CHAPTER 6

THE EFFECT OF MIXING HYDROGEN WITH SILANE ON
THE ELECTRONIC AND OPTICAL PROPERTIES OF
HYDROGENATED AMORPHOUS SILICON THIN FILMS
6.1. Introduction:

It is now well established that the electronic and optical properties of hydrogenated a-Si (a-Si:H) films depend mainly on the hydrogen content in the films as hydrogen acts as a dangling bond terminator in such films. The properties of a-Si:H films are now being extensively studied because of their importance in the fabrication of a-Si solar cells. Some of the groups engaged in the development of a-Si solar cells are using pure SiH₄ as the discharge material whereas other groups are using a mixture of SiH₄ and H₂ gases [Carlson (1980); Okamoto, Nitta, Adachi and Hamakawa (1979); Uchida, Sakai, Nishiura and Haruki (1981)]. It is therefore interesting to study the effect of mixing SiH₄ with hydrogen on the electronic and optical properties of a-Si:H films.

The influence of the addition of hydrogen in different proportions to argon on the properties of a-Si:H films prepared by the d.c. method or the r.f. sputtering method has been studied by a number of workers [Anderson and Paul (1981); Martin and Pawlewics (1981); Zemek, Zavetova and Koc (1980)]. However, no results of studies on the changes in the properties of a-Si:H prepared from a mixture of SiH₄ and H₂ by the r.f. glow discharge method have been reported. In this Chapter are given the results of our studies of the electronic and optical properties of a-Si:H films prepared by the r.f. glow discharge method from mixtures with different concentrations of H₂ in SiH₄.

The properties which have been studied are the temperature dependence of the dark conductivity and the photoconductivity,
the intensity dependence of the photoconductivity, the absorption coefficient, the spectral response and the IR vibrational spectra.

6.2. Experimental Details:

a-Si:H films were deposited onto Corning 7059 glass substrates by dissociating pure SiH$_4$ or an SiH$_4$ - H$_2$ mixture in the r.f. glow discharge apparatus described in Chapter 2. The flow rates of SiH$_4$ and H$_2$ were separately controlled by two electronic mass flowmeters and thus the ratio of H$_2$ to SiH$_4$ plus H$_2$ was accurately determined. The substrate temperature was normally kept at 250°C and the r.f. power supplied to the coil was 20 W. The H$_2$ concentration (by volume) in the H$_2$ - SiH$_4$ mixture was varied from 0% to 90%. The thickness of the films was in the range 2000 - 5000 Å and the deposition rate was 20 - 30 Å min$^{-1}$. For IR transmission measurements films with a thickness of 12000 - 13000 Å were deposited onto single-crystal silicon wafers.

Dark conductivity and photoconductivity measurements were carried out in vacuum (about 10$^{-5}$ Torr) with a gap cell geometry using vacuum-evaporated aluminium electrodes. The electric field applied to the electrodes was 1 kV cm$^{-1}$. To study the variation in photoconductivity with temperature and intensity of incident radiation a monochromator was used. Radiation with a wavelength (5600 Å) corresponding to a photon energy of 2.2 eV was selected as the exciting radiation and the intensity was varied by neutral density filters. The photoconductivity was also studied under white light of intensity 20 mW cm$^{-2}$. The absorption coefficient, transmittance and reflectance of a-Si:H films were studied with
Fig. 1. The dark conductivity plotted as a function of $1/T$ for the samples deposited with various $H_2$ concentrations in the $H_2 - SiH_4$ gas mixture: curve 1, 0% $H_2$; curve 2, 25% $H_2$; curve 3, 50% $H_2$; curve 4, 75% $H_2$; curve 5, 90% $H_2$. 

$\sigma_d (\Omega^{-1} m^{-1})$ vs. $10^3/T (K^{-1})$
The dark conductivity \( \sigma_D \) as a function of temperature was studied for a number of films prepared with different concentrations of \( H_2 \). The plots of \( \log \sigma_D \) versus \( 10^3/T \) are shown in Fig. 1. The values of the activation energies \( \Delta E \) for these films were obtained from the gradients of the curves and are given in Table 1. For a-Si:H film prepared from pure SiH\(_4\) (Fig. 1, curve 1) the activation energy at temperatures above 270°C is 0.96 eV and the plot is a straight line. This suggests that the conduction takes place by transport in the extended states. At lower temperatures the slope is less steep, suggesting a change in transport mechanism which may now involve hopping through the localized states near the conduction band. As the concentration of \( H_2 \) increases (25\%; Fig. 1, curve 2) the straight portion of the \( \log \sigma_D \) versus \( 10^3/T \) curve, which has a corresponding activation energy of 1.01 eV, extends to a lower temperature than does curve 1. The \( \sigma_D \) values for curve 2 are also lower than those for curve 1. These results indicate that with glow discharge using \( H_2 - \text{SiH}_4 \) mixtures where the \( H_2 \) concentration is low the passivation of dangling bonds is more effective than for the films prepared from pure SiH\(_4\). The increase in the activation energy also indicates the incorporation of a larger quantity of bonded hydrogen in the a-Si:H films. With a further increase in the \( H_2 \) concentration in the discharge gas mixture (Fig. 1, curve 3), the conductivity starts to increase again and
Table 1. Activation energies, band gaps and conductivity prefactors of a-Si:H films prepared with different percentages of H₂ in the SiH₄ - H₂ gas mixture.

