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Tritium Dynamics
in the
Amorphous Silicon Semiconductor

by

Lakhbeer Singh Sidhu

A thesis submitted in conformity with the requirements for the
degree of Doctor of Philosophy
Graduate Department of Electrical and Computer Engineering
University of Toronto

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Tritium Dynamics in the Amorphous Silicon Semiconductor.

Doctor of Philosophy, 1997

Lakhbeer Singh Sidhu

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ABSTRACT

For the first time, Tritium has been bonded into a semiconductor. The decay of tritium in the amorphous silicon network is a unique source of disorder.

Infrared spectroscopy of this semiconductor identifies the various bonding sites of tritium in the amorphous silicon matrix. Tritium behaves as a heavy hydrogen atom. Raman and optical absorption analysis indicate that tritium decay does not lead to enhanced structural disorder of the amorphous network.

Inelastic collisions of $\beta$ particles, produced as a result of the tritium decay, with the amorphous silicon network results in the generation of electron-hole pairs. Radiative recombination of these carriers is observed.
The bonded tritium that undergoes nuclear decay, creates a dangling bond defect at its bonding site. This defect behaves as a non-radiative recombination center. Tritium decay is used to probe the effect of dangling bond concentration on luminescence, thus, providing further understanding of disorder in amorphous silicon.
Acknowledgements

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I would like to express my deepest gratitude to my friend, Alexander Tkachenko. I thank him for his interest in my work, and the many scientific and non-scientific discussions in the Second Cup.

Finally, I would like to thank my parents, and my brother, Sukhjit, and sisters, Suki (happiness) and Deepa, for their love and support, without either this work would not have been possible.

This work is dedicated to my mother Saranjit Kaur Grewal-Sidhu, who taught me so much.
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Chapter 1

Basic Concepts of Amorphous Silicon

*O my mind, thou art the essence of light.*  
Guru Amar Das

1.1 Introduction

Hydrogenated amorphous silicon is both fundamentally and technologically an important material. Fundamentally, it represents one of the simplest examples of an amorphous solid, and therefore, forms the basis for the study of more complex systems. Technologically, it is cheap to deposit, and has many diverse applications, such as: solar cell power generation, and flat panel displays.

While much has been done, there are still many aspects of this
semiconductor which are not fully understood. In particular, there are questions regarding the hydrogen bonding configurations. This is important because modelling the electronic structure of hydrogenated amorphous silicon requires knowledge of the hydrogen bonding. Furthermore, hydrogen bonding provides information on the growth processes.

Devices made from hydrogenated amorphous silicon degrade with time due to material degradation. The material properties such as dark conductivity, photoconductivity, and luminescence degrade - resulting in dramatic changes in device performance. In many cases, both the process of defect generation, and the identity of the defect are not well understood. Furthermore, measurement of the defect concentration is subject to considerable error. Defects in hydrogenated amorphous silicon arise in a wide variety of ways: doping with the common dopants phosphorous for donors or boron for acceptors [1,2], quenching from elevated temperatures (=220 °C) [3], exposure to strong light [4], the passage of forward currents in device structures [5], formation of a space-charge region [6], and widely varying deposition conditions [7]. All the defects originating from the above mentioned ways show the presence of paramagnetic centers, and therefore,
have been assigned to dangling bond defects. However, it is unclear whether the paramagnetic center alone is responsible for the degradation of the material properties, or, if additional disorder exists. In order to understand and prevent material degradation leading to device failure, a better understanding of the dangling bond is needed.

In this thesis, the unstable hydrogen isotope, tritium, has been bonded into a semiconductor for the first time. Tritium is used to study hydrogen bonding, and dangling bond defect creation in amorphous silicon. The decay of bonded tritium produces an identifiable defect center - a dangling bond, the concentration of which can be accurately determined. Thus, degradation of material properties as a function of defect concentration can be investigated.

In this chapter the amorphous silicon semiconductor is introduced in section 1.2. In section 1.3 the role of hydrogen in amorphous silicon is discussed. The final section, briefly, discusses the role of tritium as a means of probing the properties of amorphous silicon and the technological applications of its decay in the amorphous silicon network.
1.2 Amorphous Silicon

The main distinction between an amorphous material and its crystalline counterpart is the disorder of the atomic structure. Crystalline semiconductors are defined by the periodic arrangement of atoms. This periodicity leads to Bloch's theorem [8] which underlies band theory. Electron and hole wavefunctions are extended in space and characterized by dispersion relationships $E(k)$, $k$ denoting the crystal momentum wave vector and $E$ the energy of the particle. The theory of lattice vibration has a similar basis in the lattice symmetry.

A different theoretical approach is used to model amorphous semiconductors. This approach is based on the chemical bonding between the atoms, with emphasis on the short range bonding interactions.

Amorphous semiconductors are not completely without order. In amorphous silicon the local structure is essentially tetrahedral in nature, and much the same as in crystalline silicon, with four nearest neighbour and twelve next nearest neighbour atoms [9,10]. The disorder in the amorphous network is described by the atomic pair distribution function, which
provides a measure of the expected number of atoms lying between radii \( r, r + \Delta r \) given there is an atom at the origin [11]. In Figure 1.1 the pair distribution function for crystalline silicon and amorphous silicon are shown. The crystalline pair distribution consists of a number of delta functions, while in the amorphous case the peaks are much broader. This indicates that the structure of amorphous silicon is highly ordered in the short-range, but, completely disordered in the long range. The short range order indicates that the average bond lengths and bond angles are similar to those occurring in crystalline silicon which has a bond length of 2.35Å, and a bond angle of 109°28 [9]. The broadness of the amorphous peaks are due to slight fluctuations in the bond angles and bond lengths. As the pair separation is increased, these short range fluctuations compound, resulting in the observed long-range disorder. Coordination defects contribute to the long range disorder. For example, although amorphous silicon, like crystalline silicon, displays four fold coordination, most preparation techniques give material containing relatively large numbers of voids [13]

The electronic structure of a solid arises from its constituent bonds. For both crystalline and amorphous silicon, the constituent silicon atoms
Figure 1.1. The atomic pair distribution functions of c-Si and a-Si. The atomic pair distribution function of a typical gas is also shown for the purpose of comparison [12.]
bond in the \( \text{sp}^3 \) configuration. Four equivalent \( \text{sp}^3 \) orbitals arise from the two \( s \) and two \( p \) orbitals of the ground state of an individual atom. Two interacting \( \text{sp}^3 \) orbitals on neighbouring atoms form a bonding and an antibonding orbital, introducing an energy gap. In a solid, interacting bonding and antibonding levels form the valence and conduction bands, respectively. Thus, the concepts of energy bands and gaps are applicable in any solid, crystalline or amorphous. Figure 1.2 illustrates the formation of energy bands.

Bonding is a local phenomena, the bond strength being most influenced by the nearest neighbour interactions. As a result, it is expected that short-range order will play the dominant role in influencing the electronic properties of the solids. As the short-range order of most amorphous semiconductors is similar to that of their crystalline counterparts, it would be expected that the gross features of their electronic structures is similar [14,15]. In particular, it would be expected that the electronic properties of an amorphous semiconductor are governed by interactions within and between essentially empty conduction band states and full valence band states.
Figure 1.2. Formation of energy bands in c-Si and a-Si [14]
The principal features of the structure of amorphous semiconductors are the short range order of the ideal network, the long-range disorder, and the coordination defects. While, the distribution of states in a defect free crystalline semiconductor terminates abruptly at the band edge, in an amorphous semiconductor, a tail of states extends into the energy gap. The tail states originate from the deviations of the bond length and angle arising from the long range structural disorder. Analysis shows that many of the tail states are localized by the site disorder, which leads to quantum confinement [16]. The band tails are most important, despite their relatively small concentration (10^{19}-10^{20} \text{ cm}^3 \text{ in amorphous silicon [17]}), because electronic transport occurs at the band edge. Tail states trap conducting charge carriers, thus reducing the effective mobility by several orders of magnitude. The probability of optical transitions between filled and empty tail states is limited to a large extent by quantum confinement. Transitions are allowed if there is spatial overlap of the localized wavefunctions.

Electronic states deep within the band gap arise from departures from the ideal network, such as coordination defects - dangling bonds. These gap states determine many electronic properties by controlling trapping and
recombination. The electronic structure of an amorphous semiconductor is shown in Figure 1.3. The boundaries (mobility edges) between the localized (band tails) and extended states (band states) are indicated.

1.3 Hydrogenated Amorphous Silicon

The recognition of the importance of hydrogen in amorphous silicon dates back to the 1970s when it was demonstrated that the addition of hydrogen during the deposition of amorphous silicon by sputtering led to a marked improvement in the material's properties [18,19]. By then it had been shown that amorphous silicon prepared by the glow-discharge decomposition of silane had a low density of gap states and as a consequence could be doped n- or p-type by adding phosphine or diborane to the plasma. Infrared spectroscopy [20] and hydrogen evolution [21] experiments demonstrated that material prepared in this way could contain up to 50% hydrogen. It was concluded that hydrogen plays the all important role of passivating dangling bonds, thereby removing states in the gap and
Figure 1.3. A typical distribution of states for an amorphous semiconductor. The mobility edges are represented by the dotted lines. There exist two mobility edges, one associated with the conduction band, the other associated with the valence band. Below these mobility edges, the states are localized; above the edges, the states are extended.
permitting the Fermi level to be shifted from near the mid-gap position to the conduction or valence band edges.

Hydrogen has additional effects on the electronic structure of amorphous silicon. If saturation of dangling bonds (of concentration $= 10^{20}$ cm$^3$) were the only contribution of hydrogen, addition of a fraction of a percent would suffice. Yet the improvement in properties, for example the increase in photoconductivity, continues up to a hydrogen content of about 15%. In fact, hydrogen also modifies the underlying amorphous network by inserting itself into weak bonds, thereby removing band tail states, widening the gap and sharpening the optical absorption edge [22].

Today hydrogenated amorphous silicon is a technologically important material, noted for its excellent properties and wide range of photoelectronic applications; see Tables 1.1 and 1.2. The potential for large area photoelectronic applications has made hydrogenated amorphous silicon one of the leading materials in the field.
Table 1.1: Commercially available products using a-Si:H.

<table>
<thead>
<tr>
<th>Device</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photovoltaic cell</td>
<td>Calculators, watches, battery chargers etc.</td>
</tr>
<tr>
<td>Photoreceptor</td>
<td>Electrophotography, LED printers, etc.</td>
</tr>
<tr>
<td>Photoconductors, image sensors</td>
<td>Color sensors, light sensors, etc.</td>
</tr>
<tr>
<td>Heat control layer</td>
<td>Heat reflecting float glass, etc.</td>
</tr>
<tr>
<td>Thin-film FETs</td>
<td>Displays, televisions, logic circuits, etc.</td>
</tr>
<tr>
<td>High-voltage thin-film transistors</td>
<td>Printers etc.</td>
</tr>
</tbody>
</table>

From LeComber [23]

Table 1.2: Other proposed applications for hydrogenated amorphous silicon

<table>
<thead>
<tr>
<th>Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>Image pick-up tubes</td>
</tr>
<tr>
<td>Optical recording</td>
</tr>
<tr>
<td>LEDs</td>
</tr>
<tr>
<td>FETs for ambient sensors</td>
</tr>
<tr>
<td>Passivation layers</td>
</tr>
<tr>
<td>Fast detectors and modulators</td>
</tr>
<tr>
<td>Charge-coupled devices</td>
</tr>
<tr>
<td>Diodes</td>
</tr>
<tr>
<td>Memories</td>
</tr>
<tr>
<td>DiFETs</td>
</tr>
<tr>
<td>Strain gauges</td>
</tr>
<tr>
<td>Bipolar transistors</td>
</tr>
<tr>
<td>Photolithographic masks</td>
</tr>
<tr>
<td>Optical waveguides</td>
</tr>
<tr>
<td>X-ray detectors</td>
</tr>
<tr>
<td>Optically modulated neural networks</td>
</tr>
<tr>
<td>Charged particle detectors</td>
</tr>
</tbody>
</table>

From LeComber [23]
1.4 Tritiated Amorphous Silicon

Tritium is a hydrogen isotope, and as such should readily substitute hydrogen in amorphous silicon. It is expected that bonded tritium will introduce new infrared vibrations, thus, providing further insight into growth processes and hydrogen bonding.

The instability of tritium poses interesting possibilities. Tritium is a pure beta (β) emitter. It undergoes radioactive decay according to the reaction

\[ T \rightarrow ^3He^- + \beta^- + \bar{\nu} \; , \tag{1.1} \]

where \( \bar{\nu} \) is the antineutrino. The probability of tritium decay is \( 1.78 \times 10^{-9} \text{ s}^{-1} \) or equivalently it has a half-life of 12.3 y. The β particle has a maximum energy of 18.6 keV and a mean energy of 5.69 keV [24]. The antineutrino is virtually unreactive and travels unimpeded through all matter.

Tritium decay has the potential of introducing new phenomena in amorphous silicon, and can provide further understanding on the role of disorder (defects). It is expected that the β particle will interact with the
amorphous network to generate electron-hole pairs. Furthermore, tritium decay is a unique form of disorder and its affect on the structural and electronic properties of this material will be investigated. In this thesis tritium decay is used to probe the properties of amorphous silicon by creating dangling bond defects, the concentration of which, can be accurately determined. On the technological side, the radioactivity may be converted to useful electrical and optical power. For example, the excess electron-hole pairs created by β particle interaction with the amorphous silicon matrix can be separated by the electric field of a pn-junction, thus, producing a current. This is the equivalent of a solar cell but with no external excitation. Another possible application is luminescent material resulting from the radiative recombination of β generated electron-hole pairs. Clearly, tritiated amorphous silicon is an example of a happy marriage between interests in fundamental and applied research.

This thesis is organized in the following manner. In chapter two, deuterium incorporation into amorphous silicon is studied for the purpose of determining deposition parameters favouring tritium incorporation. In chapter three infrared spectroscopy is used to identify tritium bonding
environments and the concentration of bonded tritium. Raman spectroscopy and optical absorption studies were used to characterize tritiated amorphous silicon. Defect generation and radiative recombination in tritiated amorphous silicon is studied in chapter four. Finally, the conclusions are drawn in chapter five.
Chapter 2

Preparation of Tritiated Amorphous Silicon

*Four things do not come back: the spoken word; the sped arrow; time past; the neglected opportunity.*

Al Halif Omar Ibn

2.1 Introduction

This chapter concerns tritium incorporation into the amorphous silicon matrix. Using a glow-discharge of a silane and tritium gas mixture, tritiated amorphous silicon films were prepared. Film growth parameters favoring tritium incorporation were determined by studying another
hydrogen isotope, deuterium, and its incorporation into amorphous silicon.

In the next section the dc saddle-field glow-discharge deposition technique is briefly described. Section 2.3 presents the results of an isotopic study of the dc saddle-field glow-discharge growth of deuterated hydrogenated amorphous silicon. Deuterium is used to correlate the species present in both plasma and films. This is done by performing mass spectrometry on the plasma, followed by secondary ion mass spectrometry (SIMS) on the deposited films. The final section of this chapter gives details concerning tritiated film deposition parameters.

2.2 The Saddle-Field Glow-Discharge Deposition Technique

High quality hydrogenated amorphous silicon may be prepared by the dc saddle-field glow-discharge decomposition of silane [25-27]. This deposition technique involves the generation of radicals through the
dissociation of silane, followed by radical diffusion and reaction processes with the growth surface.

A saddle-field may be established using a symmetric arrangement of three electrodes; a central mesh anode, maintained at a positive dc bias, positioned between two grounded mesh cathodes. In Figure 2.1, a schematic of the dc saddle-field glow-discharge deposition system is shown. The saddle-field electrode configuration is symmetric with respect to the central anode. Only one of the two outer electrodes is used as a substrate holder while the other is used to perform plasma analysis using a mass spectrometer. The chamber was manufactured of stainless steel, its volume being approximately 13 L. The electrodes were stainless steel mesh, circular, and approximately 20 cm in diameter.

