Chapter 7
Discussion

7.1 Introduction

Amorphous silicon prepared by plasma deposition from silane has hydrogen involving and participating in the reactions for film formation. Most hydrogen in the silane gas is dissociated from Si in the deposited film but a certain percentage gets incorporated into the film. These incorporated hydrogen plays an important role in reducing defect in the film. However, not all the hydrogen incorporated are effective in reducing defects. It is the way the hydrogen gets incorporated that determines the effectiveness of defect reduction. In this work, the hydrogen content in the film is determined by two different techniques, the Valence Electron Model (VEM) and the Chemical Bonding Infra-red Model (IRM). Initially in Section 7.2, the growth mechanism of a-Si:H thin film is presented, and later followed by the hydrogen diffusion and evolution mechanisms in annealed a-Si:H in Section 7.3. These two sections are presented to relate these growth, diffusion and evolution
mechanisms to the hydrogen content in as-prepared and annealed films in Sections 7.4 and 7.5 respectively. Section 7.4 specifically discusses the effectiveness of helium dilution of silane in the dc plasma glow discharge in increasing the deposition rate and improving the homogeneity of the film. Section 7.6 starts off with discussing the effects of annealing on the hydrogen content as calculated by the VEM and the IRM and these hydrogen content are then related to the hydrogen content in the film at the monohydride and polyhydride bonding sites of H atoms to Si atoms. The hydrogen content calculated by the VEM is found to be strongly linked to the hydrogen content at the Si-H bonding sites and this link is strongly supported when the VEM hydrogen percentages are related to the optical energy gap, the dc dark conductivity and density of states at the fermi level of the film.

The hydrogen percentage calculated by the IRM model is the total hydrogen percentage in the film and this section concludes that both the H percentages are important in determining the film quality.

7.2 Review of Growth Mechanism of a-Si:H Film

The main emphasis of this work is to study the hydrogen content in a-Si:H film and the effect of hydrogen on some of the film properties. Thus, a brief review on the growth kinetics of a-Si:H film prepared from plasma discharge of silane (SiH₄) is presented to effectively discuss the incorporation of hydrogen in these films later. Since for each Si atom there are four H atoms in SiH₄, most of the H is dissociated in the deposition process. It is the result of incomplete dissociation of SiH₄ that that caused H being incorporated into
the film. In this work, a-Si:H film is prepared from the dc glow discharge of pure SiH₄ or SiH₄ diluted in helium, thus the H present in the film are mainly from the hydrogen radicals in the plasma dissociated from SiH₄ molecules and not from the dilution of SiH₄ by hydrogen.

Thin films of a-Si:H are the product of numerous reactions that is the homogeneous reactions which influence the composition of the discharge atmosphere, and the heterogeneous reactions which occur at the substrate surface. The homogeneous reactions are initiated by electron-impact dissociation of SiH₄ gas molecules into radicals ready to react with surface sites of the growing film. Electron impact SiH₄ that occurs most frequently are¹

\[
\begin{align*}
\text{SiH}_4 & \xrightarrow{4.4 \text{ eV}} \text{Si} + 2\text{H}_2 \quad \text{(7.1)} \\
\text{SiH}_4 & \xrightarrow{5.9 \text{ eV}} \text{SiH} + \text{H}_2 + \text{H} \quad \text{(7.2)} \\
\text{SiH}_4 & \xrightarrow{2.2 \text{ eV}} \text{SiH}_2 + \text{H}_2 \quad \text{(7.3)} \\
\text{SiH}_4 & \xrightarrow{4.4 \text{ eV}} \text{SiH}_3 + \text{H} \quad \text{(7.4)}
\end{align*}
\]

