000  1 # si  1
  8.03000  10.61000 11.45000  1 # si  2
 15.92000  4.43000  8.39000  1 # si  3
 13.30000  6.81000 15.72000  1 # si  4
 11.28000  2.01000 10.26000  1 # si  5
 15.81000 15.23000 14.44000  1 # si  6
 16.48000 15.00000 11.13000  1 # si  7
  7.31000 15.83000  3.21000  1 # si  8
 15.50000 14.25000  3.77000  1 # si  9
 13.76000  8.37000 12.25000  1 # si 10
  8.43000 14.34000 12.25000  1 # si 11
  7.75000  7.41000  6.12000  1 # si 12
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6.14366 17.36130 28.59330 2 # H 2573

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NonCollinearSpin F # Default value
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LongOutput F # Default value
NumberOfSpecies 2
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Write Mulliken Pop 0 # Default value
MeshCutoff 100.0000000 Ry
# Above item originally: MeshCutoff 100.0000000 Ry
NetCharge 0.000000000 # Default value
MaxSCFIterations 50
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DM.NumberBroyden 0 # Default value
DM.MixSCF1 F # Default value
DM.PulayOnFile F # Default value
DM.MixingWeight 0.300000000
DM.OccupancyTolerance 0.1000000000E-11 # Default value
BIBLIOGRAPHY


