CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Hydrogenated amorphous silicon (a-Si:H) is currently the most widely employed thin film semiconductor. The main applications are in large-scale devices such as photovoltaic modules, active matrix liquid crystal (AM-LCD) and large area imaging sensors. The advantages of a-Si:H for devices are mainly due to its controllability of material properties and flexible design capability of the device structures. The material has a low defect density, thus allowing it to behave like a true semiconductor that exhibits doping effect. Besides being economical, this effect has contributed to the success of a-Si:H in microelectronics technology.

The major features of amorphous silicon arise from the chemical bonding which is completely covalent. Amorphous silicon\(^1,2\) have four outer electrons and thus each atom is in its lowest energy state when it is surrounded by a regular tetrahedron like atoms which is each covalently sharing one electron with the central atom. A regular array of such tetrahedron forms a diamond structure of crystalline silicon. In order to obtain amorphous silicon, a disordered structure must be produced.

However, amorphous semiconducting silicon cannot be obtained by rapid quenching from the melt because the short-range order of liquid silicon is metallic in nature. Amorphous films are commonly obtained by one of four main methods that is vapor deposition, sputtering in argon, electrolitically from
solutions of materials and by means of a glow discharge from silane or germane gas.

In the two main fabrication processes of the a-Si:H, that are glow discharge and reactive cathodic sputtering, the films are deposited in a plasma. Although all experimentalists found great sensitivity of the plasma to the various parameters, the derivation of the dominant features is still unknown. For glow discharge decomposition of silane, Brodsky\textsuperscript{3} emphasized the substrate temperature and silane pressure but then in his work with Deneuville\textsuperscript{4}, Brodsky emphasized flowrate in addition to his previous work while Fritzsc\textsuperscript{5}he highlighted the role of either cathodic or anodic deposition and Knights et al\textsuperscript{6} emphasized the argon dilution of the silane. For reactive cathodic sputtering, Paul\textsuperscript{7} and co-workers used the substrate temperature and the partial pressure of hydrogen in the reactive gas mixture. In this work, amorphous silicon film was produced by plasma glow discharge from silane gas.

2.2 The Structure of Amorphous Silicon

X-ray and electron diffraction experiments have contributed to the knowledge of the structure of amorphous silicon. Results have shown that the atoms in the amorphous solids are surrounded by a tetrahedron or other atoms with an average separation essentially equal to that in the corresponding crystal. There is a possibility that the amorphous material is made up of microcrystallites\textsuperscript{8} of about 20A. Another possibility is based on the fact that two possible crystal structures, the diamond and the wurtzite lattices, have identical tetrahedrally coordinated nearest-neighbor environment\textsuperscript{9-12}. However, the
second nearest-neighbor environment of these two structures is different. The diamond lattice only have "staggered" six-membered rings whereas the wurtzite structure have "eclipsed" six-membered rings. Figure 2.1 shows the configuration of both structures.

![Diagram of staggered and eclipsed structures](image)

**Figure 2.1:** (a) "staggered" (chain) configuration. (b) "eclipsed" (boat) configuration.

In the random network model which has been constructed by Polk\textsuperscript{13}, all atoms are surrounded by four covalent bonded atoms at the proper interatomic separation which leads to the refusal of any internal dangling bonds nor bond-angle distortion greater than 20°. Polk found that such a structure could be extended to fill all space with 97% of the density of the periodic crystal.

The density of amorphous silicon is found to be 5 to 30% less than its crystalline density. Donovan et al\textsuperscript{14,15} reported a 12 to 15% density decrease on carefully prepared films. This result is expected since density is a macroscopic property which includes voids, cracks and pinholes, all commonly found in thin films. The highest value obtained is the nearest to the ideal density of an
amorphous material and thus we can conclude that the density of amorphous silicon is quite close to the density of its crystal.

An ideal amorphous state\textsuperscript{16,17} is a state with near perfect short-range order without any long-range order. It has no internal dangling bonds and all valence requirements in the interior are locally satisfied. This state is metastable and represents a local energy minimum with respect to atomic rearrangements. On the other hand, as-deposited amorphous silicon is far from the ideal state and contains many voids within the structure. These voids lead to interior dangling bonds and they can dominate the electrical properties of amorphous materials. However, these voids can be made to disappear by annealing the amorphous films below the crystallization temperature.