Since the average electron energy in glow discharge is 1 - 2 eV, thus most of the reactive species in the plasma are neutral radicals². However, there is no straight forward correlation with the concentrations of radicals SiH₂ and SiH₄ in the gas phase to SiH and SiH₂ groups in the resulting film¹. The heterogeneous reactions which occurs at the film surface can be expressed by the following equation¹,

\[ \text{SiH}_3 \text{ (plasma)} \leftrightarrow \text{Si (solid)} + \text{XH (plasma)} \quad \text{(7.5)} \]
The forward reaction represents film deposition while the reverse reaction represents hydrogen "etching" of the film surface. The reverse reaction occurs even in the case of pure SiH₄ plasma deposition. This hydrogen "etching" process preferentially eliminates weak or strained bonds, which normally would require a rather high process temperature to remove. Energetically unfavourable configurations will be eliminated during film growth, so that the surviving configurations tend to be energetically more stable. Some studies on the heterogeneous reactions on the film surface as a result of plasma-discharge of SiH₄ suggest that the growth process on the substrate is strongly influenced by the disproportionate reactions for the SiH₂ radicals

\[
\text{SiH}_2 (g) \rightarrow \text{SiH}_x (s) + \text{SiH}_4 (g) + H_2 (g) + H_2 (g) \quad \text{(7.6)}
\]

\[
\text{SiH}_2 (g) \rightarrow \text{SiH}_x (s) + (1 - 0.5x)H_2 \quad \text{(7.7)}
\]

Excited hydrogen also plays an important role in the chemical process of a-Si:H growth as demonstrated by the following heterogeneous reactions

\[
\text{SiH} + H \rightarrow \text{Si} (s) + H_2 (g) \quad \text{(7.8)}
\]

\[
\text{SiH} + H \rightarrow \text{SiH}_2 (g) \quad \text{(7.9)}
\]

The SiH₂ molecules may then be converted to adsorption state of SiH to create solid silicon surface through the reactions

\[
\text{SiH}_2 (g) + \text{Si} (s) \rightarrow \text{SiH} (a) \quad \text{(7.10)}
\]

or

\[
\text{SiH}_2 (g) + H (g) \rightarrow \text{Si} H (a) + H_4 (g) \quad \text{(7.11)}
\]

Neutral radicals - such as H, SiH, SiH₂ and SiH₃ are possible chemical intermediates responsible for a-Si:H growth from SiH₄ plasma however SiH
and SiH₂ are more easily inserted into SiH surface bonds rather than SiH₃ since SiH₄ requires generation of a free Si bond to be incorporated⁸⁻⁹.

7.3 Hydrogen Diffusion and Evolution Mechanism in Annealed a-Si:H

Plasma-deposited a-Si:H from SiH₄ contains a significant H atomic fraction¹⁰,¹¹,¹² as mentioned earlier. The deposition temperature strongly determines the hydrogen content in the film. Annealing of plasma-deposited a-Si:H films from SiH₄ provides information concerning the H bonding configuration in the film.

For a-Si:H deposited at low substrate temperature (high H concentration) there are two H temperature evolution peaks when the film is annealed. One occurs near 300 °C and the other at 500 °C¹³,¹⁴. Low temperature evolution is associated to SiH₂ complexes while Si-H type bonds account for the higher temperature peak¹³. Samples with low H concentration exhibit only the high temperature peak since H remains primarily in Si-H bonding configurations even following diffusion¹³,¹⁵. Annealing at temperatures less than the deposition temperature for high H content samples only reshuffles hydrogen while at the same time removes active dangling bonds and other midgap defects¹³,¹⁴. The H content remains virtually unchanged. Annealing these samples at higher temperature causes the release of weakly bonded hydrogen as indicated by the first evolution peak¹⁴. When the annealing temperature exceeds 400 °C, a net decrease of defect density results and also a small concentration of dangling bonds appears caused by the failure of broken Si-H bonds to build reconstructed Si-Si bonds. Several models are proposed to
explain the diffusion and evolution of H caused by annealing of a-Si:H samples. R.A. Street et al.\textsuperscript{16} proposed a diffusion mechanism whereby interstitial H insert itself into weak Si-Si bonds which are usually due to overstretched or distorted bonds, forming new Si-H bonds and dangling bonds. As the H atom moves into another interstitial position it leaves behind an unterminated Si bond which can recombine with the dangling bond formed by the hydrogen insertion to reform a covalent Si-Si bond. This mechanism as illustrated in Figure 7.1 shows that H hops from one bonded site to another which constitutes the basic diffusion step. The final step in this mechanism leads to the out-diffusion of H from the film when the sample is annealed at 400 °C or higher.