The mesh anode is semi-transparent to the passage of electrons. At low pressures a significant number of electrons are accelerated through the apertures in the anode, and on reaching the cathode are deflected back towards the anode, where once again they experience the attraction of the anode. Thus, electrons can follow an oscillatory trajectory along the axis of the chamber between electrodes [28,29]. In such a configuration the
Figure 2.1. A schematic of the dc saddle-field glow discharge deposition system.
electron path length can be considerably longer than the electrode spacing. Positively ionized radicals created in the discharge are accelerated towards the two mesh cathodes. In the plasma the oscillating electrons collide with the source gas, transferring energy to the gas and causing excitation, impact ionization and fragmentation of the gas molecules. Below are listed the major electron-impact dissociative processes creating neutral primary radicals in a glow discharge [30]

\[
e^{-} + SiH_4 \rightarrow SiH + H_2 + H + e^- \quad \Delta H=5.7eV \quad (2.1(a))
\]

\[
e^{-} + SiH_4 \rightarrow Si + 2H_2 + e^- \quad \Delta H=4.2eV \quad (2.1(b))
\]

\[
e^{-} + SiH_4 \rightarrow SiH_3 + H + e^- \quad \Delta H=4.0eV \quad (2.1(c))
\]

\[
e^{-} + SiH_4 \rightarrow SiH_2 + H_2 + e^- \quad \Delta H=2.2eV \quad (2.1(d))
\]

The high transparency of the cathodes means that a significant number of ionized radicals will be transmitted through the mesh and to the substrate where film growth occurs. The primary ions impinging on
to the substrate are created by the following dissociative ionization processes [31]:

\[ e^- + SiH_4 \rightarrow SiH^+ + H_2 + H + 2e^- \quad \Delta E_a = 16.1\,eV \quad (2.2(a)) \]

\[ e^- + SiH_4 \rightarrow SiH_3^- + H + 2e^- \quad \Delta E_a = 12.3\,eV \quad (2.2(b)) \]

\[ e^- + SiH_4 \rightarrow SiH_2^- + H_2 + 2e^- \quad \Delta E_a = 11.9\,eV \quad (2.2(c)) \]

\[ e^- + SiH_4 \rightarrow Si^- + 2H_2 + 2e^- \quad \Delta E_a = 11.7\,eV \quad (2.2(d)) \]

Where, \( E_a \) represents the minimum energy at which the process occurs with no excess energy imparted to the products.
2.3 Deuterium Incorporation into Amorphous Silicon

This section concerns deuterium incorporation into amorphous silicon, when introduced into the deposition chamber in the form of molecular deuterium. The deuterium in the film can originate from the $D_2$ gas directly, or, from a deuterated silane radical originating from an isotope exchange process, i.e., from $\text{SiH}_x\text{D}_y$ ($x+y=4$). It is very likely that in the plasma, exchange reactions occur in which some hydrogen atoms in silane are replaced by deuterium atoms. These exchange reactions are investigated. Furthermore, the contribution of isotope exchange processes to deuterium incorporation into amorphous silicon is estimated.

To produce the plasma a mixture of silane and molecular deuterium was allowed to flow through the growth chamber at a constant rate. These gases were dissociated in a dc glow-discharge, excited using the saddle-field electrode configuration. A VG 300 plasma sampling quadropole mass spectrometer, operated in the ionizer on and ionizer off modes was used to monitor the plasma. Films were grown on crystalline silicon wafers.
(Czochralski grown, (100) orientation, with both sides polished), mounted on a heated and electrically grounded substrate holder, exposed to the plasma at steady state.

SIMS analysis of the films was performed using a Cameca IMS 3f at the university of Western Ontario. Films were bombarded by a primary beam of Cs ions, resulting in material being sputtered from the surface. In multi atom materials, the sputtered atoms are not proportional to their atomic concentrations at the film surface, as sputtering is dependent on the mass of the atom and its binding energy in the solid. Mass analysis of the secondary ions, created from Cs ion bombardment of the film surface, is then compared with calibrated mass spectra data from reference samples having a known implanted dose; thus the concentration in the sample is estimated. Table 2.1 summarizes the preparation conditions of the deuterated films. To help resolve the influence of deuterium on both plasma and film, additional films were grown under identical conditions, but with hydrogen replacing the deuterium in the gas mixture.
Table 2.1: Summary of the preparation conditions. The deposition temperature was near 200 °C, and the current density used was 300 μAcm⁻². Films deposited under identical conditions as those listed in the table but with hydrogen substituting the deuterium are referred to as h₁, h₂, ... h₆, in the text.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiH₄ Flow Rate (sccm)</th>
<th>D₂ Flow Rate (sccm)</th>
<th>Pressure (mTorr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₄</td>
<td>2</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>d₃</td>
<td>5</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>d₂</td>
<td>6</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>d₁</td>
<td>8</td>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>d₅</td>
<td>20</td>
<td>6</td>
<td>75</td>
</tr>
<tr>
<td>d₆</td>
<td>21</td>
<td>8</td>
<td>150</td>
</tr>
</tbody>
</table>

In Figure 2.2(a,b) part of the mass spectra of d₄, and its corresponding hydrogenated counterpart h₄, is shown. These results are representative of all the plasmas. The mass spectra (obtained with the ionizer in the on mode) of the deuterated plasma exhibited a large peak.
Figure 2.2(a). Part of the mass spectra of d4 and its hydrogenated counterpart h4. The mass 2 signal is about two orders of magnitude larger than the mass 30 signal of Figure 2.2(b).
Figure 2.2(b). Part of the mass spectra of d4 and its hydrogenated counterpart h4.
at 3 a.m.u. which is attributed to the HD molecule. The intensity of this HD signal is similar to that of the D₂ signal, suggesting a strong mixing between hydrogen and deuterium in the plasma. In the range 28-31 a.m.u. the deuterated and hydrogenated plasmas exhibit little difference, the intensity of these peaks resembling the silane cracking pattern [32]. However at 32 a.m.u. the deuterated plasma exhibits a substantially enhanced peak (the 32 a.m.u. peak in the hydrogenated discharge is from the $^{29}\text{SiH}_3^+$). This enhancement is clearly deuterium related and can be assigned to $^{28}\text{SiH}_2\text{D}^+$ whose parent molecule is $\text{SiH}_3\text{D}$. The apparent absence of peaks 33 a.m.u. and higher shows that relatively little $\text{SiH}_2\text{D}_2$, $\text{SiHD}_3$, and $\text{SiD}_4$ are present in the discharge.

The formation of $\text{SiH}_3\text{D}$ in the deuterated plasma may be attributed to the highly favourable recombination reaction [32]

$$D + \text{SiH}_3 \rightarrow \text{SiH}_3\text{D} \quad \Delta H = -4.14 \, \text{eV} \quad (2.3)$$

The deuter-silane, $\text{SiH}_3\text{D}$, will be continuously created and dissociated in the glow discharge. Radicals produced from its fragmentation are likely to contribute to deuterium incorporation into the growing film.
The ionized species in the plasma were also studied. Figure 2.3 plots the mass spectrum of positively charged radicals in the h4 discharge, the energy band pass filter of the plasma probe was set to the average energy of the impinging ions (180 eV) with a window of about ±10 eV. The mass 28 and 29 signals are the dominant ion signals in the plasma and are attributed to the Si\(^+\) and SiH\(^+\) ions (Equation 2.2(d) predicts that Si\(^+\) formation is energetically the most favourable ionization process). Therefore, it can be concluded that the substrate current is largely due to Si\(^+\) and SiH\(^+\) ions. The substrate current for typical deposition rates of 1 Å/s is 4 mA, indicating that ions can account for only about 10\% of the deposition rate. The ion spectrum for the deposition conditions of d4 displayed a very similar spectrum to that of h4, indicating that there is negligible contribution of deuterium related ions.

Plotting the deuterium to hydrogen ratio in the deposited films (as determined by SIMS) against the deuterium to hydrogen ratio of the species H\(_2\), HD, and D\(_2\), observed in the plasma using mass spectrometry, (see Figure 2.4) provides further insight on deuterium incorporation into amorphous silicon. A good correlation exists between
Figure 2.3. Part of the ion spectrum of plasma h4. The mass 28 signal is about an order of magnitude smaller than the mass 30 signal of Figure 2.2(b).
the plasma and the films, suggesting that it is the deuterium originating from molecular form \( (D_2 \text{ or HD}) \) that is incorporated into the film most probably via surface reactions. It is to be noted that the relative amount of deuterium originating from the \( \text{SiH}_3D \) as shown in the mass spectra of Figure 2.2(b) is insufficient to account for the deuterium incorporated into films. The radical \( \text{SiH}_2D \) will compete with the equivalent radical \( \text{SiH}_3 \) (31 a.m.u.) and the primary neutral radicals \( \text{SiH}_2, \text{SiH}, \text{and Si} \) for incorporation into the amorphous film. Considering competition only with \( \text{SiH}_3 \), for every deuterium there are a total of five hydrogen atoms that can be incorporated into the film. Furthermore, from Figure 2.2(b) the intensity of the \( \text{SiH}_2D \) signal is much weaker than that of the \( \text{SiH}_3 \) signal. Therefore, deuterium incorporation via an exchange process is expected to be marginal. However, the ratio of molecular deuterium to molecular hydrogen in the plasma, is in agreement with the ratio of deuterium to hydrogen in the films, as shown in Figure 2.4. Consequently, it can be concluded that it is mainly the molecular deuterium \( (D_2 \text{ and HD}) \) in the plasma that is directly incorporated into the film via surface reactions with the growth surface. The surface

\text{31}
Figure 2.4. Deuterium to hydrogen ratio in plasma versus deuterium to hydrogen ratio in films
reaction between molecular deuterium and the amorphous silicon network can be described as an insertion reaction. A deuterium molecule interrupts a strained silicon-silicon bond, breaking it and inserting two deuterium atoms (or one deuterium atom and one hydrogen atom in the case of a HD molecule) to form SiDDS\textsubscript{i} (or SiHDS\textsubscript{i}) [33]. Another, parallel process for deuterium incorporation into amorphous silicon is by a process of substitution. The deuterium originating from the HD or D\textsubscript{2} molecule substitutes a hydrogen atom that terminates a silicon dangling bond at the film surface. The resulting, free hydrogen atom, forms a molecule with the hydrogen or other deuterium that was previously bonded to the incorporated deuterium.

Table 2.2 lists the SIMS deuterium and hydrogen concentration of the deuterated films. Film d\textsubscript{4}'s deuterium concentration exceeds its hydrogen concentration, suggesting that at low flow rates deuterium is more readily incorporated into the film than is hydrogen. Furthermore, both d\textsubscript{3} and d\textsubscript{4} were grown under identical deposition conditions except d\textsubscript{4} had about half the total flow rate of d\textsubscript{3}, and showed a larger SIMS deuterium to hydrogen fraction than that of d\textsubscript{3}. By reducing the flow
rate, the flushing of gas from the chamber is reduced, as a consequence, the plasma residency time in the chamber increases, leading to longer interaction times between the plasma and the film growth surface. This is expected to increase the probability of hydrogen and deuterium insertion, and substitution reactions. It is possible that deuterium may be more readily incorporated into the film than hydrogen due to its greater mass and so reduced diffusivity on the growth surface resulting in a longer interaction time between deuterium and the film surface.

Table 2.2: SIMS deuterium and hydrogen content of deuterated films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deuterium (atomic % ±20%)</th>
<th>Hydrogen (atomic % ±20%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d4</td>
<td>7</td>
<td>4.5</td>
</tr>
<tr>
<td>d3</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>d2</td>
<td>3.4</td>
<td>8</td>
</tr>
<tr>
<td>d1</td>
<td>3.3</td>
<td>9</td>
</tr>
<tr>
<td>d5</td>
<td>.8</td>
<td>8.4</td>
</tr>
<tr>
<td>d6</td>
<td>1.8</td>
<td>12</td>
</tr>
</tbody>
</table>

Figure 2.5 exhibits the deuterium and hydrogen profiles of sample...
Figure 2.5. Deuterium and hydrogen profiles of sample d3 as obtained by SIMS. The deuterium and hydrogen concentrations begin to fall off at 1.2 micro m, at the film-substrate interface.
D3 as obtained by SIMS. These flat profiles are representative of all deuterated films. Furthermore, the total deuterium and hydrogen SIMS concentration for all the films remained fairly constant at $12 \pm 1.5$ atomic %. The similarity in the profiles and the constant total (hydrogen + deuterium) concentration indicates that deuterium substitutes hydrogen in the amorphous silicon network. The total (hydrogen + deuterium) concentration in the films is primarily controlled by substrate temperature and discharge power.

Positively biasing the substrate holder is a major deposition parameter [34]. Electrically floating the substrate holder during film deposition also leads to a positive biasing of the substrate. Floating the substrate holder establishes a positive voltage of $\approx 100$ V for the deposition parameters of Table 2.1 (samples d1-d4). At these voltages, the silicon ions impinging on the substrate experience a retarding potential and are decelerated. In order to determine how the energy of the ions is influenced by the application of substrate bias, two plasma measurements were made for the deposition conditions of sample d4. Firstly, the mass spectrometer was grounded and the energy distribution
of the Si\(^+\) ion was sampled. Then the mass spectrometer was electrically floated and the energy distribution of the Si\(^+\) ion again sampled. In Figure 2.6 the normalized, and smoothed ion energy distribution for the two measurements are displayed. Clearly, on application of a positive bias, the Si\(^+\) ion energies are reduced by approximately 100 eV. We have recently performed a study on the effects of ion bombardment on amorphous silicon during deposition [35]. Our results indicate that films deposited on floating substrates display distinctly different properties from films deposited on grounded substrates. In the dc saddle-field glow discharge, ions account for only 10% of the film deposition rate, yet, play an important role in film growth. Energetic ions can disrupt and break surface bonds, to cause surface sputtering, and can penetrate and bond underneath the top surface layers. Broken silicon-silicon bonds at the surface will also react with silane radicals to incorporate further silicon. As a consequence, the film growth processes are modified resulting in films having different properties from films deposited under relatively low ion energy (\(\leq 100\) eV) bombardment. Our results show that films deposited on floating substrates display an increased order in the amorphous
Figure 2.6. Normalized silicon ion (28 a.m.u.) energy spectra at two substrate biases.
network, a larger optical gap, and an increased hydrogen content (≈25% more hydrogen) relative to their grounded counterparts. The enhanced hydrogen content is particularly important for tritium incorporation into amorphous silicon.

2.4 Tritiated Amorphous Silicon Films

Having determined the deposition parameters favouring deuterium incorporation into amorphous silicon, similar deposition parameters were chosen for tritium incorporation. In addition, films were deposited onto electrically floating substrates which leads to enhanced hydrogen incorporation relative to films deposited on electrically grounded substrates [35]. Depositions were performed at Ontario Hydro Technologies. A dc saddle-field glow-discharge similar to the one described in section 2.2 was used. The deposition conditions of tritiated films and deuterated and hydrogenated films are listed in Table 2.4. For purposes of comparison the deuterated and hydrogenated films were
grown under very similar conditions to those of the tritiated films.

Table 2.4: Deposition Parameters of tritiated, deuterated, and hydrogenated films. Substrate temperature was 150°C. Chamber pressure was 50 mTorr. Silane flow rate was 2.5 sccm. Isotope gas flow rate was 2.5 sccm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isotope gas</th>
<th>Substrate current (mA)</th>
<th>Substrate voltage (V)</th>
<th>Anode current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UT</td>
<td>T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>A214, A215</td>
<td>T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>≈300</td>
<td>≈27</td>
</tr>
<tr>
<td>D2</td>
<td>D&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5</td>
<td>0</td>
<td>28</td>
</tr>
<tr>
<td>D1</td>
<td>D&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>110</td>
<td>30</td>
</tr>
<tr>
<td>H2</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>H1</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>125</td>
<td>30</td>
</tr>
</tbody>
</table>
2.5 Summary

Deuterium was used to probe hydrogen isotope incorporation into amorphous silicon. Mass spectrometry and SIMS analysis suggests that deuterium incorporation into the growing film occurred primarily by direct reaction between molecular deuterium and the growth surface. It is expected that tritium will behave similarly.
Chapter 3

Vibrations in the Amorphous Silicon Matrix

I believe in work, hard work and long hours of work. Men do not break down from overwork, but worry and dissipation.