The independence of unpaired spin density on thickness implies that the dangling bonds are distributed throughout the entire film, rather than being restricted to the surfaces. Since the unpaired spins are concentrated at the inner surfaces of voids rather than being randomly arranged, it is unfair to apply the concept of an average separation. If the size of the voids is assumed about $5\text{Å}$, then the average distance between voids of $10\text{Å}$ will result in a 12% density deficiency.

The absence of the electron paramagnetic resonance (EPR) signal in amorphous-silicon prepared by means of a radio frequency glow discharge from silane gas as reported by Brodsky\textsuperscript{18} proves that dangling bonds are not necessarily present in all amorphous-silicon films. It is likely that silicon prepared by this technique contains residual hydrogen that congregates in the voids and saturates the potential dangling bonds.
2.3 The Hydrogen Content

Amorphous silicon is a highly defective material due to its large density of dangling bonds. Addition of hydrogen results in structural relaxation in the covalent random network thus turning it into a material of high electronic quality.

In a-Si:H, hydrogen is incorporated in the silicon to reduce the number of dangling bonds. a-Si:H deposited by silane (SiH₄) glow discharge is found to have structural, chemical and electronic properties, which depend greatly on the deposition conditions. Therefor the hydrogen in the a-Si:H can be bonded in many phases such as the mono-hydride SiH, the dihydride SiH₂, the trihydride SiH₃ and the poly-hydride (SiH₂)n. Hydrogen presence is crucial in producing device-quality material. Therefor it is important to determine the hydrogen content of the material in order to reduce defects.

The properties of the a-Si:H films obtained either by glow discharge or reactive sputtering are very sensitive to plasma behavior. In a-Si:H prepared by glow discharge decomposition of silane, Brodsky et al¹⁹ showed an important concentration of hydrogen (14% < H/Si < 45%), the occurrence of SiH and/or SiH₂ bonding³ are being very dependent on the preparation parameters. With a similar type of preparation on spin free samples, Solomon et al²⁰ proposed an alloy type description of a-Si:H. Solomon prepared on the hydrogen concentration range of 10 to 15% and his proposal is mainly based on the increase of the optical gap when the atomic concentration increases within the films.
In an a-Si:H sample prepared by radio frequency cathodic sputtering of a-Si target in a hydrogen/argon reactive gas, Freeman and Paul\textsuperscript{7} found different optical gaps for the same hydrogen content (0-26\%) within the film and reported a monotomic increase of the gap with relative content of SiH\textsubscript{2} in the material. The different relationship found between hydrogen parameters and optical gap on limited preparation ranges suggests that a more general physical description of a-Si:H should be found.

Bruyere\textsuperscript{21} reported on the optical properties of a-Si:H prepared by cathodic sputtering of a-Si target in an 80\% argon and 80\% hydrogen reactive gas at about 9 \times 10\textsuperscript{-3} torr. Their results imply the occurrence of hydrogen atoms not bonded in the usual SiH or SiH\textsubscript{2} forms. The optical energy gap decreases with increase in deposition rate and is independent of the substrate temperature for deposition rates less than 30A/min. For higher deposition rates, the optical energy gap decreases as the substrate temperature increases. On the other hand, the refractive index increases toward the crystalline value as deposition rate increases and substrate temperature decreases. From the infrared stretching mode absorption curve, they found a dominance of the 2.000 cm\textsuperscript{-1} mode that usually attributed to the SiH site\textsuperscript{3,7} assuming that a single hydrogen atom is attached to a single Si dangling bond. Their results shows that deposition rate is an important parameter that decreases the hydrogen content within the layer monotonically without significant variation with substrate temperature. Bruyere suggested equilibrium between hydrogen bonds as SiH, SiH\textsubscript{2} and other forms and that the optical gap is controlled by the deformation of the silicon matrix by the various hydrogen species.
Brodsky et al\textsuperscript{19} reported total value of hydrogen between 50\% and 14\% in glow discharge from variations of the silane pressure and substrate temperature. Freeman and Paul\textsuperscript{7} obtained values between 26\% and 0\% by cathodic reactive sputtering from variation of the partial pressure of hydrogen in the reactive mixture and substrate temperature.