Another model which is proposed by S.T. Pantelides\textsuperscript{17} is based on the existence of two primitive intrinsic point defects, namely dangling bonds and floating bonds. A dangling bond is three-fold coordinated Si atom and a floating bond has an extra atom thus is five-fold coordinated Si atom. Floating bonds can migrate very efficiently by bond switching. The extra bond is passed from one Si atom to another with only small movements of a few atoms, as shown in Figure 7.2. The description of defect dynamics by this model start off with the migrating floating bond reacting with Si-H bonds and releasing H in an interstitial configuration. In the following two reactions, FB denotes a floating bond, $\text{H}_i$ denotes interstitial H and $\square$ denotes a four-fold coordinated network.

$$\text{FB} + \text{SiH} \leftrightarrow \square + \text{H}_i \quad \cdots \cdots \cdots \cdots \cdots (7.12)$$

The reverse reaction or an interstitial H running into a floating bond result in the formation of Si-H bond.

$$\text{H}_i + \text{FB} \leftrightarrow \square + \text{Si H} \quad \cdots \cdots \cdots \cdots \cdots (7.13)$$
Figure 7.1: Schematic diagram indicating the hydrogen diffusion mechanism, by which the hydrogen moves from a Si-H bond into an interstitial position, inserts into a strained Si-Si bond, and finally passivates preexisting dangling bond. [after J. Kakalios et al.18]
Figure 7.2: Schematic illustration of the mobility of a floating bond by bond switching. [after S.T. Pantelides\textsuperscript{17}]

Figure 7.3: Passivation of floating bond by a hydrogen atom. [after S.T. Pantelides\textsuperscript{17}]
This reaction describes the passivation of a floating bond as illustrated in Figure 7.3. The spontaneous "Frenkel"-pair creation

\[ \emptyset \leftrightarrow \text{FB} + \text{DB} \]  

is another defect dynamic reaction, where DB stands for dangling bond. The reverse reaction is the mutual annihilation that occurs when a migrating FB encounters a DB. The reaction viewed in either direction is illustrated schematically in Figure 7.4.

The last reaction describing this model is the hydrogenation of dangling bonds i.e.

\[ \text{H}_2 + \text{DB} \leftrightarrow \emptyset + \text{SiH} \]  

The above reaction can be used to explain the reduction of defects by hydrogen and the evolution of H from the film at fairly low temperature due to annealing.