Charles Evans Hughes

3.1 Introduction

This chapter concerns the local bonding of tritium in the amorphous silicon matrix. Tritium being a hydrogen isotope should readily substitute for hydrogen in amorphous silicon. As silicon-hydrogen bonds have dipole moments which can be modulated by infrared (IR) radiation, so too must silicon-tritium bonds. Therefore, IR spectroscopy is an ideal tool to study tritium bonding in amorphous silicon.
In the next section IR vibrations and hydrogen bonding in hydrogenated amorphous silicon will be briefly reviewed. Following this an induction mechanism is used to model how changes in the electronegativity of the neighbourhood of the Si-H group affect the IR vibrational frequency of the Si-H stretching bond. From this result the medium range environment of hydrogen bonds can be estimated. In section 3.3, the IR spectra of hydrogenated amorphous silicon (a-Si:H), deuterated amorphous silicon (a-Si:H,D), and tritiated amorphous silicon (a-Si:H,T) films are compared and using the induction model, the tritium bonding environment is identified. Section 3.4 discusses IR absorption intensities and the bonded tritium content. The final section of this chapter concerns silicon-silicon bond strain derived from Raman spectroscopic analysis of films and optical absorption studies.

3.2 Hydrogen Bonding in Amorphous Silicon

Hydrogenated amorphous silicon does not represent a single semiconductor but a family of semiconductors. The hydrogen content of
device quality films can vary between 4-35 atomic % [22,36,37]. The optical gap of this material ranges from 1.6 to 2.1 eV [22,36,37]. The physical properties of a-Si:H depend greatly on the Si-H bond configurations, and the incorporated hydrogen content. For example, material that has hydrogen bonded predominantly in monohydrde form (only one hydrogen atom is bonded to a silicon atom) demonstrates superior electronic properties (such as improved carrier mobility, strong photo response) to material having multiple hydrogen atoms bonded to a silicon atom [38-41]. An increasing hydrogen content leads to an increasing optical gap [22,38,39] corresponding to a redistribution of conduction and valence band states. It is therefore essential that hydrogen bonding in the deposited films be carefully identified to determine to what sub-set of the hydrogenated amorphous silicon our films belong.

Hydrogen in amorphous silicon exists in a variety of bonding configurations. IR spectroscopy shows that monohydrde (SiH), dihydride (SiH$_2$), polymeric (SiH$_2$)$_n$, and trihydride (SiH$_3$) complexes exist in the silicon matrix. Briefly, the IR spectrum of a hydrogenated amorphous silicon film having hydrogen bonded in monohydrde form shows absorption in two
regions - a wagging mode at 640 cm\(^{-1}\) and a stretching mode centered at 2000 cm\(^{-1}\) [20,42-44]. The other hydrogen bonding configurations (involving more than one hydrogen) introduce a shift in the stretching mode and a third region of absorption between 800 and 950 cm\(^{-1}\). SiH\(_2\) complexes show a single absorption peak near 875 cm\(^{-1}\) [20,42-44] interpreted as due to Si-H\(_2\) bending (scissor) mode and have a silicon-hydrogen stretching frequency at 2090 cm\(^{-1}\). Incorporation of hydrogen in (SiH\(_2\))\(_n\) or SiH\(_3\) groups will result in two doublets one having peaks near 845 and 890 cm\(^{-1}\) associated with (SiH\(_2\))\(_n\) groups and the other with peaks near 862 cm\(^{-1}\) (symmetric deformation) and 907 cm\(^{-1}\) (asymmetric deformation) for the SiH\(_3\) groups [20,43-45]. The silicon-hydrogen stretching frequencies of (SiH\(_2\))\(_n\) complexes occur between 2090 and 2100 cm\(^{-1}\), whilst those of SiH\(_3\) groups occur near 2140 cm\(^{-1}\) [43,45]. The shift in the stretching frequencies relative to that of the monohydride complex is due to an increase in the force constant of the silicon-hydrogen bond. All SiH\(_2\), (SiH\(_2\))\(_n\), and SiH\(_3\) species show absorption near 640 cm\(^{-1}\). Figure 3.1 illustrates the bond stretching, bond bending, and bond wagging modes of silicon-hydrogen complexes in hydrogenated amorphous silicon.
Figure 3.1. Schematic illustration of the bond-stretching $\omega^S$ (top row), bond-bending $\omega^B$ (middle row), and bond wagging $\omega^W$ (bottom row) modes of silicon-hydrogen complexes in a-Si (from [20]). SYM or ASYM indicate symmetric asymmetric modes.
3.3 The Induction Model

In this section the silicon-hydrogen stretching vibration frequencies in amorphous silicon are used to identify the local bonding environment of hydrogen. It has been observed that the frequency of the silicon-hydrogen stretching absorption band in substituted silane molecules, SiHR,R,R, shifts in a systematic way with the electronegativities of the substituting atoms or groups R1,R2, and R3 [46,47]. Electronegativity is a measure of the ability of a bonded atom to attract the electrons in the bond from the other atom or atoms to which it is bonded, and is determined from bond energies [48]. For example, the frequency of the silicon-hydrogen bond of trichlorsilane, SiHCl3, is at 2274 cm⁻¹ whilst that of trimethyl silane, SiH(CH3)3, is at 2118 cm⁻¹. These differences in frequencies result from modifications in the electron distribution about the silicon atom that are induced by the substituting atoms or groups [46]; leading to a change in the silicon-hydrogen interatomic distance [49] and so, the effective force constant, and are referred to as induction effects.

All types of vibrations display induction effects to varying degrees.
Silicon-hydrogen stretching vibrations show relatively strong induction effects, whilst bond bending modes show weak induction effects [49]. In the analysis that follows, the silicon-hydrogen stretching absorption band is studied.

Table 3.1 summarizes the preparation conditions of a series of films that were used to investigate the induction effect. Substrate temperature was the variable. Sample FL7, a reference sample, was grown under conditions very different from other films. Deposited films were about 1 μm in thickness.

Table 3.1: Preparation conditions for films. The discharge power density used was 0.2 W/cm². Sample FL7, a reference sample, was deposited at a chamber pressure of 250 mTorr, all other samples were deposited at a chamber pressure of 50 mTorr.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiH₄ (SiH₄ + H₂)</th>
<th>Flow Rate (sccm)</th>
<th>Substrate Temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T35</td>
<td>0.5</td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>T85</td>
<td>0.5</td>
<td>5</td>
<td>85</td>
</tr>
<tr>
<td>T150</td>
<td>0.5</td>
<td>5</td>
<td>150</td>
</tr>
<tr>
<td>T200</td>
<td>0.5</td>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>T300</td>
<td>0.5</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>T400</td>
<td>0.5</td>
<td>5</td>
<td>400</td>
</tr>
<tr>
<td>FL7</td>
<td>0.86</td>
<td>28</td>
<td>250</td>
</tr>
</tbody>
</table>
as determined using a surface profiler. IR spectra were taken in the range 370 - 5200 cm\(^{-1}\), using a Perkin Elmer 2000 Fourier transform IR spectrometer, purged with dry air. Measurements were made in the single-beam mode, in which the transmittances of the amorphous silicon film and a reference crystalline silicon substrate were measured and ratioed in rapid succession. Twenty ratios were accumulated and averaged to obtain the film transmittance spectrum. The resolution of the measurements was ±2 cm\(^{-1}\).

The absorption spectrum was obtained from the relation

\[
\alpha(\omega) = -\frac{1}{d} \ln \frac{T(\alpha)}{T(\alpha=0)}
\]  

(3.1)

where \(\alpha(\omega)\) is the absorption coefficient and \(\omega\) is the wavenumber, \(d\) is the film thickness, and \(T(\alpha=0)\) is the transmittance with no absorption (bare substrate). The error in the value of \(\alpha\) is about ±10 % mainly due to the error in determining the film thickness.

The IR spectra of all the films displayed a non-symmetric silicon-hydrogen stretching absorption band. In order to identify which of the silicon-hydrogen complexes contributed to the stretching vibration, the experimental stretching band was Gaussian deconvolved.
The absorption $\alpha(\omega)$ in the stretching region 1850-2250 cm$^{-1}$ was fitted using a superposition of two gaussian functions having a total of six free parameters i.e. amplitude, peak frequency, and standard deviation $\sigma_i$, that is

$$\alpha(\omega) = \sum_{i=1}^{2} A_i \exp[-\frac{(\omega - \omega_{\text{peak},i})^2}{2\sigma_i^2}].$$

(3.2)

A typical deconvolution result of one of the samples (T150) is illustrated in Figure 3.2. The experimental silicon-hydrogen stretching absorption peak is located at 2052 cm$^{-1}$ and has a shoulder near 2000 cm$^{-1}$. Gaussian deconvolution of the experimental peak identifies two peaks located at 2092 and the other at 2020 cm$^{-1}$. We assigned the absorption band peaking at 2092 cm$^{-1}$ to (SiH$_2$)$_n$ complexes due to the presence of a doublet near 845 and 890 cm$^{-1}$. The band peaking at 2020 cm$^{-1}$, we attributed to a monohydride type of bonding.

To clearly identify the origin of the 2020 cm$^{-1}$ absorption band, a reference sample FL7 was deposited under growth conditions (see Table 3.1) that promote monohydride bonding in the amorphous network [50]. The
Figure 3.2. Deconvolution of the Si-H stretching band at 2052 cm$^{-1}$ of sample T150 yields two bands located at 2020 cm$^{-1}$ and 2092 cm$^{-1}$. 
measured IR spectrum of this sample exhibited strong absorption at 2003 and near 640 cm\(^{-1}\), and very weak absorption at approximately 875 cm\(^{-1}\). Gaussian deconvolution of the experimental stretching absorption band yielded two peaks at 2003 and 2088 \(cm^{-1}\). Figure 3.3 shows the experimental and deconvolved stretching peaks. The area of the 2003 cm\(^{-1}\) gaussian band was more than an order of magnitude greater than that of the 2088 cm\(^{-1}\) gaussian curve. The weak stretching mode at 2088 \(cm^{-1}\) is in accordance with the weak bending mode near 875 cm\(^{-1}\) and therefore we attribute these two modes to the SiH\(_2\) complex. In the literature, the silicon-hydrogen stretching vibration of isolated monohydrides is assigned 2000 cm\(^{-1}\) [20,42,43]. We assign the absorption band with peak at 2003\(\pm2\) cm\(^{-1}\), of the reference sample FL7, to an isolated monohydride stretching mode.

We attribute the gaussian peak at 2020 cm\(^{-1}\) in Figure 3.2 to a modified monohydride stretching vibration and associate the increase in the stretching frequency with an induction effect. The IR stretching absorption band of the remaining films was deconvolved and the results are tabulated in Table 3.2. The deconvolution shows that the stretching mode consists of two bands - a low frequency band and a high frequency band each of varying
Figure 3.3. Deconvolution of Si-H stretching band of reference sample FL7. The experimental peak position lies at the same position as the dominant gaussian peak at 2003 cm$^{-1}$.
intensity. The high frequency band is ascribed to SiH₂ complexes.

Table 3.2: Measured and deconvolved peak position(s) of the IR Si-H stretching mode peak, and hydrogen content of films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Si-H Stretching Frequency (±2 cm⁻¹)</th>
<th>After Deconvolution (High Frequency Peak cm⁻¹)</th>
<th>After Deconvolution (Low Frequency Peak cm⁻¹)</th>
<th>Hydrogen Content (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T400</td>
<td>2016</td>
<td>2085</td>
<td>2004</td>
<td>7±1</td>
</tr>
<tr>
<td>FL7</td>
<td>2003</td>
<td>2088</td>
<td>2003</td>
<td>7±1</td>
</tr>
<tr>
<td>T200</td>
<td>2082</td>
<td>2091</td>
<td>2015</td>
<td>10±2</td>
</tr>
<tr>
<td>T300</td>
<td>2061</td>
<td>2090</td>
<td>2011</td>
<td>11±1</td>
</tr>
<tr>
<td>T35</td>
<td>2032</td>
<td>2100</td>
<td>2026</td>
<td>9±1</td>
</tr>
<tr>
<td>T85</td>
<td>2042</td>
<td>2093</td>
<td>2024</td>
<td>13±1</td>
</tr>
<tr>
<td>T150</td>
<td>2052</td>
<td>2092</td>
<td>2020</td>
<td>16±1</td>
</tr>
</tbody>
</table>
In Figure 3.4 (a) and 3.4 (b), the temperature dependence of the peak position of the low and high frequency deconvolved peaks is plotted. The low frequency peak position which we have attributed to modified monohydrides displays a linear dependence on deposition temperature. The high frequency peak position does not have a linear dependence and in the deposition temperature range of 35-300 °C there is little change. Clearly then, the complexes responsible for the modified monohydride frequencies are strongly dependent on growth temperature. The growth temperature changes the neighbourhood of the silicon-hydrogen group resulting in changes in the vibrational frequency.

To identify the complex or complexes producing the modified monohydride vibrations, we applied the induction model of Lucovskv [49]. Lucovskv has developed an empirical relationship for the vibrational frequencies of silicon-hydrogen groups in amorphous solids such as a-Si and a-SiO2, and shown that they vary systematically with the electronegativities of neighbouring atoms of the network. The model assumes that the silicon-hydrogen vibrational frequency ω is directly proportional to the average electronegativity of the neighbouring environment, i.e.
Figure 3.4(a). Monohydride stretch frequency versus deposition temperature. A linear relationship is observed. Resolution was 2 cm\(^{-1}\).
Figure 3.4(b). Stretch frequency of SiH\textsubscript{2} complexes versus deposition temperature. A non-linear relationship is observed relative to the monohydride-like vibration frequencies shown in Figure 3.4(a).
\[ \omega = \omega_0 + b \sum_i X_{Ai} \]  

(3.3)

where the constants \( \omega_0 \) and \( b \) are determined empirically, \( X_{Ai} \) is the stability-ratio electronegativity (as defined by Sanderson [51]) of a group and the sum is over three neighbouring groups of the silicon-hydrogen bond. To determine the number of atoms to be considered for the neighbouring group that would correctly describe the electronegativity of neighbouring groups, we estimated the stability-ratio sum of the silicon-hydrogen bond for substituted silane molecules. We considered two cases: (i) the group consisting of the nearest neighbours only, and (ii) that group of atoms consisting of the nearest neighbour to the silicon-hydrogen bond in question and its three other neighbours (see Equation (3.5)). In Table 3.3 the two approximations are compared to the actual stability-ratio sum. The nearest neighbour approximation is poor when compared to case (ii). Consequently, in the analysis of silicon-hydrogen bond stretching vibrations in the amorphous silicon matrix, each neighbouring group consisted of groups of atoms consisting of the nearest neighbour and its three other neighbours. Stability ratio electronegativity values for substituting atoms and for Si are: \( H = 3.55 \), 58
C=3.79, Cl=4.93, and Si=2.62 [51].