The a-Si:H layers exhibit the typical infrared absorption of the stretching modes of the Si-H bonds as SiH (2000 cm\textsuperscript{-1}), SiH\textsubscript{2} (2095 cm\textsuperscript{-1}), SiH\textsubscript{3}, (SiH\textsubscript{2})\textsubscript{n} or other sites. Anyway, the control between dominant SiH or SiH\textsubscript{2} bonding was only reported in glow discharge\textsuperscript{3,6}. Although the physical reason is unclear, Deneuville and Brodsky\textsuperscript{4} reported that as the number of recombination centers in the gap increases, the SiH\textsubscript{2} content in the film also increases. Knights et al\textsuperscript{22} reported an increase in the number of spins and a decrease of the luminescence when the (SiH\textsubscript{2})\textsubscript{n} content increases.

For reactive cathodic sputtering, Paul\textsuperscript{7} and Brodsky et al\textsuperscript{3} reported the dominance of SiH\textsubscript{2} (2095 cm\textsuperscript{-1}) or other H sites (2140 cm\textsuperscript{-1}) over SiH (2000 cm\textsuperscript{-1}). Bruyere\textsuperscript{21} only found the SiH\textsubscript{2} (2095 cm\textsuperscript{-1}) and SiH (2000 cm\textsuperscript{-1}) bands with a dominance of 70 to 90\% of SiH.

Since the size of the H atom is smaller than that of the Si atom, and the Si-H bond length lower than the Si-Si bond, the bonded hydrogen introduces a smaller decrease in the Si concentration than a substitutional atom. The hydrogen would mainly modify the short-range order in the amorphous silicon matrix. For glow discharge material, Brodsky et al\textsuperscript{19} reported a deficiency from 10\% (pure SiH) to 30\% (SiH\textsubscript{2}) compared to the Si concentration in bulk silicon.
Freeman and Paul reported a 20% decrease in their film density as the hydrogen content increases from 0 to 26%.

In their alloy model, Solomon et al.\textsuperscript{20} assumed complete homogeneous hydrogen bonding as SiH and predict a monotonic increase of the optical energy gap as SiH bonds increases. In Bruyere's\textsuperscript{21} work, although the optical energy gap decreases monotonically as the deposition rate increases, it was clearly observed that for deposition rates below 30A/min, the optical energy gap is independent of the substrate temperature. The role of the hydrogen atoms would be mainly to allow and/or induce a wide range of structure for the amorphous silicon matrix and the energy gap of a-Si:H is very dependent on the structure of the amorphous silicon matrix.

In his writing on the growth and structure of amorphous silicon, Street\textsuperscript{23} believe that exposure of the surface to atomic hydrogen increases the surface concentration and causes hydrogen to diffuse into the film. The shape of the concentration profile is the same as for the normal hydrogen diffusion, indicating that the extra hydrogen is bonded to silicon atoms. The only source of the excess Si-H bonds is from the breaking of weak Si-Si bonds as there are not enough dangling bonds in the film to absorb the extra hydrogen. Atomic hydrogen is free to move in and out of the surface during the film growth. The diffusion allows the hydrogen to react with the silicon network in the subsurface region after the silicon has attached to the surface. The hydrogen then terminates dangling bonds and removes weak bonds while excess hydrogen is evolved from the film. The hydrogen exchange between the film and the plasma establishes equilibrium between the plasma gas and the film. Thus the hydrogen
concentration in the film and the reactions in the network is dependent on the chemical potential of the hydrogen in the plasma. Weak Si-Si bonds which is below the hydrogen chemical potential are broken while stronger bonds remain.