7.4 Growth Mechanism Model of a-Si:H Films

The way H is incorporated into the structure of a-Si:H film is very effective in reducing defect density, rather than the quantity of H content in the film. Defective a-Si:H prepared at room temperature contains much more hydrogen than the device-quality material generally obtained in the range of 200-300 °C \footnote{20}, except the hydrogen is bonded in the more defective modes of SiH\textsubscript{2}, SiH\textsubscript{3}, or (SiH\textsubscript{2})\textsubscript{n} \footnote{21}. Hydrogen incorporated into a-Si:H are bonded predominantly as monohydrides, Si-H \footnote{22} are less defective and more homogeneous. Hydrogen dilution in plasma-discharged a-Si:H is known to etch away unfavourable configurations in the film structure so that surviving configurations, being less defective, tends to be energetically more stable \footnote{22}.
Figure 7.4: Schematic illustration of dangling-bond and floating bond pair creation or annihilation by bond switching. [after S.T. Pantelides]
Films grown from helium diluted SiH₄ plasma are also found to be more homogeneous irrespective of the sign of the bias voltage\textsuperscript{23}, i.e. the film demonstrate a high degree of Si-H bonding. Thus, helium dilution seems to play a role in incorporating H effectively into the film structure in such a way that the defect density is minimized. In Section 6.2.1, it is observed that the a-Si:H cathode samples from strongly diluted SiH₄ in helium plasma (SAR3B, He:SiH₄ = 20:1), have predominant Si-H bonding configuration. This observation strongly supports the fact that the helium dilution is effective in producing less defective a-Si:H film from the plasma discharge of SiH₄. Helium being a very light gas while SiH₄ being a heavy gas results in helium dilution being more effective at the cathode and SiH₄ concentration being higher at the base. However, the effect of deposition temperature, pressure and discharge power during the preparation of the films are also critical to effectively reduce defects when depositing a-Si:H film from dc discharge plasma of SiH₄ diluted in helium. Very low H content (~ 2 %) a-Si:H films illustrates inferior optoelectronic properties (refer section 6.2) especially when the substrate temperature and discharge power are relatively low. On the contrary a high deposition pressure (~ 1.4 mbar) is not necessarily due to the partial pressure of SiH₄ and He gas (compare samples SAR3 and SAR6). Deposition at a lower pressure of but with a moderate SiH₄ flow-rate results in a high H content (~ 10.5 %) and better optoelectronic properties (refer section 6.2). However, diluting silane with helium in plasma-discharged films can also be defective to the film at certain He to SiH₄ ratio, irrespective of the discharge power, deposition temperature or pressure. Preparation with a He
to Si:H$_4$ ratio of 1:1, at moderate deposition temperature of around 260 °C, discharge power of around 4 watts and deposition pressure of around 0.8mbars is found to possess oxygen contamination and H are incorporated into the a-Si:H film in bonding configurations other than pure Si-H bonds (as analysed in the previous chapter). Thus the resulting a-Si:H films have a large optical energy gap (≈ 2.16 eV) and a low dc conductivity (≈ 10$^4$ Ω$^{-1}$ cm$^{-1}$). A high conductivity is not typical for an intrinsic a-Si:H film especially when the film has a high H content of ≈12% (refer sections 6.2 and 6.3). Some form of doping are probably present in this film perhaps due to the incorporation of impurity atoms into the film. Therefore it can be deduced that the 1:1 ratio of helium to silane flow-rates is defective to the formation of a-Si:H film.

On the other hand without He dilution of SiH$_4$ in the discharge gases, produces predominant bonding species such as the Si-H$_2$ bonds, as indicated by the Si-H$_x$ stretch absorption band at ≈ 2060 cm$^{-1}$. A low optical energy gap of less than 2eV as compared to the other samples is probably due to H-related defect states and increasing columnar microstructures, especially as observed in films with dominant polyhydride bonding configurations$^{34}$. The low density of states at the Fermi level N(E$_f$) of ≈ 10$^{16}$ eV$^{-1}$ cm$^{-3}$ indicates that the sample has a low dangling bond and floating bond density, thus removal of defects by bond switching are also less probable. Thus, helium dilution of a-Si:H film specifically as demonstrated by the samples produced by our system can be effective in producing respectable quality films with predominant a-Si-H bonding configuration, that is if the helium to silane ratio is optimized and the deposition pressure maintained so that the deposition pressure is due to the
total partial pressure of the reactive and diluent gases, provided the deposition temperature is maintained within the range of 200 °C to 300 °C.

A mechanism on the growth process of a-Si:H film prepared from the dc glow discharge of SiH₄ diluted in helium is proposed here in this work. High deposition pressure which is due to the total pressure contributed by the reactant and diluent gases results in a high ionization current. Homogeneous reactions as in equations 7.1 to 7.4 due to ion-impact dissociation is highly enhanced by the presence of helium in the discharge gases, irrespective of the potential across the electrodes. This enhancement in ion-impact dissociation is mainly due to the more frequent collisions since the high concentration of ions and atoms in the plasma results in a smaller mean free path. Also since the electron energy is lower because of the more frequent collisions and the lower voltage across the electrode, reaction following 7.3 is more dominant. Consequently, results in a higher concentration of Si-H₂ radials and H₂ molecules in the plasma. Since the growth process on the substrate is also strongly influenced by the disproportionate reactions for the Si-H₂ radials especially following reactions 7.6 and 7.7 thus the growth process is strongly enhanced by this effect. Helium atoms also aids the migration of the adsorption species to the site that incorporates the atom into the film structure, hence increasing the deposition rate. The He atoms being small are packed very close together in the vicinity of the substrate thus producing a shielding effect to the growing film from damaging ion bombardment. This shielding effect can also allow etching of defects from the film by the insertion of interstitial H into weak Si-Si bonds as proposed by R.A. Street et al. and
bond-switching mechanism as proposed by S.T. Pantelides\textsuperscript{17}, described by reactions in equations 7.12 to 7.15. These two mechanisms due the helium dilution of silane in dc plasma discharge can also result in an increase in the deposition rate and a reduction of defects in the film. However, it is suggested that the helium to silane ratio must be optimized, the deposition pressure to be maintained at a pressure equal to the total partial pressure of the gases and the deposition temperature to be within the range of 200°C to 300°C.