Table 3.3: Stability ratio sum approximations for nearest neighbour (n.n.) and next-nearest neighbours (n.n.n.)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Stability ratio sum (n.n.)</th>
<th>Stability ratio sum (n.n.n.)</th>
<th>Stability ratio actual value [42]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH(C₂H₅)Cl₂</td>
<td>13.65</td>
<td>13.52</td>
<td>13.48</td>
</tr>
<tr>
<td>SiH(C₂H₅)₂Cl</td>
<td>12.51</td>
<td>12.26</td>
<td>12.17</td>
</tr>
<tr>
<td>SiH(C₂H₅)₂CH₃</td>
<td>11.37</td>
<td>10.83</td>
<td>10.85</td>
</tr>
<tr>
<td>SiH(C₂H₅)₃</td>
<td>11.37</td>
<td>10.83</td>
<td>10.86</td>
</tr>
</tbody>
</table>

The low frequency deconvolved peak positions of the experimental data lie in the range 2003-2026 cm⁻¹ (see Table 3.2). We have attributed these vibration frequencies to monohydride-like vibrations. Consequently, we propose the following monohydride-like structures, as illustrated in Figure 3.5, to explain the origin of the low frequency stretching modes.

The silicon-hydrogen stretching frequency \( \omega_{\text{Si-H}} \) can be expressed in
Figure 3.5. Monohydride clusters. (a) An isolated monohydride. (b) A one dimensional monohydride chain. (c) A two dimensional monohydride chain.
terms of the stability-ratio electronegativity by the following relation [49]

\[ \omega_{Si-H} = a + 34.7 \sum_{j=1}^{3} X_{A_j} , \] (3.4)

where \( a \) is a constant and \( X_{A_j} \) represents the stability-ratio electronegativity of a nearest neighbour and its three neighbouring atoms. We express \( X_A \) by the following relation

\[ X_A = [X_{nn} (X_{nn1}) (X_{nn2}) (X_{nn3})]^{1/4} , \] (3.5)

where \( X_{nn} \) is the stability-ratio electronegativity of the nearest neighbour, and \( X_{nn(1)(2)(3)} \) is the stability-ratio electronegativity of the three other neighbours of one of the nearest neighbour to the silicon-hydrogen bond in question.

The silicon-hydrogen stretching vibrations occurring near 2000 cm\(^{-1}\), we attribute to the monohydride clusters as shown in Figure 3.5(a,b,c). Figure 3.6 shows the relationship between the stability-ratio electronegativity sum \( \sum X_{A_j} \) and the one dimensional monohydride chain length, \( n \) (see Figure 3.5(b)). The average silicon-hydrogen electronegativity sum of a chain of length \( n \) increases and begins to saturate with increasing \( n \). The
Figure 3.6. Mean electronegativity sum for a Si-H bond in a one-dimensional monohydride chain.
corresponding silicon-hydrogen stretching frequency as a function of monohydride chain length is displayed in Figure 3.7. The calculated frequencies represent the average vibration frequency of a chain of monohydrides of length n. From Figure 3.7 and Table 3.2 we can conclude that films deposited at substrate temperatures of 200 and 300 °C display silicon-hydrogen stretching frequencies attributable to one-dimensional monohydride chains (Figure 3.5(b)). Considering the accuracy of the measurement, ± 2 cm⁻¹, the monohydride complexes (SiH)₂ and (SiH)₃ are most probably present in the films at these substrate temperatures.

The calculated silicon hydrogen stretching frequency of the one-dimensional monohydride chain saturates at 2017 cm⁻¹. To explain the silicon-hydrogen stretching frequencies occurring at 2020 cm⁻¹ and higher, as shown in Figure 3.4(a), we employed the two dimensional monohydride chain of Figure 3.5 (c). Figure 3.8 plots the silicon-hydrogen stretching frequency of the two dimensional chain as a function of chain length n. The deconvolved low frequency silicon-hydrogen stretching vibrations at 2020, 2024, and 2026 cm⁻¹ (resolution ±2 cm⁻¹) can then be explained by the increase in the stability ratio sum for the silicon-hydrogen bond due to two
Figure 3.7. Mean frequency of a Si-H stretching vibration in a one-dimensional monohydride chain.
Figure 3.8. Mean frequency of a Si-H stretching vibration in a two-dimensional monohydride chain.
dimensional monohydride chain structures.

The above analysis demonstrates that monohydride chains exist in the amorphous silicon network.

3.4 Infrared Spectroscopy of Hydrogenated, Deuterated, and Tritiated Amorphous Silicon

Infrared spectroscopy of the deposited films was taken in the range 30-5200 cm\(^{-1}\) using the Perkin-Elmer 2000 FTIR spectrometer. Figure 3.9(a,b) displays the spectral range of the highest frequency vibrations occurring in the IR spectra of hydrogenated (H1,H2), deuterated (D1,D2), and tritiated (A214,UT) amorphous silicon films. These vibrations are attributed to stretching modes. The vibrations near 2100 cm\(^{-1}\) in the hydrogenated samples indicate the dominance of SiH\(_2\) complexes. Very similar hydrogen peaks are observed in the deuterated and tritiated spectra. Consequently, it is expected that bonded deuterium and tritium will exist in dihydride-like complexes, that is, combinations of HD, DD, and HT, TT, will be bonded to silicon. The low frequency vibrations in the deuterated and tritiated films
Figure 3.9(a). High frequency IR vibrations of samples: $H_1$, $D_1$, and $A_{214}$. Both $D_1$ and $H_1$ have been shifted up with respect to $A_{214}$ by about 500 and 1100 cm$^{-1}$, respectively.
Figure 3.9 (b) High frequency IR vibrations of samples: H2, D2, and UT. Both D2 and H2 have been shifted up with respect to UT by about 250 and 750 cm\textsuperscript{-1}, respectively.
are attributed to silicon-deuterium and silicon-tritium stretching modes. The greater reduced mass of the Si-D and Si-T oscillators relative to that of the Si-H oscillator, is responsible for the shift to lower frequencies. Differences in the nuclear mass of the bonded atoms have virtually no effect on the bonding strengths, and thus different isotopic species of the same molecule or complex will have the same force constants. Thus, the frequency of vibration of isotopically substituted complexes can be modelled on the mass of the atoms comprising the complex.

The simplest model for a solid is a linear chain of atoms, each of mass m, and separated by the unit cell of length a. A first approximation is nearest-neighbour interactions. Therefore, if the energy between two neighbours at a distance a is $\varphi(a)$, the total energy of a chain of N atoms, when each atom is at rest, is

$$E = N\varphi(a).$$  \hspace{1cm} (3.6)

Assuming each atom has a small vibrational motion about its equilibrium position, the displacement of an atom along the chain can be represented by the symbol $u$. If the displacements are small in comparison with a, then the
energy of the vibrating chain can be calculated using a Taylor series.

Summing over all the atoms:

\[ E = N\phi - \sum_{s=1}^{S} \frac{1}{s!} \frac{\partial^s \phi}{\partial u^s} \sum_n (u_n - u_{n-1})^s, \]  

(3.7)

where \( u_n \) is the displacement of the \( n \)-th atom from its equilibrium position.

By making the harmonic approximation (the \( s=2 \) term) the harmonic energy of the chain is

\[ E^{\text{harm}} = \frac{1}{2} \sum_n (u_n - u_{n-1})^2; \quad J = \frac{\partial^2 \phi}{\partial u^2}. \]  

(3.8)

The energy of the chain is then the same as the energy of a set of harmonic oscillators. The equation of motion of the \( n \)-th atom is obtained from the classical Newton equation and is

\[ \frac{m \partial^2 u_n}{\partial t^2} = -\frac{\partial E^{\text{harm}}}{\partial u_n} = -J(2u_n - u_{n-1} - u_{n-1}). \]  

(3.9)

The solution of the harmonic equation of motion is a sinusoidal wave, so the
motion of the whole system will correspond to a set of travelling waves.

When studying the vibration frequencies of three dimensional disordered solids, the analysis becomes far more complex due to the large number of vibrating bodies involved and the loss of periodicity. However, approximations can be made. For hydrogenated amorphous silicon, silicon-hydrogen related vibrations occur at frequencies greater than that of the amorphous silicon matrix. Therefore, silicon-hydrogen vibrations can be treated as localized vibrations, where the amplitude of vibration of the silicon-hydrogen oscillation decays exponentially into the amorphous silicon matrix. When investigating localized vibrational modes, much of the neighbouring environment of the localized oscillator can be ignored. In the case of the silicon-hydrogen stretching vibration in amorphous silicon, the silicon-hydrogen bond can be considered as a diatomic molecule and all other atoms ignored.

Using the harmonic potential approximation the stretching frequencies of the Si-D(T) bonds can be calculated with respect to the Si-H stretching frequency i.e.
\[
\frac{\omega_{\text{Si-D(T)}}}{\omega_{\text{Si-H}}} = \sqrt[3]{\frac{m_H (m_D(T) + M_{\text{Si}})}{m_D(T) (m_H + M_{\text{Si}})}}.
\tag{3.10}
\]

where, \(\omega_{\text{Si-H(D,T)}}\) is the stretching frequency of the Si-H(D,T) bond, \(m_{\text{H(D,T)}}\) denotes the mass of the hydrogen (deuterium, tritium), and \(M_{\text{Si}}\) represents the mass of silicon. The calculated Si-D, and Si-T stretching frequencies are in close agreement with measurement. Table 3.4 shows good agreement between experimental and calculated ratios.

Table 3.4: Ratio of stretching frequency of Si-D and Si-T bonds with respect to Si-H bonds

<table>
<thead>
<tr>
<th>Ratio of Frequencies</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_{\text{Si-D}}/\omega_{\text{Si-H}})</td>
<td>0.73</td>
<td>0.72</td>
</tr>
<tr>
<td>(\omega_{\text{Si-T}}/\omega_{\text{Si-H}})</td>
<td>0.61</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Using the induction model developed in section 3.3, the IR stretching absorption band of the films were deconvolved. Table 3.5 lists the peak
frequency position of the two gaussians used to fit the IR stretching vibrations of each of the samples.

Table 3.5: Deconvolution of stretching absorption bands.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si-H Experimental Peak Position (cm⁻¹)</th>
<th>Deconvolved Si-H Peaks (cm⁻¹)</th>
<th>Si-D, Si-T Experimental Peak Position (cm⁻¹)</th>
<th>Deconvolved Si-D, Si-T Peaks (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>2082</td>
<td>2021, 2094</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H2</td>
<td>2079</td>
<td>2015, 2091</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D1</td>
<td>2083</td>
<td>2019, 2092</td>
<td>1515</td>
<td>1497, 1526</td>
</tr>
<tr>
<td>D2</td>
<td>2084</td>
<td>2014, 2090</td>
<td>1511</td>
<td>1476, 1522</td>
</tr>
<tr>
<td>A214</td>
<td>2086</td>
<td>2021, 2094</td>
<td>1267</td>
<td>1260, 1272</td>
</tr>
<tr>
<td>UT</td>
<td>2079</td>
<td>2017, 2092</td>
<td>1259</td>
<td>1224, 1268</td>
</tr>
</tbody>
</table>

It can be seen that the deconvolved hydrogen related stretching components of hydrogenated, deuterated and tritiated films are very similar, indicating the presence of two dimensional monohydride clusters and dihydride complexes. The corresponding monodeuteride and monotritide cluster
stretching frequencies are expected to occur at approximately 1475 cm\(^{-1}\) 
\((2020 \text{ cm}^{-1} \times 0.73)\) and approximately 1232 cm\(^{-1}\) 
\((2020 \text{ cm}^{-1} \times 0.61)\), respectively. The dideuteride and ditritide frequencies are expected to occur 
at approximately 1527 cm\(^{-1}\) 
\((2092 \text{ cm}^{-1} \times 0.73)\) and approximately 1276 cm\(^{-1}\) 
\((2092 \text{ cm}^{-1} \times 0.61)\), respectively. Inspection of the last column 
of Table 3.5 shows that the samples D2 and UT display both monodeuteride 
clusters and dideuterides, and monotritide clusters and ditritides, 
respectively. However, the floating samples, D1 and A214 show frequencies 
typical of dideuterides and ditritides. Clearly, the deuterium and tritium 
bonding configurations are influenced by electrically floating the substrate 
during film deposition. Further evidence supporting the designation of the 
deconvolved peaks is the presence of scissor mode vibrations in the mid IR 
frequency range and not a doublet which corresponds to polymeric or 
trideuteride or tritritide complexes. These issues will be discussed shortly.

The deconvolved deuterium and tritium related frequencies for 
samples D1 and A214 are interpreted in terms of symmetric and asymmetric 
stretching vibrations (see Figure 3.1). Lucovsky [52] has developed an 
expression relating the square of the asymmetric stretching vibration \((u_a)\) of
a SiX$_2$ complex (where X is some different atom) to that of the symmetric stretching vibration $v_s$ as is given below

$$\frac{v_a}{v_s}^2 = \frac{1 + 2M \sin^2\theta}{1 + 2M \cos^2\theta} \cdot \frac{1 - \gamma}{1 + \gamma}, \quad (3.11)$$

where $M$ is the mass ratio of $m(X)/m(Si)$, and $\gamma$ is the ratio of the three-body to two-body bond-stretching frequencies $\gamma(Si-X)_\pi/\gamma(Si-X)_r$. $\theta$ is half of the H-Si-H bond angle which is assumed to be equal to the tetrahedral bond angle of 109.47°. In Table 3.6 are listed the experimentally derived ratios from the deconvolution and the calculated ratios. The values are in agreement.
Table 3.6: Asymmetric and Symmetric stretching frequency ratios. \( \gamma(\text{Si-X})_\pi / \gamma (\text{Si-X})_\sigma = 0.01 \) [52].

<table>
<thead>
<tr>
<th>Complex</th>
<th>((v_\sigma/v_\pi)) Experiment</th>
<th>((v_\sigma/v_\pi)) Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH(_2)</td>
<td>-</td>
<td>1.00</td>
</tr>
<tr>
<td>SiD(_2)</td>
<td>1.02</td>
<td>1.01</td>
</tr>
<tr>
<td>SiT(_2)</td>
<td>1.01</td>
<td>1.02</td>
</tr>
</tbody>
</table>

In the case of SiH\(_2\), the splitting is very small (3 cm\(^{-1}\), \( v_\sigma/v_\pi = 1.001 \)) and consequently, difficult to observe from the deconvolution of the experimental silicon-hydrogen stretching band which was measured with a resolution of \( \pm 2 \) cm\(^{-1}\).

Figure 3.10(a,b) displays the mid and far IR spectra. The vibrations occurring in the frequency range 700-900 cm\(^{-1}\) are suggestive of bending (scissor) mode vibrations. The hydrogen related vibrations show a double peak near 886 and 844 cm\(^{-1}\). The low frequency peak near 844 cm\(^{-1}\) is identified as the splitting of scissor modes due to interactions between neighbouring SiH\(_2\) groups in (SiH\(_2\))\(_n\) complexes [44], the high frequency peak is attributed to the SiH\(_2\) scissor mode.
Figure 3.10(a). Mid and far IR vibrations of samples: H1, D1, and A214. H1 and D1 have been shifted up with respect to A214.
Figure 3.10(b). Mid and far IR spectra of samples: H2, D2, and UT. H2 and D2 have been shifted up with respect to UT.
For the analysis that follows, it was necessary to determine the scissor mode vibration of a single SiH$_2$ complex. From Figure 3.10(a,b) it can be seen that polyhydrides exist in all the films and consequently the SiH$_2$ scissor mode vibration will experience a blue shift due to the increased electronegativity sum of the neighbouring environment. All SiH$_2$ groups contribute to the relatively strong absorption near 890 cm$^{-1}$, whereas only near-neighbour pairs of SiH$_2$ groups or large chain segments, (SiH$_2$)$_n$, contribute to a strong absorption near 845 cm$^{-1}$. Therefore, the ratio of the integrated absorption of the 845 cm$^{-1}$ absorption band to that of the 890 cm$^{-1}$ absorption band is considered to be a measure of the (SiH$_2$)$_n$ chain formation.