The concentration of hydrogen in the a-Si:H films actually decreases when hydrogen is added to the plasma. This is an indication of the complex interaction between the hydrogen and the silicon bonding structure. The reconstruction of the silicon network might shift from a low to a higher chemical potential, replacing weak bonds with stronger bonds.

The optimum growth temperature of a-Si:H film is about 200 to 300°C. This can be explained by the hydrogen interactions in which at much lower temperatures, the diffusion coefficient is too low to allow structural equilibrium while at much higher temperatures, the chemical potential is lower and hydrogen does not remain in the film thus does not remove weak bonds. Both conditions result in a more disordered structure.

Excess hydrogen also induces a transition to microcrystalline silicon. This is due to too many weak bonds in the minimum disorder of an amorphous network thus inducing crystallization. The most ordered structure should occur when the hydrogen chemical potential is at the highest and this corresponds to the conditions for microcrystalline growth.

2.4 The Role of Argon

It has been indicated that argon atoms play the role of steric hindrance against not only H₂ effusion but also thermal arrangement of H local environments, but due to its non-chemical reactivity, less attention has been
paid to it. Tanaka et al\textsuperscript{24} had studied the role of argon involved in plasma-deposited a-Si:H. They found that argon atom is inevitably incorporated into a-Si:H as an impurity depending on deposition conditions such as gas pressure and radio frequency power.

Argon atoms incorporated in the films never effuse at least up to annealing temperature of 400\textdegree C. For some reactive sputtering samples, evolution of argon occurs explosively at 450 to 500\textdegree C depending on the film thickness, which simultaneously accompanies destruction of the film. Argon atom does not show any characteristic behavior against annealing. It was noted that films prepared by sputtering and glow-discharge techniques show the similarity in the manner that they release hydrogen despite the essential difference in the deposition kinetics.

Films involving a larger amount of argon release their hydrogen at higher temperatures compared to films with small amount of argon. It suggests that in the a-Si:H film, the steric hindrance role played by argon against H diffusion is independent of preparation techniques. Microscopically, argon atom seems to inhabit a structural defect, which is possibly a void, associated with dihydride (SiH$_2$). This is due to the striking difference in hydrogen effusion between argon-rich and argon-poor films, which is originated in the difference in effusion rates of H from dihydride sites.

Tanaka et al\textsuperscript{24} also observed an increase in argon content with an increase in radio frequency power. The strong relation between argon content and median wave number may be ascribed to two independent effects: One is the role of argon as steric hindrance associated with SiH$_2$ and two is an indirect effect

14
essentially prevailing in plasma deposition process. Knights\textsuperscript{25} has reported that higher radio frequency power produces a-Si:H films with lower ratio of monohydrite to dihydrite mode absorptions.

Das et al\textsuperscript{26} studied the structure of the hydrogenated amorphous and microcrystalline silicon films deposited by radio frequency glow discharge decomposition of silane diluted in argon. In their work, they observed that argon acts as a passive diluent gas as well as playing an important role in the growth of the amorphous or microcrystalline network. Calculation of the variation of equilibrium concentration of argon atoms with argon dilution shows that at high argon dilution, equilibrium concentration of argon rises sharply with increase in argon dilution. Variation of structural properties with argon dilution suggests that involvement of these excited states of argon in the growth process.

Through TEM studies, Das et al\textsuperscript{26} observed structural changes at the amorphous-microcrystalline boundary. Argon diluted samples were deposited at 35 mW/cm\textsuperscript{2} radio frequency power density. The inhomogeneities on the scale of about 50 nm observed in the micrograph may result either from density variation of the amorphous material or due to some structures on the film surface. However, when scanned by electron microscopy, no surface structures of that particular scale have been observed. Therefore it is probable to conclude that film deposited with 95% argon dilution has some variations in bulk density. On increasing the radio frequency power density at the same argon dilution, small dark spots surrounded by dark patches appear in the TEM micrograph. However, the corresponding diffraction pattern does not show any evidence of microcrystallites.
Increasing the argon dilution to 98% while keeping the radio frequency power density at 160 mW/cm² results in the formation of microcrystallites. The corresponding transmission electron diffraction pattern shows the sharp ring for Si\(111\) planes.