7.5 Hydrogen Content: Comparison between the Chemical Bonding Infra-red Model and the Valence Electron Model.

As mentioned earlier in this chapter, the effectiveness of hydrogen in reducing defects in a-Si:H films is strongly dependent on how the H atom is incorporated into the film and not on the H content in the film. In general, a-Si:H prepared from plasma discharge of SiH\textsubscript{4} shows a two-phase structure, one being the H-diluted with randomly distributed monohydride phase and the other is a tightly clustered hydrogen rich phase\textsuperscript{24,25}. The second phase is known to contain structural inhomogeneities like voids, vacancies etc. and it has been observed that trapped molecular hydrogen are present in the microvoids\textsuperscript{26,27}.

In this work, the valence electron model (VEM) and the chemical bonding infra-red model (IRM) which was described in detail in sections 6.3.1 and 6.3.2 respectively are used to determine the H content in the film. Our discussion here will be based on the assumption that only small difference in H concentration occurs between films that are deposited on intrinsic silicon and fused silica substrates within the thickness range of the films in this work. It is
to be emphasized here that the main aim of this work is not to optimize deposition parameters but instead to look at the role and content of hydrogen in the film since it was rather difficult to maintain a fixed deposition parameter using our home-built glow discharge system, and therefore the following discussion will be based fully on annealed samples. The effect of annealing on the optoelectronic properties of the film is suitable for the discussion on the H content calculated by these two techniques since variation of the H content in the film is only due to the heat treatment induced by the process of annealing. Figures 7.5(a) and (b) shows the effects of annealing on the H percentages as calculated by the valence electron model[H% (VEM)] , the chemical bonding infra-red model for Si-H\textsubscript{x} stretch peak at \(\sim 2000 \text{ cm}^{-1}\) [H% (2000 cm\(^{-1}\))], for Si-H wagging peak at \(\sim 611 \text{ cm}^{-1}\) [H% (600 cm\(^{-1}\))] and for the total H percentage due to these two infra-red peaks[ H% (IRM) ] as extracted from section 6.4. These informations caused by annealing lead us to the proposal that the H percentage calculated by the VEM arises from the H atoms on the Si-H bonding sites including those that are bonded or coupled to other atoms [e.g. O-(Si=)-H bonds]. It is therefore deduced the H percentage calculated by the IRM model is the total H percentage arising from the Si-H\textsubscript{x} stretch modes and the Si-H wagging modes, which includes the Si-H, Si-H\textsubscript{2} and (SiH\textsubscript{2})\textsubscript{n} bonding sites.

In the case of a-Si:H deposited from pure silane a significant proportion of the H atoms bonded to Si atoms are in the Si-H\textsubscript{2} bonding configuration (refer to section 6.2). On the contrary samples deposited from helium diluted silane display H atoms bonded to Si atoms in the Si-H configuration, whereby
Figure 7.5(a) : Variation of hydrogen percentage calculated by the Valence Electron Model, H\%(VEM) and the Chemical Bonding Infra-red Model at the Si-H stretching mode, H\%(2000cm\(^{-1}\)) , at the Si-H wagging mode H\%(600cm\(^{-1}\)) and at both these modes , H\%(IRM) for sample SAR7B.