A series of films were deposited with varying degrees of polymerization as determined by deconvolving the doublet near 845 and 890 cm$^{-1}$ and taking their integrated ratios R. In Figure 3.11(a,b) are plotted the scissor mode and interaction mode frequency as a function of polysilane formation, R. It can be seen that the scissor mode and interaction mode frequencies show very different behaviour indicating different types of vibration. As the degree of polymerization increases the scissor mode frequency continues to
Figure 3.11(a). Dependence of scissor mode frequency on polymerization.
Figure 3.11(b). Dependence of the low frequency peak position of the \((\text{SiH}_2)_n\) doublet on polymerization.
increase while the interaction mode frequency appears to saturate. The line in Figure 3.11(a) is a least squares fit to the data points. Extrapolating to \( R=0 \) for the case of no polymeric bonding in a film, the scissor mode frequency of a single \( \text{SiH}_2 \) was determined to be 875 ±2 cm\(^{-1}\). This value will be used in the calculations.

For a \( \text{SiH}_2 \) complex the force constants determining the scissor mode vibration are the H-Si-H angular force constant and the H-Si-Si force constant. In Figure 3.12 the scissor mode vibration of an \( \text{SiH}_2 \) complex is depicted with its angular force constants. The \( \text{SiH}_2 \) scissor mode vibration shown in Figure 3.12 is modelled as a diatomic molecule in Figure 3.13. For this system the reduced mass of the oscillator is the reduced mass of the vibrating H-H pair.

All the films show that hydrogen bonds in both \( \text{SiH}_2 \) and \( (\text{SiH}_2)_n \) form. The deuterated and tritiated films do not display doublets indicative of polymeric bonding, therefore, it is expected that in the deuterated and tritiated samples the following complexes are also present \( \text{SiHD}, \text{SiD}_2, \text{SiHT}, \text{SiT}_2 \), respectively. The isotopic bonding suggests that the \( (\text{SiH}_2)_n \) structures in the film arise from clustering of silane radicals in
Figure 3.12. A ball and stick model of an SiH$_2$ complex undergoing bending mode vibration. X,Y represent hydrogen and its isotopes. The large spheres represent silicon atoms.

Figure 3.13. The bending mode vibration of Figure 3.12 is modelled by the stretching vibration of a diatomic molecule.
the plasma which are incorporated into the film. We use Equation (3.12) to model the scissor mode vibration frequency of these complexes

$$\frac{\omega_{XY}}{\omega_{HH}} = \sqrt{\frac{m_X + m_Y}{m_X m_Y} \frac{m_H}{2}} . \quad (3.12)$$

where $\omega_{XY}$ is the scissor mode frequency of an X-Y vibrating pair, X, Y, can represent H, D, or T. Table 3.7 lists the experimental and calculated frequencies for the three films. Our calculated values were determined using the experimental SiH$_2$ scissor mode at 875 cm$^{-1}$. The SiD$_2$ scissor mode has been observed near 650 cm$^{-1}$ [20,42,53] but in Figure 3.10(a,b) it is hidden by the strong silicon-hydrogen wagging vibration near 640 cm$^{-1}$. The calculation predicts a low frequency SiT$_2$ scissor mode at 505 cm$^{-1}$, the IR spectrum of the tritiated film shows a peak at 490 cm$^{-1}$. This peak we assign to a SiT$_2$ scissor mode. The calculated frequencies are in good agreement with the experimental values. Further evidence indicating that the vibration at 490 cm$^{-1}$ is a SiT$_2$ scissor mode and not one of the silicon matrix's vibration modes (the transverse optic-like vibration near 480 cm$^{-1}$, see Figure 3.14 and the accompanying text) can be seen from the intensity of the peak near 200
cm⁻¹ in all three spectra of Figure 3.10(b). This peak is identified as the transverse acoustic (T.A.)-like vibration mode of the silicon-matrix and has a similar intensity in all the spectra. If the absorption at 490 cm⁻¹ was due to tritium decay induced silicon-silicon vibrations, the absorption near 200 cm⁻¹ in the tritiated film UT should be enhanced relative to that observed in the other films H2 and D2. The similar intensities indicate that there is no enhanced tritium decay induced absorption of the silicon matrix. The high frequency peaks superimposed on the broad T.A.-like peak are due to water vapour absorption inside the FTIR.

Table 3.7: Scissor mode vibrations in hydrogenated, deuterated and tritiated amorphous silicon

<table>
<thead>
<tr>
<th>Scissor Mode</th>
<th>Experiment (cm⁻¹)</th>
<th>Calculated (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{\text{HH}}$</td>
<td>875</td>
<td>875*</td>
</tr>
<tr>
<td>$\omega_{\text{HD}}$</td>
<td>782</td>
<td>758</td>
</tr>
<tr>
<td>$\omega_{\text{HT}}$</td>
<td>755</td>
<td>714</td>
</tr>
<tr>
<td>$\omega_{\text{DD}}$</td>
<td>650 [13,35,46]</td>
<td>619</td>
</tr>
<tr>
<td>$\omega_{\text{TT}}$</td>
<td>490</td>
<td>505</td>
</tr>
</tbody>
</table>

*This frequency was experimentally derived and is used in the calculation.
The temperature rise in the tritiated film due to tritium decay is discussed in section 3.6. Tritium decay results in a 0.003 K increase in film temperature which is insignificant, and further indicates that the vibration near 490 cm$^{-1}$ in the tritiated film is not due to tritium decay energy transferred to the amorphous network but to the IR active silicon-tritium bond.

Using the Si-H wagging frequency $\omega_H$, we can approximate the wagging frequencies of the Si-D and Si-T bonds by

$$\frac{\omega_X}{\omega_H} = \sqrt{\frac{m_H}{m_X}},$$  \hspace{1cm} (3.13)

where $\omega_X$ is the wagging frequency of a Si-D or Si-T bond, $m_X$ is the mass of a deuterium or tritium atom, and $m_H$ is the mass of a hydrogen atom. Table 3.8 lists the experimental and calculated frequencies. The experimental Si-T wagging vibration is quite accurately predicted by Equation (3.13), however, the experimental Si-D wagging vibration is underestimated. This is explained by noting that the Si-D wagging vibration falls very close to the transverse-optic (T.O.) like vibrational band (-480 cm$^{-1}$) of the Si-Si matrix [54].
Table 3.8: Wagging mode vibrations in hydrogenated, deuterated and tritiated amorphous silicon

<table>
<thead>
<tr>
<th>Wagging mode</th>
<th>Experiment (cm(^{-1}))</th>
<th>Calculated (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_H)</td>
<td>645</td>
<td>645(^{**})</td>
</tr>
<tr>
<td>(\omega_D)</td>
<td>515</td>
<td>456</td>
</tr>
<tr>
<td>(\omega_T)</td>
<td>373</td>
<td>372</td>
</tr>
</tbody>
</table>

This frequency was experimentally derived and is used in the calculation.

The IR absorption spectrum of pure amorphous silicon and hydrogenated amorphous silicon are shown in Figure 3.14. In Figure 3.15 is shown the vibrational density of states of crystalline silicon. There clearly exists a similarity between the IR absorption spectra and the vibrational density of states. The conservation of crystal momentum, and symmetry selection rules, lead to zero first-order IR activity in diamond silicon. The introduction of distortions and subsequent loss of long-range order in the amorphous phase relaxes these restrictions and permits all phonons to contribute to the IR absorption. The first order IR spectrum should then consist of the phonon density of states modified by transition matrix
Figure 3.14. The experimental vibrational absorption spectra of pure (broken line) and hydrogenated (24.2%) amorphous silicon (heavy line) (from [4]).
Figure 3.15. The density of states of c-Si (from [55]).
elements [56].

The Si-D wagging vibration and the T.O.-like vibration of the amorphous network occur at similar frequencies. Depending on the degree of coupling between the Si-D wagging mode and the T.O.-like band, a broadening of the line shape and a blue shift in the Si-D wagging frequency is expected [57]. The coupling of the Si-D oscillator with that of the amorphous silicon network provides a new energy dissipation channel for the oscillator. As a consequence, the wagging mode excitation of the Si-D oscillator has a life time much smaller than that of the Si-H oscillator. Qualitatively, from the Heisenberg uncertainty principle it is expected that a reduced life time will result in a broadening of the energy level. The broadening is quite evident on comparing the Si-D wagging vibration in Figure 3.10(a,b) to the corresponding Si-H and Si-T wagging vibrations.

Gadzuk and Luntz [57] have studied the frequency shift ($\Delta \omega$) of a localized oscillator coupling to a phonon field $\rho(\omega)$. Their analysis shows that a blue shift of the oscillator frequency occurs and can be expressed by the relation
\[ \Delta(\omega_i) = \int_0^\infty \frac{2\omega |\lambda(\omega)|^2}{\omega_i^2 - \omega^2} \rho(\omega) d\omega , \]  

(3.14)

where \( \omega_i \) is the unperturbed oscillator frequency and \( \lambda(\omega) \) is the coupling coefficient. Clearly the degree of coupling determines the shift in the oscillator frequency. Another vibration that falls on the T.O.-like band is the SiT\(_2\) scissor mode. It too displays a broadened line shape compared to the other scissor modes. However, the expected blue shift is not easily observed, due to the broadness of the peak.

Further investigation of the Si-D wagging vibration in Figure 3.10(a) suggests the presence of a shoulder near 450 cm\(^{-1}\). In Figure 3.10(b), this shoulder is clearly seen for the sample D2. Lucovsky et al. [58] have attributed this shoulder to a wagging-like motion of the Si-D oscillator, where both the deuterium and silicon atom that bonds to it move in phase. The corresponding Si-H wagging-like vibration is expected to occur near 480 cm\(^{-1}\), and there does exist a very weak peak in both the IR spectra of H2 and H1. However, the tritiated samples show only the symmetric Si-T wagging vibration and no additional peak. This evidence clearly indicates that the
assignment by Lucovsky et al. [58] is incorrect. The following explanation is proposed. In hydrogenated amorphous silicon, the wagging vibration is expected to occur near 640 cm\textsuperscript{-1}. The weak peak near 480 cm\textsuperscript{-1} is due to the weakly IR active amorphous silicon matrix. In deuterated amorphous silicon, the Si-D wagging vibration couples to the amorphous silicon network vibration. As a result it becomes blue shifted and the weak shoulder near 450 cm\textsuperscript{-1} is the corresponding shifted silicon-silicon vibrations that exist in the vicinity of the Si-D oscillator. Finally, in tritiated amorphous silicon, the Si-T wagging vibration lies in that region of the host network’s vibrational density of states which is a minimum. Very weak coupling between the oscillator and the silicon network leads to no peak shift in the Si-T oscillators’s position (see Table 3.8) and little observable broadening in its line shape.
3.5 Concentration of Bonded Hydrogen, Deuterium, and Tritium

The bonded hydrogen content, \( N_{\text{Si-H}} \) (cm\(^3\)), was obtained from the integrated intensity of the silicon-hydrogen IR stretching band centered near 2000 cm\(^{-1}\), according to Kruzelecky et al. [27]

\[
N_{\text{Si-H}} = C_{\text{Si-H}} \int \frac{a(\omega)}{\omega} d\omega
\]  

(3.15)

where \( C_{\text{Si-H}} = (1.1 \pm 0.1) \times 10^{20} \) cm\(^{-2}\) is the proportionality factor for this band, obtained by the calibration of integrated intensity against the hydrogen content deduced by a \(^{15}\)N nuclear reaction analysis. The percentage of hydrogen in the films was deduced to be

\[
H \% = \frac{N_{\text{Si-H}}}{\rho_{c-Si}} \times 100
\]  

(3.16)

where \( \rho_{c-Si} = 5 \times 10^{22} \) cm\(^3\) is the atomic density of crystalline silicon. It is assumed that the concentration of silicon atoms in hydrogenated amorphous
silicon is similar to that measured in crystalline silicon.

Equation (3.17) can also be written in the form [20]

\[ N_{Si-H} = A_{Si-H} \int a(\omega) d\omega, \]  
(3.17)

where \( A_{Si-H} \) (cm\(^{-1}\)) is a modified coefficient. This expression can be directly applied to the IR spectrum. The coefficient \( A_{Si-H} \) can be expressed (in cgs units) as

\[ A_{Si-H} = \frac{c n \mu_{Si-H}}{2 \pi^2 \varepsilon_s^2}, \]  
(3.18)

where \( c \) is the speed of light, \( n \) the refractive index, \( \mu_{Si-H} \) the reduced mass of the Si-H oscillator, and \( \varepsilon_s \) the appropriate effective charge for Si-H in the amorphous silicon network. For the case of Si-D and Si-T oscillators, it is expected that differences in the nuclear mass of the bonded atoms have virtually no effect on the effective charge. Thus, different isotopic species of the same molecule or complex will have the same force constants. However, the greater reduced mass of the Si-D and Si-T oscillators relative to Si-H will clearly increase the coefficient in Equation (3.18) by a factor of about 2 and 94.
3 for $A_{\text{Si-D}}$ and $A_{\text{Si-T}}$, respectively. Thus, we expect that for the same density of oscillators, the hydrogen related absorption band will be approximately twice and three times as intense as those of the deuterium and tritium ones, respectively.

To determine the bonded deuterium and tritium contents the coefficient in Equation (3.15) had to be modified. $C_{\text{Si-H}}$ can be expressed (in cgs units) as [20]

$$
C_{\text{Si-H}} = \frac{c n \omega_t \mu_{\text{Si-H}}}{2\pi^2 e_s^2}.
$$

(3.19)

where $\omega_t$ is the stretching vibration frequency of the Si-H bond,

$$
\omega_t = \sqrt{\frac{k_{\text{Si-H}}}{\mu_{\text{Si-H}}}}.
$$

(3.20)

Therefore, $C_{\text{Si-D}} = \sqrt{2} \times C_{\text{Si-H}} = \sqrt{2}(1.1 \pm 0.1) \times 10^{20}$ cm$^2$, and $C_{\text{Si-T}} = \sqrt{3} \times C_{\text{Si-H}} = \sqrt{3}(1.1 \pm 0.1) \times 10^{20}$ cm$^2$. In Table 3.9 are listed the bonded hydrogen, deuterium, and tritium concentrations in the films.
Table 3.9: Bonded hydrogen, deuterium, and tritium content in films. Determined from IR analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydrogen content at.%</th>
<th>Deuterium content at.%</th>
<th>Tritium content at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H2</td>
<td>12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D1</td>
<td>10</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>D2</td>
<td>8</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>A214 (A215)</td>
<td>12</td>
<td>-</td>
<td>6 (6)</td>
</tr>
<tr>
<td>UT</td>
<td>9</td>
<td>-</td>
<td>4</td>
</tr>
</tbody>
</table>

3.6 Raman Spectroscopy and Optical Absorption

Raman spectroscopy is a powerful tool to study the structural order of materials. This technique provides information on the structural changes related to bond angle and bond length variations. The vibrational spectra of solids are primarily determined by nearest neighbour interactions [59].
short range order of an amorphous material is very similar to its crystalline counterpart, except for small variations in bond angle and bond length. Such differences result in a change in the vibrational energy (peak shift) as well as a broadening of the peak [60-62]. Because of the lack of long range order in amorphous materials, first order Raman scattering is possible from all the vibrational modes present in the material [59]. The spectra can be interpreted as representing the vibrational densities of states. Shuker and Gammon [63] have derived an approximate expression for the Raman scattering intensity $I(\omega)$ of an amorphous material

$$I(\omega) = \sum_b C_b [n(\omega, T) + 1] \frac{\rho_b}{\omega} .$$

(3.21)

where $n(\omega, T)$ is the Bose-Einstien distribution evaluated at temperature $T$ and frequency $\omega$, $\rho_b(\omega)$ is the density of vibrational states in band $b$, and $C_b$ contains the polarization dependence and the average coupling strength of a band to the incident radiation. $C_b$ is smoothly varying to first order [64].