At 99% argon dilution and low radio frequency power density (35 mW/cm²), the film is almost homogeneously amorphous with well separated dark patches within which dark spots appear. Increasing the radio frequency power density to 80 mW/cm² results in huge clustering of the dark spots. The corresponding diffraction pattern shows the microcrystalline nature of the film from the clear diffraction rings corresponding to different Si-crystal planes. Higher radio frequency power density reduces the size of the microcrystals and prevents the cluster formation. A distinct difference between higher radio frequency power density and addition of hydrogen in the mixture is that the dark patches surrounding the dark spots vanish in the latter case.

From the results of their experiment, Das et al\(^{26}\) has summarized that (1) microcrystal grains start to develop within a higher density region. This may result from large-scale structural variations in the bulk when the argon dilution is increased beyond 95%; (2) there is a sharp increase of the microcrystallite clustering when argon dilution is increased from 98% to 99% at a moderate radio frequency power density of 80 mW/cm²; (3) increase of argon dilution at a constant power density lowers the intensity of TA mode at 160 cm\(^{-1}\); and (4) in the argon diluted amorphous and microcrystalline samples, hydrogen content is high and hydrogen is predominantly bonded in monohydrite mode.
In their discussion, Das et al\textsuperscript{26} mentioned that the Ar density in a SiH\textsubscript{4}-Ar rf glow discharge, plasma has been observed to rise slowly with argon flow below 90% of the silane-argon mixture while above 90% argon dilution, increase of the Ar density is very sharp. Ar plays a vital role in the process of dissociation of silane at high argon dilution. Some the Ar reacts with the SiH\textsubscript{4} molecules to form radicals such as SiH\textsubscript{3} and SiH\textsubscript{2}. A more compact amorphous silicon network with lower microstructure factor is deposited when argon dilution was increased from 0% to 90%\textsuperscript{27}.

It was suggested that energy released by Ar is absorbed in the neighboring lattice which may help in the formation of a more compact a-Si:H network. This suggestion is visualized as a two-step process. First, energy released by Ar breaks up weak Si-Si bonds. A portion of the energy obtained from the deexitation of Ar may also be utilized in releasing loosely bonded hydrogen from SiH\textsubscript{2} sites. Second, the dangling bonds resulting from the breaking of weak Si-Si bonds form strong bonds with silicon or are terminated by hydrogen. As a result, there will be an increase in SiH in the material as well as a lowering of the microstructures originated from voids and strains. The presence of large quantity of bonded hydrogen in monohydrite form together with low microstructure in these materials led to less light-induced degradation of the photoconductivity\textsuperscript{27}.

The sharp increase of Ar concentration over a small increase of argon dilution is responsible for the sharp structural change from amorphous to microcrystalline. Development of the microcrystalline grains within the dense region support the role of Ar in the formation of microcrystals in the hydrogen-
depleted regions. At still higher argon dilution of 99% microcrystalline formation is observed at a lower power density of 80 mW/cm². This clearly shows the importance of Ar in the formation of large size (500Å) microcrystallites.

2.5 The Optical Energy Gap

The optical band gap depends mostly on the total hydrogen content of the film and is less influenced by neither the microstructure nor the hydrogen bonding. The optical band gap is also dependent on defects of the pure silane matrix and the actual hydrogen content of the film.

The position and shape of the absorption edges in amorphous silicon is very sensitive to the quality of the film and so is the optical absorption. Highest quality films are judged by the smallest density of dangling bonds and with sharp absorption edges near 1.0 eV.

As-deposited films generally show an exponential band tail but this tail is not intrinsic to the material and disappears upon annealing below the crystallization temperature. The EPR and structural studies have shown that such annealing results in a sharp reduction in void density. This lead to the conclusion that the absorption tail actually arises from the presence of dangling bonds in the material. The extended nature of the absorption indicates that the states resulting from these dangling bonds do not have discrete energy values. The most likely reason for this is that the voids are not just single vacancies or divacancies but represent roughly 15 to 30 missing atoms. Thus, besides the voids being structurally distinct, the long-range disorder of the material also
manifests itself over the volume of the void. However, the voids extend only over a range of the order of $10^8\text{Å}$.