<table>
<thead>
<tr>
<th>Concentration of H₂ in SiH₄-H₂ (vol. %)</th>
<th>Conductivity prefactor (n cm⁻¹)</th>
<th>Activation energy (eV)</th>
<th>ΔEₚₙ (eV)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.25 x 10⁶</td>
<td>0.96</td>
<td>0.18</td>
<td>1.76</td>
</tr>
<tr>
<td>9</td>
<td>2.25 x 10⁶</td>
<td>0.96</td>
<td>0.17</td>
<td>1.75</td>
</tr>
<tr>
<td>25</td>
<td>1.75 x 10⁷</td>
<td>1.01</td>
<td>0.13</td>
<td>1.74</td>
</tr>
<tr>
<td>40</td>
<td>1.80 x 10⁶</td>
<td>0.99</td>
<td>0.16</td>
<td>1.80</td>
</tr>
<tr>
<td>50</td>
<td>1.26 x 10⁶</td>
<td>0.96</td>
<td>0.17</td>
<td>1.82</td>
</tr>
<tr>
<td>75</td>
<td>3.56 x 10⁴</td>
<td>0.78</td>
<td>0.19</td>
<td>1.87</td>
</tr>
<tr>
<td>90</td>
<td>7.70 x 10²</td>
<td>0.66</td>
<td>0.17</td>
<td>1.91</td>
</tr>
</tbody>
</table>
the activation energy decreases. This result probably indicates an increase in the number of defect states due to excess hydrogen. The conductivities of the films prepared with 75% H₂ and 90% H₂ (Fig. 1, curves 4 and 5) are considerably higher than those prepared with pure SiH₄ and the activation energies are 0.78 eV and 0.66 eV respectively, which are much lower than the value (0.96 eV) obtained for pure SiH₄. This result together with those obtained for band gaps (reported later in the present Chapter) show that Eₚ is shifted towards the conduction band when a comparatively large amount of H₂ is present in the SiH₄ - H₂ mixture. The slopes (Fig. 1, curves 4 and 5) also change at much higher temperatures, indicating that the activated hopping mechanism has started to take place. Thus it is seen that by increasing the H₂ concentration in SiH₄ beyond a certain limit defect states are created in a-Si:H films.

The values of the prefactors σ₀ obtained from the intercept at 10³/T = 0 have also been given in Table 1. For a-Si:H films prepared without H₂ and with 25% H₂, σ₀ = 2.25 x 10⁶ Ω⁻¹ cm⁻¹. According to Fritzsehe (1980) σ₀ reaches this value when Eₚ is near the gap centre. With 25% H₂, σ₀ increases to 1.75 x 10⁷ Ω⁻¹ cm⁻¹ and, with a further increase in the H₂ concentration, σ₀ gradually decreases to 7.7 x 10² Ω⁻¹ cm⁻¹. By varying the deposition conditions in the r.f. glow discharge decomposition method, Spear, Allan, LeComber and Smith (1980) obtained 10² Ω⁻¹ cm⁻¹ < σ₀ < 10⁷ Ω⁻¹ cm⁻¹. Paul and Anderson (1981) obtained σ₀ in the range 10³ - 10⁴ Ω⁻¹ cm⁻¹ for a-Si:H films prepared by the r.f. sputtering method.
Fig. 2. Dark conductivity $\sigma_D$ (curve 1) and photoconductive gain $\sigma_{ph}/\sigma_D$ (curve 2) at 346 K as functions of $H_2$ concentration.
Fig. 3. $(\omega h)^{\frac{1}{2}}$ vs. $h\nu$ plots for a-Si:H films: curve 1, 0% H\textsubscript{2}; curve 2, 25% H\textsubscript{2}; curve 3, 50% H\textsubscript{2}; curve 4, 75% H\textsubscript{2}; curve 5, 90% H\textsubscript{2}.
The variation in the dark conductivity at 346 K with H₂ concentration is shown in Fig. 2. The ratio $\sigma_{\text{Ph}}/\sigma_D$ for the films obtained under white light radiation of intensity 20 mWcm⁻² is also shown. From this figure it can also be seen that, with the addition of a slight amount of H₂ to SiH₄, $\sigma_D$ decreases and the ratio $\sigma_{\text{Ph}}/\sigma_D$ increases: this shows a decrease in the density of dangling bonds and recombination centres. With a further increase in the H₂ concentration $\sigma_D$ increases and $\sigma_{\text{Ph}}/\sigma_D$ decreases, showing an increase in the defect density. It has also been found that, if the a-Si:H film prepared with 90% H₂ is exposed to the atmosphere for some time, the conductivity changes considerably. This type of change has been reported previously by Tanielian, Chatani, Fritzsche, Smid and Persans (1980) and by Anderson and Paul (1981). The films prepared with high concentrations of H₂ may have pores which absorb water vapour from the atmosphere. If the film is kept under vacuum for 1 h the conductivity decreases by up to one order magnitude. This effect is negligible for the films deposited at lower H₂ concentrations.