Figure 7.5(b) : Variation of hydrogen percentage calculated by the Valence Electron Model, H\%(VEM) and the Chemical Bonding Infra-red Model at the Si-H stretching mode, H\%(2000cm\(^{-1}\)) , at the Si-H wagging mode H\%(600cm\(^{-1}\)) and at both these modes , H\%(IRM) for sample SAR10C.
some of these bonds are either coupled or bonded to Si-O-Si bonds especially if these samples are oxygen contaminated (refer to section 6.2). The H% calculated from the Si-H\textsubscript{x} stretch infra-red peak at \(\sim 2000\) cm\(^{-1}\) is due to Si-H\textsubscript{2} and Si-H bonds while the H% from the Si-H wag infra-red peak at \(\sim 611\) cm\(^{-1}\) is due to Si-H bonds only. From Figure 7.5(a) it is observed that the trend in the variation of H% calculated by the VEM for with annealing temperature has a close resemblance to that H% determined from the Si-H wag infra-red peak at \(\sim 611\) cm\(^{-1}\), except for the slight differences when annealed at 100°C. Here, the slight decrease in H% calculated by the VEM is probably due to the presence of some O-(Si=)-H configuration in the film arising from oxygen contamination, but since its presence is minimal it is to be expected that the infra-red spectrum is not capable of detecting its presence. However, the dominant presence of this bonding mode is obviously represented by the significant decrease in the H%(VEM) when annealed at 100 °C and 200 °C in figure 7.5(b). Thus, the VEM includes the H% at Si-H bonding site even when it is bonded to other bonds as in this case, the Si-O-Si bond, but however it excludes the polyhydride bonding configuration of H atoms to Si atom. As shown in figure 7.5(b), the H%(IRM) initially increases when annealed at 100 °C and 200°C but decreases at 300°C and 400°C, and remains stable when annealed further at 500 °C, while in figure 7.5(a) the IRM H% reaches a maximum when annealed at 300 °C and decreases when annealed further at 400 °C and 500 °C. The initial increase in H% IRM shows that bond-switching processes are taking place and as proposed by S.T. Pantelides et al\textsuperscript{19}, this is due to the presence of intestinal H from either trapped H\textsubscript{2} present in microvoid
or weakly bonded H at these annealing temperatures. D centres (floating bonds and dangling bonds) are also passivated, as described by equations (7.13) and (7.15) in the forward direction. H evolution is represented by the decrease in the H%(IRM) due to reaction 7.12 driven in the forward direction and reactions 7.13 and 7.15 driven in the reverse direction representing breakup of Si-H bonds. Thus, these evidence fully supports the fact that the H%(IRM) represents the total H% in the film at the Si-H, Si-H2 and (Si-H2)n bonding sites, and that the contribution of the H% at other Si-Hx sites as represented by other infra-red peaks other than the Si-Hx stretch and Si-H wag peaks, are minimal when compared to the H%(IRM). Figure 7.6 shows the variation of the optical energy gap with H% calculated by the VEM for samples prepared from helium diluted silane and pure silane. A similar trend is observed by A. Deneuville et al.29 for the variation of energy gap with H concentration at Si-H sites from similar annealing experiment of their rf sputtered a-Si:H film in Ar and H2 atmosphere (see figure 7.7). This strongly strengthens the above proposal that the VEM H% represents the H content in the film at Si-H sites only.

Figures 7.8(a) and (b) shows the variation of room temperature conductivity and density of states at the Fermi level N(EF) with H%(VEM) and H%(IRM) respectively. From other workers studying the conductivity behaviour in a-Si:H with H content in the film29,30, the conductivity is observed to decrease with increasing film H content at low concentrations due to defect passivation by the incorporated hydrogen, but rises again in high hydrogen content film as H-related defect states and an increasing columnar film
Figure 7.6: Variation of the optical energy gap ($E_g$) with hydrogen percentage calculated by the valence electron model for samples.
Figure 7.7: Optical energy gap versus hydrogen concentration on Si-H site for a-Si:H films prepared by rf sputtering in H₂ and Ar gas mixture for substrate temperature of 250°C and deposition rates of ν=38(o), 66(+) and 115(x)Å min⁻¹ as the annealing temperature increases.[after A. Deneuville et al²⁸]
Figure 7.8(a) : Variation of dc current dark conductivity and density of states at the fermi level, N(E_f) with hydrogen percentage calculated by the valence electron model (VEM) for sample SAR7B.