In Bruyere’s$^{21}$ work, although the optical energy gap decreases monotonically as the deposition rate increases, it was clearly observed that for deposition rates below $30\text{Å}/\text{min}$, the optical energy gap is independent of the substrate temperature but is dependent of the substrate temperature for higher deposition rates.

Tanaka et al$^{24}$ reported that the annealing temperature that gives a maximum optical energy gap nearly corresponds to where $H$ effusion starts. It has been pointed out that optical energy gap of glow discharge films is mainly determined by the amount of bonded $H$. At annealing temperatures higher than $350^\circ\text{C}$, optical energy gap decreases because the films release their hydrogen.

2.6 The Glow Discharge Technique

Generally, the techniques for the preparation of amorphous silicon from a silane glow discharge were developed largely on an empirical basis. The following discussion is of reactors, techniques and deposition conditions that have been used to produce electronically viable amorphous silicon films.

2.6.1 Radio Frequency Deposition System

There are two groups of glow discharge deposition units differing in the method of coupling the radio frequency (rf) excitation into the plasma. The first group is glow discharge deposition that is carried out in an inductively coupled system. This method is convenient in depositing small area specimens. Figure
2.2 illustrates the method. It consists of a gas inlet, a fused silica reaction tube, a substrate holder, a heated pedestal and a rotary pump.

![Diagram](image)

**Figure 2.2:** Inductively coupled glow discharge deposition system\(^{28}\).

In this technique, the gas is passed through a fused silica reaction tube of diameter 5 to 10 cm. The pressure lies in the range of 0.1 to 1 torr at gas flow rates between 0.1 and 10 cm\(^3\)/min operating at STP. A rotary pump maintains the gas flow through the system. The substrate is held on the heated pedestal, which is immersed in the lower part of the glow discharge plasma. The plasma is excited by an external coupling coil connected to a rf generator that usually operate at a frequency of 13.56 MHz.

In this technique, the film grows in close contact with the plasma and its electronic properties are critically dependent on the interactions taking place at
the interface. The reproducibility and the quality of the specimens is possible to maintain if careful attention is taken to all the parameters involved. Sensitive variables include the height of the rf coil above the substrate, the substrate temperature and the rf power level. It has been generally found that for the lowest density of gap states, the substrate temperature values is required to be between 250°C to 330°C and the rf power is at low level of 1 to 10W. These values are just enough to maintain a weak glow discharge.

The second type of the deposition system employs capacitive coupling. Figure 2.3 illustrates a versatile unit designed by Knights. An obvious advantage over the inductive system is that the capacitative type has a parallel plate geometry that can be scaled up for the uniform deposition of larger area specimens. It can be seen that the upper electrode holding the substrates can either be connected to the rf ground potential or to the hot rf electrode. In the latter case, the substrate surface will acquire a steady negative bias, which can influence the material properties. The values of parameters such as pressure, flow rate, substrate temperature and rf power mentioned for the inductive system can well be applied to the capacitative system.

A schematic diagram of a system that has been used in the Dundee laboratories is shown in figure 2.4. The system has been designed to reduce the contamination problem and to achieve optimum versatility, particularly for the deposition of multilayer specimens. The stainless steel specimen holder and its electrically insulated heater are mounted vertically to reduce the deposition of small particles that are difficult to eliminate completely from a plasma system. The specimen holder is held in a demountable quartz enclosure and the
Figure 2.3: Capacitatively coupled glow discharge deposition system designed by Knights\textsuperscript{29}. 

\textit{Chapter 2}
rf field is applied between the external electrodes which are electrically connected together and adjusted parallel to the surface of the specimen holder. The whole of the specimen holder assembly is insulated from the ground and can easily be withdrawn from the apparatus for substrate loading. Two thermocouples are incorporated to monitor the temperature of the holder and of the substrate surface.