The above expression is for Stokes scattering. The approximations involved are that all vibrational modes in a given band are assumed to couple equally to the incident radiation.
Figure 3.16 shows a comparison of the reduced Raman scattering spectrum \( I(\omega)\omega/(n(\omega,T) + 1) \) of amorphous silicon at 27 and 300K, and the vibrational density of states (broadened from that for crystalline silicon to simulate the vibrational density of states of amorphous silicon). There is similarity between the reduced Raman spectra and the vibrational density of states. The reduced Raman spectra for the amorphous material essentially retains the features corresponding to the crystalline case, in particular the transverse acoustic (T.A.) and transverse optic (T.O.)-like bands. The position \( \omega_{\text{T.O.}} \) provides information on the strain in the amorphous silicon matrix.

Raman spectra were taken of the deposited films. Measurements were conducted at the Ontario Laser and Light wave Research Center (OLLRC). An argon-ion laser (488 nm) excited films deposited on glass substrates. Light scattered at 90° from the sample was collected by a lens and passed into a grating monochromator. The signal was detected by a liquid nitrogen cooled photomultiplier and amplified.

In Figure 3.17 is shown the T.O.-like bands for the films UT and A214 deposited on glass substrates. The measurements were made several months
Figure 3.16. (a) Reduced Raman spectra of amorphous silicon at 27 and 300K. Resolution is indicated by R. (b) Single-phonon density of states of crystalline silicon (dashed line) and density of states of a-Si (solid line) obtained by broadening the crystalline density of states [59].
Figure 3.17. Normalized T.O.-like peak position of samples A214 and UT.
after film deposition. The peak position of sample A214 is located at 469 cm\(^{-1}\) and that of UT is at 465 cm\(^{-1}\). The resolution was ±1 cm\(^{-1}\). From the peak position it can be said that the silicon matrix of A214 has a different strain energy than that of sample UT. In Table 3.10 is listed the T.O.-like peak position for tritiated and regular amorphous silicon films. It is seen that films (A214, D1, and H1) deposited on floating substrates display higher peak positions than do films (UT, D2, and H2) deposited on grounded substrates. This difference is attributed to reduced ion bombardment effects on floating substrates during film deposition [35]. There was no observable change in the width of the T.O.-like peak for the samples A214, D1, and H1, and similarly, for the samples UT, D2, and H2.
Table 3.10: T.O.-like Raman peak position of films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T.O. Peak position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A214</td>
<td>469</td>
</tr>
<tr>
<td>D1</td>
<td>470</td>
</tr>
<tr>
<td>H1</td>
<td>469</td>
</tr>
<tr>
<td>UT</td>
<td>465</td>
</tr>
<tr>
<td>D2</td>
<td>465</td>
</tr>
<tr>
<td>H2</td>
<td>461</td>
</tr>
</tbody>
</table>

Optical absorption in amorphous silicon is usually characterized by the Tauc gap [66]. The Tauc gap, $E_g$, is determined by extrapolating the linear functional dependence of the product of absorption coefficient and photon energy, i.e.
where, $B$ is a constant. $E_g$ marks approximately the transition between the virtual crystal behaviour and the exponential tail. Cody et al. [67] have experimentally shown that the Tauc gap of amorphous silicon decreases linearly with increasing width of the Urbach tail; the width of the Urbach tail is a direct measure of disorder. Thus, $E_g$ can be used as a measure of disorder.

To determine the optical gap of the amorphous silicon films, transmittance and reflectance measurements were made in the range 200-900 nm using a uv-visible spectrophotometer. The measurements were made several months after film deposition. The Tauc gap was determined using the method of Demichelis et al. [68]. In the spectral region of fundamental absorption the absorbance $\Omega(R,T)$ which is the product of absorption coefficient and film thickness can be expressed as

$$\Omega(R,T) = \ln \frac{1-R}{T},$$

where, $T$ is the transmittance, and $R$ is the reflectance. The Tauc gap is then obtained from the relation

$$[\alpha(E)E]^{1/2} = B(E-E_g),$$

(3.22)
\[(\Omega(R,T)E)^{1/2} = A(E-E_g).\] (3.24)

The term A is energy independent. Equation (3.24) has the same form as Equation (3.22). The only difference is that the gradients in the two relations are different. Extrapolating the linear dependence will yield identical values of \(E_g\). Figure 3.18 displays the Tauc plot for samples UT and A214. Extrapolating to the energy axis yields an optical gap of 1.92 eV for sample UT and 2.19 eV for A214. It has been proposed [69] that a decrease in the optical gap results from a broadening of the conduction and valence bands due to a redistribution of electronic states. Table 3.11 tabulates the Tauc gap of tritiated and regular amorphous silicon films. The films deposited on floating substrates display a larger optical gap than that of films deposited on grounded substrates. This is attributed to ion bombardment effects during film growth as discussed in chapter two.
Figure 3.18. Tauc gap of samples A214 and UT. The non-linear behaviour near the energy axis of sample UT is due to interference effects from the transmittance and reflectance measurements.
Table 3.11: Tauc gap of films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A214</td>
<td>2.19</td>
</tr>
<tr>
<td>D1</td>
<td>2.17</td>
</tr>
<tr>
<td>H1</td>
<td>2.17</td>
</tr>
<tr>
<td>UT</td>
<td>1.92</td>
</tr>
<tr>
<td>D2</td>
<td>1.92</td>
</tr>
<tr>
<td>H2</td>
<td>1.91</td>
</tr>
</tbody>
</table>

The influence of disorder on the optical gap of an amorphous semiconductor may be expressed as [67,70]

$$E_g = E_g(0) + D(<u^2>_T + <u^2>_x)$$

(3.25)

where $E_g(0)$ is the optical gap in the limit of small structural disorder at $T=0$
K, D is the deformation potential, \( <u^2> \) is an averaged square displacement of atoms due to thermal vibrations \( (<u^2>_r) \) or structural disorder \( (<u^2>_\chi) \). \( <u^2>_\chi \) can be modified by the deposition process, particularly, by high energy ion bombardment, leading to a decrease in \( E_g \).

Raman spectra, and so \( \omega_{T,O} \), are dependent on network bonding and structure. Therefore, it is expected that \( \omega_{T,O} \) and \( E_g \) should be related. Figure 3.19 clearly indicates a correlation between \( E_g \) and \( \omega_{T,O} \), two different parameters that are functions of the vibrational and electronic states in the amorphous silicon films.

From Figure 3.19 it can be seen that tritiated films possess a similar structure and optical gap to regular amorphous silicon. Clearly tritium decay does not significantly influence these two properties. Pfann and Rousbroeck [71] have estimated the radiation damage threshold for silicon to be 300 keV. A tritium decay generated \( \beta \) has a maximum energy of 18.6 keV. This energy is more than an order of magnitude below the threshold energy necessary to cause structural disorder to the silicon matrix. Consequently, no \( \beta \) induced structural disorder is expected.

The decay of a free tritium atom produces a helium isotope with recoil
Figure 3.19. Tauc gap and T.O. peak position of tritiated and regular amorphous silicon films.
energy of 3.44 eV [72]. This energy can be directly coupled into the vibrational modes available in the silicon matrix. However, both IR spectra and the above results show no enhanced disorder effects relative to regular amorphous silicon. Therefore, helium recoil induced vibration is probably not significant. To estimate the heating of sample A215 due to tritium decay, an approximate calculation was performed. An energy of 0.26 μJ was deposited into the film every second due to tritium decay. Crystalline silicon has a specific heat capacity (C) of 0.678 J/gK [73] and this value was assumed the same for amorphous silicon. The film mass (m) was 1.16×10⁻⁴g. Equating mCΔT to the tritium decay energy deposited into the film, where ΔT is the rise in film temperature, indicates a 3×10⁻³K increase in film temperature which is insignificant.

The decay of bonded tritium can lead to another form of disorder - dangling bond defects. The tritium passivated dangling bond transforms into a dangling bond defect once the tritium has undergone nuclear decay. The creation of the dangling bond is not expected to introduce additional strain into the amorphous network, since prior to decay, the vicinity of the silicon-tritium bond is relaxed. For example, in hydrogenated amorphous silicon, the
inner surface of a void has many coordination defects which result in dangling bonds that are passivated by hydrogen. It is expected that there is significant structural relaxation of the silicon network in the void.

3.7 Summary

In this chapter IR spectroscopy was used to identify the bonding of hydrogen and its isotopes in the amorphous silicon matrix. Deconvolution of the silicon-hydrogen (isotope) stretching vibrations indicated the presence of induction effects. It is concluded that monohydride clusters exist in the amorphous silicon matrix. Bonded tritium behaves as a heavy hydrogen atom. The tritium vibrations are shifted by a factor of about 0.6 relative to hydrogen vibration frequencies. Using IR spectroscopy the bonded tritium concentration was determined.

Raman spectroscopy and optical absorption analysis showed that the structure and optical gap of tritiated films were very similar to those of regular amorphous silicon films. It is concluded that tritium decay does not lead to enhanced structural disorder of the silicon matrix.
Chapter 4

Radiative Recombination in Tritiated Amorphous Silicon

*Three men are my friends—he that loves me, he that hates me, he that is indifferent to me. Who loves me, teaches me tenderness; who hates me, teaches me caution; who is indifferent to me, teaches me self-reliance.*

J. E. Dinger

4.1 Introduction

This chapter briefly reviews the theory of photoluminescence (PL) in hydrogenated amorphous silicon; a material which is an example for localized states. To understand tritium decay in the amorphous silicon matrix, the luminescence of tritiated amorphous silicon is investigated and compared with that of regular amorphous silicon. Differences are attributed to tritium decay processes.
4.2 Theory of Radiative Recombination in Amorphous Silicon

The recombination mechanisms present in hydrogenated amorphous silicon are the same as in crystalline semiconductors. Disorder does not introduce new processes but does influence which mechanisms dominate. Figure 4.1 describes radiative and non-radiative transitions in intrinsic semiconductors. The band-to-band transitions involve weakly localized states. The electron and hole therefore do not interact strongly with the matrix. The luminescence spectra resulting from this type of transition consists of very sharp zero-phonon transitions and weak phonon side bands. Electrons and holes produced by the absorption of photons can pair to form excitons. Radiative recombination of the electron-hole pair results in a narrow and sharp peak in the emission spectra. The energy of the emitted photon is equal to that of the energy gap less the binding energy of the exciton.

Recombinations at deep levels and surface states are typically non-radiative. The recombination of electrons and holes at deep levels do not
Figure 4.1. Possible types of radiative and non-radiative transitions in intrinsic semiconductors.
produce photons but instead generate multiple phonons [74]. The
dangling bond is the most common deep level and surface state in
semiconductors. Transitions involving deep levels have much stronger
phonon interactions than band edge transitions. In Figure 4.2 is shown
the coupling between electronic state and lattice vibration as a function
of configuration coordinate. The strong interaction between an electron
at a deep level and the lattice vibration is shown to cause the lattice to
relax from the original equilibrium position to a new equilibrium position.
The displacement is a measure of the coupling strength between electronic
states and lattice vibrations. The non-radiative recombination process can
be explained by this model. Electrons can go directly across the energy
intersection between the excited state and the ground state without
having to emit a photon.

The Auger recombination process involves three carriers (two
electrons and a hole or vice versa). The Auger effect occurs when the
recombination energy is given up to a third particle that is then excited
depth into one of the bands, subsequently, losing its energy by
thermalization back to the band edge [75]. This effect is present in
Figure 4.2. Configuration coordinate diagram of a localized defect with lattice relaxation, in relation to the band edges $E_v$ and $E_c$. 
amorphous silicon when electrons and holes exist in large concentrations [76,77].

In amorphous silicon, the large density of band tail states is the most influential factor in the recombination. After initial excitation above the band gap, carriers rapidly thermalize to the band tails, where they become trapped in localized states. At low temperatures recombination is determined by electron-hole pair wavefunction overlap or tunneling to defects, as there is insufficient thermal energy to excite carriers from the band tail states to the mobility edge. Thermal excitation becomes significant above about 100 K and changes the recombination mechanisms resulting in a decrease in luminescence intensity. This behaviour is referred to as thermal quenching. Thermal quenching is not a non-radiative mechanism but refers to a phenomenon where the luminescence intensity decreases with increasing temperature. Increasing the temperature excites carriers to the band edges where they can readily diffuse to non-radiative centers and there recombine.

Radiative transitions occur predominantly between carriers that are trapped in localized tail states. At low temperatures and under low
excitation, electrons and holes diffuse only a short distance apart after generation and recombine in a geminate process. A geminate pair is an electron and a hole created by the same photon - recombination of this particular pair is termed geminate recombination. Non-geminate recombination is a transition between carriers excited by different absorption events. At elevated temperatures or higher excitation intensities, electron-hole pairs separate more and more resulting in non-geminate recombinations.

The radiative recombination rate, \( P_{em} \), for a transition between an upper and lower state emitting a photon of energy \( \hbar \omega \) is given by the Fermi golden rule,

\[
P_{em} = \left( \frac{2\pi}{\hbar} \right) |M|^2 \delta(E_L - E_u + \hbar \omega)
\]

where \( M \) is the matrix element of the transition and the \( \delta \)-function conserves energy. The matrix element is

\[
M = M_0 J(\varphi_e, \varphi_h)
\]

where \( J \) is the overlap integral of the electron and hole wave functions.
Therefore,

\[ P_{\text{em}} = P_0 J^2 \]  

(4.3)

where \( P_0 \) is the transition rate for completely overlapping wave functions. A dipole-allowed transition \( P_0 \) can be expressed as (in cgs units)

\[ P_0 = \frac{8}{3} \pi^3 e^2 r_d^2 / \hbar \lambda^3 \]  

(4.4)

where \( e r_d \) is the dipole moment \( (r_d-1\text{Å}) \) from which the recombination rate, \( P_0 \), is approximately \( 10^8 \text{ s}^{-1} \). In an exciton the electron and hole have almost complete spatial overlap and the recombination life time is of the order of \( 10^{-9}-10^{-8}\text{s} \). When the electron and hole are localized, and separated by a distance \( R \) which is larger than the localization radius \( R_0 \) of the electron and hole wave functions, the overlap integral is [12]

\[ J = \exp(-\frac{R}{R_0}). \]  

(4.5)
According to Tsang and Street [78], the distance \( R \) between locally trapped electrons and holes in the band tail states of amorphous silicon determines the overlap of their wave functions. The life time for radiative recombinations \( \tau_r \) (or their radiative recombination rate \( P_r \)) is then described by

\[
(P_r^{-1} = \tau_r = \tau_{0r} \exp\left(\frac{2R}{R_0}\right)
\]

where, \( \tau_{0r} \sim 10^{-9}-10^{-8} \text{ s} \) and \( R_0 \) is the localization radius for the less localized carrier, the electron. Typical values of \( R_0 \) are between 10-12 Å [78]. Large variations in the electron-hole separation distance \( R \) therefore cause a broad distribution of lifetimes. For hydrogenated amorphous silicon radiative life times scan the range \( 10^{-8} - 10^{-2} \text{ s} \). This is shown in Figure 4.3. The distribution is peaked between \( 10^{-3} - 10^{6} \text{ s} \) [78,79]. At higher temperatures, the thermal energy becomes sufficient to release trapped electrons from tail states across the mobility edge into extended states of the conduction band. With increasing separation and mobility, carriers are more easily captured at non-radiative recombination centers.
Figure 4.3. Radiative life time distribution in hydrogenated amorphous silicon [78].
and radiative processes diminish. The defect which is the major non-radiative recombination center, in amorphous silicon, is the silicon dangling bond [80]. It is considered to be a multivalent center with three mid gap energy states: $D^-$, the negatively charged state occupied by two electrons, the paramagnetic $D^0$ state occupied by one electron and the positively charged $D^+$ state depleted of electrons [80].

Hydrogen facilitates radiative transitions in hydrogenated amorphous silicon in three ways. First, hydrogen lowers the density of mid gap defect states in amorphous silicon by passivating silicon dangling bonds. As silicon dangling bonds assume a near mid gap position in amorphous silicon, they are largely responsible for non-radiative recombinations (also referred to as "killer centers"). The silicon-hydrogen bond shifts the corresponding state deep into the valence band. Second, hydrogen breaks up highly strained Si-Si bonds, saturates the resulting dangling bonds and thereby reduces distortions of the network thus reducing deep tail states. Third, by removing deep states continuously out of the band gap, the gap widens with increasing hydrogen content $c_H$. 