From the reflectance and transmittance data the absorption coefficients $\alpha$ for the a-Si:H films were calculated. $(\alpha \ h \nu)^{\frac{1}{2}}$ is plotted in Fig. 3 as a function of the photon energy $h \nu$ for films deposited with different H₂ concentrations. From the extension of the straight portion of the curve, band gaps for the corresponding films were obtained, the values of which are given in Table 1. It can be seen that the band gap remains virtually constant up to 25% H₂ and then increases significantly as the H₂ concentration is increased further.
Fig. 4. Absorption coefficient $\alpha$ vs. frequency $\omega$ for stretching Si–H bonds in a-Si:H films: curve 1, 0% H$_2$; curve 2, 25% H$_2$; curve 3, 50% H$_2$; curve 4, 75% H$_2$. 
Fig. 5. Absorption coefficient $\alpha$ vs. frequency $\omega$ for wagging Si-H bonds in a-Si:H films: curve 1, 0\% H$_2$; curve 2, 25\% H$_2$; curve 3, 50\% H$_2$; curve 4, 75\% H$_2$. 
The IR vibrational spectra of a few a-Si:H films prepared from SiH₄-H₂ mixtures with different H₂ concentrations have been studied to obtain information about the total bonded hydrogen content and the local bonding configurations of hydrogen. The spectra obtained for a-Si:H films prepared from mixtures having 0%, 25%, 50% and 75% H₂ are shown in Figs. 4 and 5. The a-Si:H films have two main absorption peaks at 2000 cm⁻¹ (Fig. 4) and 640 cm⁻¹ (Fig. 5) which correspond respectively to stretching and wagging Si - H bonds. A weak peak was observed at 2100 cm⁻¹ which corresponds to the bond-stretching mode of SiH₂\[^{1}\text{Brodsky, Cardona and Cuomo (1977)}\]. This shows that the bonded hydrogen in the a-Si:H films prepared by us is mainly present in the monohydride form.

The concentration of bonded hydrogen in the a-Si:H films has been estimated from the intensities of IR absorption due to the Si - H wagging mode using the expression [Brodsky, Cardona and Cuomo (1977); Morimoto, Miura, Kumeda and Shimizu (1982)]

\[
N_H = A \int \frac{\alpha(\omega)}{\omega} \, d\omega
\]  

where \( \alpha \) is the absorption coefficient and \( \omega \) is the wavenumber. The value of \( A \) was taken as 1.6 x 10\(^{19} \) cm\(^{-2} \). The hydrogen contents of the films prepared with 0% H₂, 25% H₂, 50% H₂ and 75% H₂ were estimated to be 8.6 at. %, 18.6 at. %, 25.5 at. % and 10.2 at. % respectively. Thus the concentration of hydrogen in the bonded form of Si - H increases up to an H₂ concentration of 25% and then starts decreasing with a further increase in the H₂ concentration. The
Fig. 6. The product of the photoconductivity lifetime, mobility and quantum efficiency as a function of the photon energy: curve 1, 0% H₂; curve 2, 9% H₂; curve 3, 50% H₂; curve 4, 75% H₂; curve 5, 90% H₂.
band gap, however, increases monotonically with the increase in the $H_2$ concentration in the $SiH_4-H_2$ mixture. These results may be interpreted as being due to the entry of $H_2$ into the a-Si network in different configurations at different $H_2$ concentrations, which may introduce more localized states in the pseudogap. This interpretation has also been given by Freeman and Paul (1979) for similar results obtained by them with sputtered a-Si:H films.