Figure 7.8(b) : Variation of dc current dark conductivity and density of states at the fermi level, N(E_f) with hydrogen percentage calculated by chemical bonding infra-red model (IRM) for sample SAR7B.
morphology starts to develop. In general room temperature conductivity falls with decreasing sample defect-density or increasingly uniform microstructure. Since, H%(VEM) is linked to the H content in the film at the Si-H bonding sites, the decrease in conductivity with an initial increase in H content, followed by the saturation of conductivity when the H content is increased further, as observed in Figure 7.8(a), indicates that increasing Si-H bonding sites result in a more uniform microstructure in the film. Low defect density region in glow discharge a-Si:H is known to be the region where hydrogen is bonded in Si-H sites. The H% (IRM) is linked to the total H content in the film bonded in monohydride and polyhydride sites. The initial decrease in conductivity when the H content increases as shown in Figure 7.8(b) is probably due to the increase in H at Si-H bonding sites. Beyond this point, any further increase in H results in an increase in H in the polyhydride bonding sites which is associated to the formation of columnar morphology in the film, hence resulting in increasing conductivity. This is followed by decreasing conductivity as observed when the H%(IRM) increases to ~34%, probably due to the onset of microcrystalline structure in the film due to high concentration of H in the film.

The density of state at the Fermi level, N(E_F) seems to be dependent more on the H%(IRM) rather than the H% (VEM) since the variation of N(E_F) with H%(VEM) shows no definite trend after the initial decrease in N(E_F) when the H% increases. The conductivity and N(E_F) shows almost similar behaviour with H%(IRM) except that the transition from a decrease to an increase in conductivity with H% occurs at lower H% in comparison to
H%(VEM). This shows that the conductivity starts to increase before most of the dangling bond defects as represented by \( N(E\_\gamma) \) are passivated. This is clearly justified by the fact that large amounts of H are needed to passivate relatively small concentrations of D centres as observed by D. Kaplan et al\(^{15} \), and that hydrogen-related defects resulting in columnar microstructures are able to develop even before most of the D centres are passivated which are indicated by the early increase in conductivity when the H content increases.

An interesting behaviour in the variation of conductivity and \( N(E\_\gamma) \) are observed when plotted against the fraction of H%(VEM) with H%(IRM) is portrayed in Figure 7.9. Both conductivity and \( N(E\_\gamma) \) both decrease initially with the increase of this fraction up to a transition point of \( \sim 0.5 \), and a further increase in this fraction increases both the conductivity and \( N(E\_\gamma) \) again. The initial decrease in conductivity and \( N(E\_\gamma) \) is probably due to bonded hydrogen existing in the dilute phase consisting of isolated Si-H bonds which produces a uniform microstruture in the film. When the fraction of hydrogen at Si-H bonding sites to the total H content in the film is increased beyond the transition fraction, in this case is \( \sim 0.5 \), bonded hydrogen which earlier existed in the dilute phase are transformed to the clustered phase, as described by J. Kakalios et al.\(^{18} \) in their work. Thus, H bonded to Si in the Si-H bonding configuration does not always produce low defect dilute phase structure. This suggests that there must be a balance between the monohydride and the polydyride bond configuration of Si bonded to H atom in a-Si:H films in order to produce a low defect density material.
Figure 7.9: Variation of dc current dark conductivity and density of states at the fermi level, $N(E_F)$, with the ratio of valence electron model hydrogen percentage, $H%_{(VEM)}$, to chemical bonding infra-red model hydrogen percentage, $H%_{(IRM)}$. 
Chapter 7

Discussion

7.6 References