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Broadband PL emissions with peak energies up to 2.05 eV (605 nm) have been observed for hydrogen contents of 40 at. %. [81].

The thermally activated hopping apart of carriers during thermalization causes the thermal quenching of PL. The thermal quenching can be calculated from the thermalization depth of the carriers in the band tails [82,83]. This varies with time as

\[ E_d = kT \ln (v_0 t) \]  \hspace{1cm} (4.8)

where, \( k \) is the Boltzmann constant, and \( v_0 \) is the hopping frequency \( - 10^{11} - 10^{13} s^{-1} \) [84,85]. A demarkation energy \( E_d \) is defined for the radiative lifetime \( t = \tau_r \), such that carriers above \( E_d \) will hop away to defects to recombine non-radiatively, while carriers below \( E_d \) will remain trapped and recombine radiatively. It is generally accepted that the band tails are described by an exponential density of states \( N(E) \), of slope \( kT_c \), [86] that is

\[ E_g = 1.5 + 0.015 c_H . \]  \hspace{1cm} (4.7)
\[ N(E) = N_0 \exp\left(-\frac{E}{kT_c}\right), \quad (4.9) \]

where \( N_0 \) is the total density of states below the mobility edge and is on the order of \( 10^{19}\text{-}10^{20} \text{ cm}^{-3} \) [17]. The luminescence efficiency is thus determined by the fraction of carriers trapped below \( E_d \),

\[ \eta = \exp\left(-\frac{E_d}{kT_c}\right) = \exp\left(-\frac{kT \ln(v_0 \tau_r)}{kT_c}\right). \quad (4.10) \]

The experimental variation of the PL efficiency of hydrogenated amorphous silicon is described by [87]

\[ \eta = \eta_0 \exp\left(-\frac{T}{T_L}\right), \quad (4.11) \]

where \( \eta_0 \) is the efficiency in the low temperature limit. Equation (4.10) has the same form if
Equation (4.11) describes the thermal quenching in hydrogenated amorphous silicon where \( T_L \) is a characteristic temperature.

At temperatures below 100 K thermally activated hopping is absent. The PL efficiency depends on the defect concentration. The electron-hole pair will recombine non-radiatively if they are formed within the tunnelling capture radius \( R_c \) of a non-radiative recombination center [88]. The relative efficiency is given by the probability of having no defects within the distance \( R_c \),

\[
\eta = \eta_0 \exp\left(-\frac{4\pi}{3}R_c^3N_d\right),
\]  

(4.13)

where \( N_d \) is the defect density and identified as the density of silicon dangling bonds. The capture radius \( R_c \) is defined as where the radiative and non-radiative tunnelling rates are equal,

\[
T_L = \frac{T_c}{\ln(v_0\tau_r)}.
\]  

(4.12)
\[ R_e = \frac{R_0}{2} \ln (v_0 \tau_r), \]  

(4.14)

where \( \tau_r \) is the radiative life time and the non-radiative life time \( \tau_{nr} \) for tunnelling is given by

\[ \tau_{nr} = \frac{1}{v_0} \exp \left( \frac{2R}{R_0} \right), \]  

(4.15)

where \( v_0 \) is the hopping frequency and \( R_0 \) is the Bohr radius of the localized state.

4.3 Experimental set-up for PL Measurement

In Figure 4.4 is shown a block diagram of the PL apparatus. The main components of the PL system are described below.

(I) Excitation source

The source of optical excitation was a CW Ar\(^+\) ion laser (Spectra...
Figure 4.4. Schematic diagram of the luminescence measurement set-up.
Physics model 165). The laser was set to operate at 490 nm (2.53 eV). The output power was measured to be 100 mW with a stability of ±5%. The laser beam was defocussed to a spot size of 5 mm to improve the uniformity of the laser power distribution at the film surface and to reduce the power density.

The laser beam was modulated at 45 Hz using an optical chopper.

(ii) Cryogenic system

The cryogenic system was used to cool the amorphous silicon samples. It consisted of a refrigeration sub-system, an optical cold head and a temperature controlled sub-system.

The amorphous silicon sample was mounted on a cold finger. A quartz window allowed the excitation light to enter and the luminescence to exit. Before cooling, the chamber was evacuated using a mechanical pump in series with a turbomolecular pump to a pressure of about $10^{-5}$ Torr.

The sample temperature was controlled in the range 10-300 K. The temperature was measured by a silicon diode sensor mounted directly on
the cold finger.

(iii) Monochromator

A Perkin-Elmer model E1 monochromator was used for the luminescence spectrum measurement. The monochromator was a 3/4 m (focal length) grating instrument. For the PL measurement a 1440 line/mm grating was used to measure the spectral response in the range 400 - 1100 nm. The spectral resolution was 4 nm.

(iv) Optical detection system

The optical detection system consisted of a photodiode to transform the optical signal into an electrical current signal and a circuit to amplify the photo-generated current signal. The amorphous silicon films displayed a luminescence peak in the near infrared. A silicon detector (Oriel 7180 photodiode) having a spectral response in the range 300 - 1100 nm was used to detect the radiation.

Sensitivity is an important issue in these measurements. The photodiode has a noise equivalent power (NEP) of $1.7 \times 10^{-14}$ W/Hz$^{1/2}$. 

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A 1 Hz frequency bandwidth was used.

4.4 Radiative Recombination in Regular Amorphous Silicon

Having studied the equations which describe radiative recombination in amorphous silicon, luminescence in regular amorphous silicon films deposited by the dc saddle-field glow-discharge technique were investigated. The luminescence spectra of sample D1 displayed typical luminescence behaviour of regular films deposited by this deposition technique. Furthermore, as D1 was deposited under very similar conditions to the tritiated films A214 and A215, its PL spectra can be compared to the PL spectra of tritiated films with little ambiguity.

Figure 4.5 shows the temperature dependence of the PL spectra of sample D1. This figure contains a wealth of information on radiative transitions in amorphous silicon. Up to about 100 K, there is little change in the luminescence intensity. At higher temperatures the luminescence intensity drops significantly. This behaviour is described by Equation
Figure 4.5. Temperature dependence of regular PL spectra of sample D1. The shoulder near 1.2 eV is attributed to absorption from the silicon substrate. For the sake of clarity, all the spectra were shifted upward from the zero value by the same amount.
(4.11). At temperatures above 100 K, the defect recombination mechanism changes gradually from tunneling to direct capture of a mobile electron or hole at a defect. The PL intensity decreases by more than an order of magnitude on going from the low temperature regime \((T<100 \text{ K})\) to 230 K. Figure 4.6(a) shows the relative luminescence intensity as a function of inverse temperature. In Figure 4.6(b), the high temperature region is fitted to Equation (4.11). The theory is in good agreement with experiment. From the fit, \(T_L\) was found to be 37 K, which is a typical value found in the literature [89].

It is interesting to note that with increasing temperature, the PL intensity of all the spectra decrease except for the case near 60 K which displays the strongest PL intensity. This apparent increase in intensity relative to the spectrum at 10 K is attributed to strong Auger recombination at the lower measurement temperature.

In Figure 4.7 is shown the large PL peak shift toward lower energies with increasing temperature. This behaviour is characteristic of transitions via tail states. The shift is caused by thermal excitation of weakly bound carriers above the mobility edge. As these carriers generally recombine
Figure 4.6(a). Relative luminescence intensity of sample D1 as a function of temperature.
Figure 4.6(b). PL temperature dependence in the high temperature region of sample D1. Data has been fit to Equation (4.11).
Figure 4.7. PL peak energy shift with temperature of sample D1.
non-radiatively, luminescence becomes increasingly dominated by carriers localized in deeper lying states. The temperature shift of the band gap for the temperature range in Figure (4.7) is about 0.05 eV [78], and is considerably smaller than the observed 0.23 eV shift of the luminescence peak energy.

4.5 Radiative Recombination in Tritiated Amorphous Silicon

Tritium decays by emitting a β particle. The β particle can generate electron-hole pairs in amorphous silicon. Considering the energy gap of amorphous silicon to be on the order of 2 eV, a single β particle, of mean energy 5.7 keV, is capable of producing many electron-hole pairs.

The β decay of a tritium atom bound to the silicon matrix is expected to lead to two primary processes in amorphous silicon: (i) the generation of electron-hole pairs by inelastic collisions between the β particle and the amorphous silicon network, and (ii) the creation of a dangling bond at the site of the decayed tritium atom. The β-
luminescence ($\beta$L) of tritiated amorphous silicon will provide evidence of electron-hole pair generation. Information on dangling bond concentration can be deduced from changes in the PL of tritiated amorphous silicon. Dangling bonds facilitate non-radiative recombination and when concentrations exceed $\sim 10^{17}$ cm$^3$, the PL efficiency of hydrogenated amorphous silicon decreases [90].

To identify $\beta$L of tritiated amorphous silicon an experimental set up similar to that shown in Figure 4.4 was used. In this case the film was not excited by a laser. To modulate any $\beta$L the chopper was placed directly in front of the sample. Measurements were taken at different temperatures.

Figures 4.8 and 4.9 display the temperature dependent $\beta$L of the tritiated films: A214 and A215. These results clearly demonstrate that $\beta$ generated electron-hole pairs exist in tritiated amorphous silicon. The peak position of the $\beta$L occurs near 1.6 eV for both spectra. The broad spectra suggest band tail processes. The Tauc gap of these films was about 2.19 eV (see section 3.6). A 0.6 eV difference between the Tauc gap and the $\beta$L peak position further indicates band tail related luminescence.
Figure 4.8. Beta luminescence of tritiated film A214. Considering the error bar, the 10 K measurement cannot be clearly, attributed to an Auger effect. The data has been smoothed.
Figure 4.9. Beta luminescence of tritiated film A215. Considering the error bar, the 10 K measurement cannot be clearly, attributed to an Auger effect. The data has been smoothed.
Using the transfer function in Appendix A, the 10 K \( \beta \)L efficiency was calculated for samples A214 and A215. Figure 4.10 shows the \( \beta \)L power spectrum of sample A215. The total \( \beta \)L power emitted by the film was 13nW (film volume was \( 5 \times 10^{-5} \text{ cm}^{-3} \)). This was estimated using geometric optics and noting that only the cone of luminescent light of half angle \( \theta - 20^\circ \) (refractive index of a-Si is \( -3.5 \)) is emitted from the film surface. It was assumed that the c-Si substrate absorbs all incident radiation. In Figure 4.5, absorption in the substrate begins at an energy near 1.2 eV; c-Si has an optical gap of 1.2 eV at 10K. Furthermore, little reflection of radiation from the back surface of the film is expected due to the similar index of refraction of a-Si and c-Si. The theoretical \( \beta \) power was estimated to be 0.26 \( \mu \)W. Thus, the \( \beta \)L efficiency is a few percent of the \( \beta \) power. A similar efficiency was obtained for sample A214.

To test the validity of the power measurement the \( \beta \)L power at the detector was calculated. The full width half maximum of the \( \beta \)L was 300 nm and the resolution of the monochromator was set to 4 nm. The average output power from the monochromator was then \( 3 \times 10^{-12} \) W. There were a total of six optical elements in the optical path (two
Figure 4.10. Beta luminescence power spectrum of sample A215 at temperature of 10K.
windows, one lens, two mirrors, and one grating). A 10% intensity loss was estimated for each optical element. The power at the detector was calculated to be $1.6 \times 10^{-12}$ W. The NEP of the detector was $1.7 \times 10^{-14}$ W at 1 Hz bandwidth.

To understand the consequences of the decay of tritium in tritiated amorphous silicon, PL spectra were taken of tritiated films as a function of temperature. Figure 4.11 shows typical luminescence spectra of a tritiated amorphous silicon film (sample A215). PL conditions were chosen to be identical to those used in obtaining the spectra of regular amorphous silicon, sample D1 as shown in Figure 4.5. The PL spectra of sample A215 display a broad peak in the energy range 1.4-1.6 eV. Furthermore, little temperature dependence is observed. This behaviour is very different from that of regular amorphous silicon.

Figure 4.12 displays the temperature dependence of the relative PL intensity of samples A215 and D1. D1 exhibits behaviour typical of good quality amorphous silicon [90]. However, the tritiated film displays weak relative PL intensity and little temperature dependence. These results indicate that in tritiated amorphous silicon a strong, non-radiative
Figure 4.11. Temperature dependence of PL of tritiated sample A215.
Figure 4.12. Relative luminescence intensity of D1 and A215.
recombination channel exists. At room temperature, there was no observable luminescence from either of the samples.

The temperature dependent spectra of tritiated amorphous silicon resembles that of amorphous silicon material having high dangling bond defect concentrations $\sim 10^{18}$ cm$^{-3}$. Street et al. [90] have studied the role of dangling bond density on luminescence efficiency in hydrogenated amorphous silicon. The results are displayed in Figure 4.13. This figure shows the temperature dependence of the luminescence intensity measured at low and high excitation power for samples of different dangling bond concentrations. Evidently, the presence of dangling bonds changes the temperature dependence of the PL. Tsang and Street [88] have shown that the luminescence efficiency, $\eta$, is exponentially dependent on the dangling bond defect concentration, as expressed by Equation (4.13). The temperature dependent PL of tritiated amorphous silicon suggests that tritium decay in amorphous silicon produces non-radiative recombination centers - dangling bond defects.

To better understand the role of dangling bond density and luminescence efficiency, PL measurements were conducted on a freshly
Figure 4.13. Temperature dependence of the luminescence intensity measured at high (H) and low (L) excitation power for samples of different dangling bond density $N_S$ [83].
deposited tritiated sample as a function of time. The tritiated film DK was grown under the deposition conditions listed in Table 4.1.

Table 4.1: Deposition parameters of tritiated film DK.

<table>
<thead>
<tr>
<th>T₂ Flow (sccm)</th>
<th>H₂ Flow (sccm)</th>
<th>Pressure (mTorr)</th>
<th>Temperature (°C)</th>
<th>Vₐnode (kV)</th>
<th>Iₐnode (mA)</th>
<th>Vsubstrate (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>50</td>
<td>225</td>
<td>1.1-0.66</td>
<td>≥22</td>
<td>≥370</td>
</tr>
</tbody>
</table>

The PL as a function of time was then measured. The laser power was 100 mW. In Figure 4.14 is shown the luminescence spectra as a function of time. Clearly the luminescence intensity decreases with time. The variation with time of the ratio of the integrated luminescence spectra relative to that measured at time t = 5 h is shown in Figure 4.15. The data displays an exponential behaviour. This decrease in intensity is attributed to an increasing dangling bond concentration.

We believe that the creation of a dangling bond ("killer center") arises from the decay of a bonded tritium atom. The helium atom has an ionization energy of 24.62 eV [91], (the highest ionization energy of any element in the periodic table) and silicon has an ionization energy of 8.16
Figure 4.14. PL spectra of sample DK at different times. Sample temperature was 10K.
Figure 4.15. Relative integrated PL intensity decay with time of freshly deposited tritiated film DK.
eV [91]. Therefore, it is expected that the helium ion, produced by tritium decay, will succeed in ionizing that silicon atom, which was bonded to the tritium atom before the decay; thereby, becoming a neutral helium atom located in an interstitial site. The silicon atom will be left with a dangling bond in a positive charge state. Further evidence supporting the helium ion's ability to capture an electron and become a neutral, unbonded atom, is the decay of the tritiated hydrocarbon, monotritiated methane (CH$_3$T). The predominant process is one in which the neutral helium separates, leaving a positively charged methyl group [92]. Similar results are reported with tritiated ethane (C$_2$H$_5$T) [93]. Carbon is a group IV element like silicon. It has an ionization energy of 11.29 eV [91] and in the molecules CH$_3$T and C$_2$H$_5$T, it becomes positively ionized after $\beta$ decay. A silicon atom has a smaller ionization energy, and consequently, the decay of bonded tritium will lead to a positively charged dangling bond defect. The reaction below describes the Si-T decay process and creation of a positively charged dangling bond defect in the amorphous silicon matrix,
\[ =Si - T \rightarrow =Si^+ - + ^3He + \beta^- , \quad (4.16) \]

where \( =Si^+ - \) represents a three fold coordinated, positively charged silicon atom. This process occurs throughout the amorphous silicon matrix, wherever bonded tritium is found.