The photocurrents ($i_{ph}$) of the films deposited with different hydrogen concentrations were measured as a function of wavelength using a monochromator. From the values of $i_{ph}$ and the absorption coefficient ($\alpha$) at different wavelengths the product $\eta \mu \tau$ was calculated using the equation (6) of Chapter 2. The values of $\eta \mu \tau$ have been plotted against $h\nu$ in Fig. 6. For energies above the band gap $\eta$ should be unity [Zangucchi, Wronski and Carlson (1977)]. If we assume that $\mu$ is the same for all the samples then the electron lifetimes for the samples deposited with higher hydrogen concentrations are less as shown in Fig. 6.

The variation in the photoconductivity with $10^3/T$ shown in Figs. 7 and 8 for different intensities of incident radiation for a-Si:H films prepared from pure $SiH_4$ and a mixture of $SiH_4$ and $H_2$ with 75% $H_2$. It can be seen that near room temperature there is a small depression in the $\sigma_{ph}$ versus $10^3/T$ plots which is more prominent at lower intensities. The depression may be explained as being due to the existence of a hole trap level which starts de-populating at that temperature and which may enhance the recombination process. A further quenching of $\sigma_{ph}$ occurs at a higher
Fig. 7. Photoconductivity $\sigma_{ph}$ of the films deposited with pure SiH$_4$ as a function of $1/T$ at various light intensities: curve I1, $1.60 \times 10^{11}$ photons cm$^{-2}$ s$^{-1}$; curve I2, $5.45 \times 10^{12}$ photons cm$^{-2}$ s$^{-1}$; curve I3, $6.65 \times 10^{13}$ photons cm$^{-2}$ s$^{-1}$; curve I4, $8.29 \times 10^{14}$ photons cm$^{-2}$ s$^{-1}$. 
Fig. 8. Photoconductivity $\sigma_{ph}$ of the films deposited with 75% H$_2$ in the H$_2$-SiH$_4$ mixture as a function of $1/\theta$ at various light intensities: curve I1, $2.92 \times 10^{11}$ photons cm$^{-2}$s$^{-1}$; curve I2, $4.92 \times 10^{12}$ photons cm$^{-2}$s$^{-1}$; curve I3, $6.35 \times 10^{13}$ photons cm$^{-2}$s$^{-1}$; curve I4, $7.50 \times 10^{14}$ photons cm$^{-2}$s$^{-1}$. 
Fig. 9. Temperature dependence of the parameter $\gamma$ in $\sigma_{\text{Ph}}^{\gamma}$:
- curve 1, 0% H$_2$;
- curve 2, 9% H$_2$;
- curve 3, 75% H$_2$. 
temperature (about 400 K). This might be explained as due to the presence of another hole trap at a higher energy which gets depopulated at this temperature and thus enhancing recombination. The existence of a depression in the $\sigma_{ph}$ versus $10^3/T$ plot has also been reported and discussed by Paul and Anderson (1981).

The intensity dependence of the photoconductivity can be written as

$$\sigma_{ph} = K I^\gamma$$

where $K$ is a constant and $I$ is the incident light intensity. The value of $\gamma$ determines the nature of the recombination mechanism. Figure 9 shows the variation in $\gamma$ with $10^3/T$ for samples deposited with 0%, 50%, and 75% H$_2$. At lower temperatures $\gamma \approx 0.5$, which indicates a predominance of bimolecular recombination process. $\gamma$ increases gradually with increasing $T$ but, at some higher temperature it again decreases towards the value 0.5, indicating again the predominance of a bimolecular recombination process. From Figs. 7, 8 and 9 we see that this occurs after the first quenching of $\sigma_{ph}$. With further increase of temperature $\gamma$ again approaches a value of 1.0 where second quenching of $\sigma_{ph}$ occurs (Figs. 7 and 8).

In the low temperature region where $\gamma \approx 0.5$, i.e. where a bimolecular recombination process is predominant [Spear and LeComber (1976)],

$$\sigma_{ph} \propto \exp \left[ - \frac{E_c - E_A}{kT} \right]$$

where $E_c - E_A$ is a measure of the extent of the localized tail
states. From the slopes of the log $\sigma_{ph}$ versus $10^3/T$ curves we have calculated the values of $\Delta E_{Ph} = E_c - E_A$ for films deposited at different $H_2$ concentrations; these are given in Table 1. It can be seen from Table 1 that, with a slight addition of $H_2$, the width of the tail states decreases but, with a further increase in the $H_2$ concentration, this width increases again.

6.4. Conclusions:

It can be seen that small but significant changes in the electronic and optical properties of a-Si:H films prepared by r.f. glow discharge decomposition occur when $H_2$ is added to SiH$_4$. The quality of the film improves with the addition of a small quantity of $H_2$ and it deteriorates with a further increase in the concentration of $H_2$.

Although we have seen that the presence of only a small quantity of $H_2$ in SiH$_4$ - $H_2$ mixtures is beneficial for producing a-Si:H films suitable for solar cells, the best composition will depend on various deposition parameters including the geometry of the apparatus.