The gas handling system is made entirely from stainless steel and consists of the five channels, all connected to the mixing chamber. Each channel is fitted with a mass flow meter and a piezoelectric valve for electronic flow and ratio control. For safety purposes, nitrogen flushing lines are provided at several parts of the apparatus. The whole system is normally kept under high vacuum that helps in reducing cross contamination from gases that have been used in previous depositions. During a deposition run, the cryo-pump is shut off and the gas flow is maintained by the rotary pump. The tubular furnace mounted in front of the pump decomposes the hydrides, which reduces contamination of the pump oil and adds to the safety of the system. The mass spectrometer is a useful part of the unit that allows examination of a gas sample before deposition. Finally, to comply with safety regulations, the whole apparatus, including the gas supplies are kept in a continuously ventilated enclosure.

2.6.2 The Deposition Rate

Experiments have shown that high quality amorphous silicon films are obtained when prepared in the silane glow discharge at deposition rates of less than about 3 Å/s and the rf power is at and the minimum. Under these
conditions, ion and electron energies in the plasma remain sufficiently low to reduce defect formation at the growing surface.

Scott et al\textsuperscript{30} have investigated the deposition and electronic properties of glow discharge amorphous silicon specimens produced from di-silane (Si\textsubscript{2}H\textsubscript{6}) and tri-silane (Si\textsubscript{3}H\textsubscript{8}), both of which form less stable molecules than the monosilane. The encouraging result was that with a low rf power, the deposition rate from the higher silanes was more than 20 times larger than that obtainable from SiH\textsubscript{4}. Moreover, films up to 20 μm thick could be deposited. This is probably because of reduced film-substrate strain. In monohydride depositions, such thicknesses are difficult to achieve without flacking-off, which suggests that structural and morphological differences may exist between the films produced by the two methods.

In their discussion on the deposition mechanism, Scott et al\textsuperscript{31} suggest that the initial rate-determining step in the decomposition of silanes involves formations of the SiH\textsubscript{2} diradical with the following equations.

\[
\text{SiH}_4 \longrightarrow \text{SiH}_2 + \text{H}_2 \\
\text{Si}_2\text{H}_6 \longrightarrow \text{SiH}_2 + \text{SiH}_4
\]

The significant point is that the reaction in the latter equation is about 100 times faster at 400°C than that given by the former. This leads to the conclusion that the higher deposition rate obtainable in Si\textsubscript{2}H\textsubscript{6} decomposition is closely related with the greater rate of SiH\textsubscript{2} production in the plasma.
Figure 2.4: Vertical glow discharge deposition system used at the Dundee laboratory\textsuperscript{28}.
2.6.3 Recent Studies of the Silane Plasma

In spite of the widespread use of the glow discharge techniques, the reactions taking place in the silane plasma and particularly at the plasma-substrate interface, are still not properly known.

Experimental works done on the silane plasma has a twofold objective, that is first, to identify the species and reactions involved in the growth of the film and second is to relate well characterized plasma conditions to the electronic properties of the amorphous specimens. The most commonly used method is optical emission spectroscopy by which the radiation from the de-excitation of atoms and molecules in the plasma can be studied. The main advantage of this approach is that it does not perturb the plasma and can also be used as a permanent monitor to achieve reproducible plasma conditions. However, this technique is only applicable to emitting species and it is essential to complement it by other techniques such as mass spectroscopy.

The weak glow discharge usually employed in glow discharge decomposition produces a dilute plasma state, which comprises a wide variety of species including electrons, ions, excited neutrals and photons. All these particles participate in the interactions to varying degrees. The rf glow discharge is maintained by inelastic electron collisions, which in the case of the silane plasma lead to reactive neutral species such as SiH, SiH₂, SiH₃, Si₂H₆, H, H₂ and ionized species.

In the recent works, the optical emission intensities have been investigated as a function of deposition parameters such as flow rate, growth rate, pressure and rf power. The experiments have also been extended to plasmas containing
dopant gases, SiH₄-SiF₄ mixtures and gaseous impurities. Some of the results suggest a relationship between the intensities of the H and SiH lines and the IR absorption in the Si-H vibrational band of the film.

2.7 References