Knowing the bonded tritium concentration from IR spectroscopy and the half-life of tritium, the dangling bond concentration as a function of time can be accurately expressed by the relation

\[ N_d(t) = N_T [1 - \exp(-\lambda t)] \quad (4.17) \]

where \( N_d(t) \) is the dangling bond concentration at time \( t \), \( N_T \) is the bonded tritium concentration estimated by IR spectroscopy, and \( \lambda \) \((=1.78237 \times 10^9 \text{ s}^{-1} [24])\) is the decay constant. The bonded tritium content of the film was estimated to be 7 at. \% or \( 3.5 \times 10^{21} \text{ cm}^{-3} \) Si-T bonds. This suggests that a potential \( 3.5 \times 10^{21} \text{ cm}^{-3} \) dangling bond defect concentration can arise in the amorphous silicon matrix. Figure 4.16 displays the tritium decay generated dangling bond concentration as a function of time in the tritiated film. Initially a sharp exponential
Figure 4.16. Tritium decay generated dangling bond defect concentration as a function of time in a freshly deposited tritiated film, DK.
increase in dangling bond defects is predicted.

Figure 4.17 plots the integrated luminescence intensity relative to that measured at time $t=5$ h against dangling bond density. At time $t=5$ h the dangling bond density was estimated to be $10^{17}$ cm$^{-3}$. In hydrogenated amorphous silicon a defect density equal or less than $10^{17}$ cm$^{-3}$ has small effect on the PL intensity [87]. It was therefore assumed that the PL efficiency of our sample was unity at the measurement time of 5h. From Figure 4.17 it can be seen that as $N_d$ increases the relative integrated intensity decreases.

In Figure 4.18 the experimental data was fit to Equation (4.13) which describes luminescence efficiency as a function of dangling bond density. The two parameters $\eta_0$ and $R_c$ were used to fit the data. $\eta_0$ was determined to be 1.11 and $R_c$ was 69Å. Typical values of $R_c$ are between 100 and 120Å [90]. The fit becomes poor for $N_d$ exceeding $2 \times 10^{18}$ cm$^{-3}$; the theory over estimating the decrease in luminescence efficiency.

Tsang and Street [88] have modelled the luminescence efficiency by defining a critical radius $R_c$ (see Equation (4.14)). The luminescence efficiency is then given by the fraction of electron-hole pairs which are
Figure 4.17. Luminescence efficiency versus dangling bond defect density.
Figure 4.18. Equation 4.13 (the model of Tsang and Street [89]) fails to accurately estimate the PL efficiency of the tritiated film DK for dangling bond concentrations exceeding $2 \times 10^{18}$ cm$^{-3}$. 

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created further than $R_c$ from the nearest defect. The distribution of distances is the nearest neighbour distribution function, $G(R)$, for randomly dispersed defects of density $N_d$, which is [94]

$$G(R) = 4\pi R^2 N_d \exp\left(-\frac{4}{3}\pi R^3 c \frac{N_d}{3}\right). \quad (4.18)$$

The luminescence efficiency is obtained by integrating $G(R)$ from the limits $R_c$ to $\infty$ and is given by Equation (4.13). Physically, radiative centers whose nearest non-radiative neighbours are less than $R_c$ away are assumed to have zero efficiency, and those pairs separated by more than $R_c$ have unit efficiency. This assumption, however, is only valid for low defect densities and at high defect densities the radiative contribution from pairs separated by less than $R_c$ cannot be neglected. As a consequence, the model of Tsang and Street [88] will always overestimate the decrease in luminescence efficiency [95].

To better describe the low temperature, PL efficiency of the tritiated film, the following approach was undertaken. In the case of two directly competing radiative and non-radiative processes with transition
rates $P_r$ and $P_{nr}$, respectively, the luminescence efficiency $\eta$ is given by

$$\eta = \frac{P_r}{P_r + P_{nr}}$$

(4.19)

and can be expressed as

$$\eta = \frac{\tau_r^{-1}}{\tau_r^{-1} + P_{nr}} = \frac{1}{1 + \tau_r P_{nr}}$$

(4.20)

where, $\tau_r$ is the radiative life time. $P_{nr}$ is a function of the dangling bond concentration, and therefore, is expected to increase with increasing defect concentration. For the sake of simplicity a single average $\tau_r$ has been used.

We shall now develop an expression for low temperature non-radiative tunnelling. As luminescence is a band tail process, the extended states will be ignored in the analysis that follows. The simplest situation is one where an electron is localized in a band tail state of energy $E_i$, a distance $R'$ from a localized hole in the valence band tail state. Here, the hole is considered fixed for simplicity and the motion of only the
electron is considered. These two carriers are surrounded by randomly distributed non-radiative centers of density \( N_d \). It is assumed that the defects are located at some energy \( E_i \) in the mid-gap states. At low temperatures the electron can tunnel only to low energy states. The hopping transition from electron state to defect state occurs by quantum mechanical tunnelling and is described by the relation

\[
v_{ij} = v_o \exp(-2R_{ij}/R_0), \quad E_j \leq E_i
\]  

where, \( R_{ij} \) represents the distance between electron and a defect state, and the other parameters have been described elsewhere.

The electron transition rate to a defect is a strong function of the density of defects. The average separation between electron and defect can be obtained from

\[
R_{ij} = \left(\frac{4}{3\pi N_d}\right)^{1/3}.
\]  

The typical tunnelling rate \( v_{\gamma\gamma} \) to defect states of density \( N_d \) can then be expressed as
Clearly, as the defect concentration increases the average separation between electron and defect state will decrease resulting in an exponential rise in $v_{pp}$. This approach has the virtue that exponentially fast rates (corresponding to rare, small separations) are not allowed to dominate the averages, which would be unphysical since only a small fraction of carriers are expected to be located in close proximity to a defect.

Equating the non-radiative tunnelling rate to the $v_{pp}$ tunnelling rate i.e.

$$P_{nr} = v_{pp},$$

(4.24)

enables the modelling of the luminescence efficiency as a function of $N_d$. This is shown below
In Figure 4.19 the luminescence data of Figure 4.17 is fitted to Equation (4.25). The two parameters $R_0$ and the product term $\tau_\nu_0$ were used to fit the experimental results. It can be seen that the fit is in good agreement with the data. A localization radius $R_0$ of 32Å was obtained from the fit. This value is larger than the localization radius of 12 Å estimated by Tsang and Street [78].

The localization radius of a localized electron wave function in the band tail states should have the form

$$R_0 \propto \frac{1}{(E_c - E)^v}, \quad E < E_c$$

(4.26)

where $E_c$ represents the conduction band edge and $E$ is the energy of the electron in a band tail state. $v$ is expected to be 0.5. As the electron moves deeper into the band tail states its wave function should become more localized. Spear and Cloude [96] have studied how the localization radius
Figure 4.19. Equation (4.25) fit to the PL efficiency of the tritiated film DK. There is good agreement between experiment and calculation.
of the electron wave function depends on energy. They estimate $v = 0.6$ in Equation (4.26). Their results indicate that $R_0$ can range from 13Å near the bottom of the tail states to values of 100 Å near the conduction band edge, corresponding to delocalized electron wave functions. Furthermore, the localization radius of a phosphorous donor in amorphous silicon is estimated to be 23 Å at an energy of 120 meV below the conduction band edge [97]. The localization radius of 32Å obtained from our PL data is therefore a reasonable value.

The varying localization radius does not significantly affect the analysis of the luminescence efficiency since at low temperatures, the distribution of trapped carriers in the band tail states is expected to follow the density of states. There is no direct evidence that the capture cross-section of a tail state depends significantly on its energy [98]. As band tails are described by exponential functions, the effective carrier population can be considered to have a mean energy and so a mean localization radius can be used.

The product term $v_0 \tau_r$ was determined to be 120 from the fitting of the luminescence data. Using a typical value
for $u_0$ of $10^{11}$ s$^{-1}$, $\tau_r$ was estimated to be $-10^{-9}$ s. This value is comparable to $\tau_{or}$ (see Equation (4.6)) and suggests a localized exciton emission process (where the electron and hole have almost complete spatial overlap) rather than radiative tunnelling, where $\tau_r$ is expected to lie in the range $10^{-6}$-$10^{-3}$ s. Radiative recombination in the nano-second time scale has been observed in amorphous silicon [99].

Finally, it should be noted that our description of the luminescence efficiency is fundamentally approximate and descriptive.

The Raman spectra and optical absorption analysis of tritiated amorphous silicon (in section 3.6) show that the structural disorder is similar to that of regular amorphous silicon. It can therefore be said that the decay of bonded tritium produces dangling bond defects with no enhanced disorder to the amorphous structure. This result is significant for luminescence studies, as luminescence can now be studied as a function of dangling bond density, independent of any other disorder effect. Prior to this, the luminescence as a function of dangling bond density was investigated by growing amorphous silicon material under widely varying deposition conditions. As the dangling bond concentration
in the material varied so too did the degree of structural disorder. Therefore, dangling bond density was not an independent variable in luminescence studies. This could be another reason why Tsang and Street's model [88] fails to accurately describe the low temperature photoluminescence efficiency of tritiated amorphous silicon.

The relatively weak temperature dependence of PL in tritiated films, as displayed by sample A215 in Figure 4.12, compared to regular amorphous silicon can thus be explained by the direct tunnelling of trapped carriers to large concentrations of non-radiative recombination centers. At the time of measurement the dangling bond concentration of the tritiated film was on the order of $10^{19}$ cm$^{-3}$. The efficiency of thermal quenching is significantly reduced in the tritiated film due to the very effective non-radiative tunnelling to defect states. Evidently, the presence of a large dangling bond concentration changes the temperature dependence of PL.
4.6 Significance on Applications and Future Directions

The PL results indicate that devices fabricated entirely from tritiated amorphous silicon films will fail over time. The creation of large, dangling bond defect densities will degrade material properties, leading to degradation in device performance. Active regions of a device should therefore be free of bonded tritium. The injection of β particles from a tritiated region of the device (the tritiated region acting, only, as a source of β particles) into a non-tritiated, active region, is one possible solution for taking advantage of β generated electron-hole pairs, without the corresponding problem of dangling bond defect creation in the active region. Another possibility, is low concentrations (~0.05%) of bonded tritium in amorphous silicon. This will reduce both the rate of defect generation, and, the total defect density in devices.

On a fundamental note, the strength of optical absorption by defects in mid-gap states provides useful information on defect densities. Photo deflection spectroscopy (PDS) [12] is a technique used to
investigate defect absorption. PDS can be used to correlate defect densities and dangling bond defect concentrations in tritiated amorphous silicon. Thus, providing further understanding on the role of dangling bond associated optical transitions.

Hydrogenated amorphous carbon is another semiconductor suited to tritium incorporation. Tritium should readily substitute hydrogen in this material. The visible, room temperature, luminescence properties of hydrogenated amorphous carbon [100] offers interesting and practical applications for β luminescent material. Furthermore, the role of the dangling bond defect in this semiconductor can be investigated using tritium decay.
4.7 Summary

In this chapter tritium decay in amorphous silicon was investigated by studying luminescence.

Energy exchange between β particles and the amorphous silicon matrix resulted in the generation of electron-hole pairs. Radiative recombination of these excess carriers was observed. The βL efficiency was on the order of a few percent.

Photoluminescence was used to probe radiative transitions in tritiated amorphous silicon. Tritiated films displayed relatively weak luminescence intensities and little temperature dependence.

The low temperature photoluminescence spectra of a freshly deposited tritiated amorphous silicon film was measured as a function of time. The luminescence intensity decreased exponentially with time. The decrease in luminescence was attributed to an increasing concentration of non-radiative centers - dangling bond defects created from the decay of bonded tritium atoms. A simple model was developed to describe the dependence of luminescence efficiency on dangling bond density.
Chapter 5

Conclusions

If you would increase your happiness and prolong your life, forget your neighbor's faults. ...Forget the peculiarities of your friends, and only remember the good points which make you fond of them. ...Obliterate everything disagreeable from yesterday; write upon today's clean sheet those things lovely and loveable.

Anonymous

The semiconductor tritiated amorphous silicon has been investigated for the first time. The deposition parameters for tritium incorporation into the amorphous network were determined by studying deuterium incorporation into amorphous silicon using a dc saddle-field glow discharge.

Infrared spectroscopy of deposited films identified the bonding of hydrogen and its isotopes. Induction effects were observed and related to monohydride clustering. The vibration frequencies of the silicon-tritium
bond indicates that tritium behaves as a heavy hydrogen atom. The silicon-tritium wagging frequency and absorption line shape have helped to identify the corresponding silicon-deuterium bond's wagging frequency and absorption line shape as due to a coupling of the silicon-deuterium wagging vibration and the amorphous silicon network. The concentration of bonded tritium was estimated from the integrated intensity of the silicon-tritium stretching vibration.

Raman spectra and optical absorption analysis of tritiated and regular amorphous silicon films indicate similar structure. These results suggest that tritium decay in amorphous silicon does not lead to enhanced disorder of the amorphous silicon matrix.

Luminescence spectroscopy was used to probe tritium decay in amorphous silicon. Evidence of β generated electron-hole pairs was observed from the self-luminescence of tritiated amorphous silicon.

A novel technique of introducing identifiable and accurately determinable defect concentrations into amorphous silicon is presented. The decay of a bonded tritium atom results in the creation of a defect- a silicon dangling bond. This defect is a non-radiative recombination center. The
concentration of these defects with time could be accurately estimated from radioactive decay analysis. The photoluminescence intensity of freshly deposited tritiated amorphous silicon decreases with time due to defect generation. An independent study of the role of dangling bond defects and luminescence efficiency was made. Analysis indicates that non-radiative recombination is due to the direct tunnelling of carriers to dangling bond defects.
Appendix A

Calibration of PL System

A 200 W quartz-iodine lamp (Qi CIN2) was used for the calibration. The spectral irradiance of the lamp had been calibrated (center of lamp filament to pressed MgO equals 43 cm) at a current of 6.5 A and 28.04 eV at the National Research Council. In Figure A1 is plotted the spectral irradiance at a distance of 43 cm. The spectral irradiance $I(\lambda)$ ($\lambda$ is the wavelength) from these lamps is based on the spectral radiance $M_\lambda$ of a black body as defined by Planck's equation

$$M_\lambda = \frac{2\pi \hbar c^2}{\lambda^5} \frac{1}{e^{\frac{\hbar c}{\lambda kT}} - 1}.$$  \hspace{1cm} (A.1)
Figure A1. Spectral irradiance of lamp.
Fitting this equation to the experimental data allowed the estimation of the irradiance for longer wavelengths. Figure A2 shows the fit.

In Figure A3 is shown the lamp's luminescence spectrum as measured by the PL system. A $\text{MgCO}_3$ block was exposed to the lamp radiance. Using geometric optics the power/nm at the monochromator slit was determined, see Figure A4.

To determine the transfer function relating the optical power incident on the slit of the spectrometer and the luminescence spectrum, the data in Figure A4 is ratioed with the data in Figure A3. Figure A5 shows the transfer function.

The βL spectrum in chapter 4 was measured with a sensitivity of 300 $\mu$V.
Figure A2. Equation A.1 fitted to spectral irradiance of lamp.
Figure A.3. Quartz-Iodine lamp spectrum measured using PL system.
Figure A.4. Lamp power spectrum at monochromater slit.
Figure A.5. Transfer function of PL system.
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