CHAPTER 7

PROPERTIES OF UNDOPED AND BORON DOPED HYDROGENATED AMORPHOUS SILICON CARBIDE FILMS
7.1. Introduction:

It was first shown by Anderson and Spear (1977) that the optical band gap of hydrogenated amorphous silicon carbide film increases with increasing carbon content. Since then a-SiC:H films have received considerable attention both from scientific and technological points of view. The p-type a-SiC:H films with comparatively high band gap has proved to be very useful as window material in p-i-n structure a-Si solar cells.

Till now most of the investigations on a-SiC:H films have been confined to infrared absorption studies [Wieder, Cardona and Guarnieri (1979); Morimoto, Miura, Kumeda and Shimizu (1982); Nakazawa, Ueda, Kumeda, Morimoto and Shimizu (1982); Tawada, Tsuge, Kondo, Okamoto and Hamakawa (1982)]. Some works have also been done on photoluminescence, E.S.R. [Morimoto, Miura, Kumeda and Shimizu (1982)] and N.M.R. [Nakazawa, Ueda, Kumeda, Morimoto and Shimizu (1982)] studies of undoped films. Tawada et al (1982a, 1982b) have studied some electrical and optical properties of undoped and p-type a-SiC:H films. The main purpose of their studies was to develop suitable material for improving the efficiency of amorphous silicon thin film solar cells.

In this Chapter the results of detailed studies on the electrical and optical properties of undoped and p-type a-SiC:H films have been presented. The dark conductivity, photoconductivity, optical absorption and band gap of these films prepared under different conditions have been studied. These data have been
analysed to yield information about the transport mechanism, density of recombination centers, effects of boron doping etc. For this purpose the information obtained by other workers from IR absorption and ESR studies have been considered. The undoped a-SiC:H films have been deposited at different compositions of silane-methane mixture, substrate temperature and r.f. power. The p-type a-SiC:H films have been prepared at different concentrations of diborane in silane-methane mixtures of two different compositions.

7.2. Experimental:

The apparatus for the preparation of a-SiC:H films by r.f. glow discharge decomposition method has been described in Chapter 2, section 1. The undoped a-SiC:H films were deposited on Corning 7059 glass substrates from a mixture of silane and methane gases. The p-type a-SiC:H films were prepared from a mixture of diborane, methane and silane gases. The silane gas was supplied by British Oxygen Co. (Electra II grade) diborane (1 % B₂H₆ in H₂, Air Products, U.K.) and methane (Matheson Inc., U.S.A.) gases were of Electronic grade.

For the undoped a-SiC:H films the substrate temperature was varied from 423K to 553K and the r.f. power supplied to the induction coil around the reaction tube was 2, 10 and 20 Watts which for convenience shall be referred to later in this Chapter as low, medium and high power, respectively. The concentration (by volume) of methane x in the mixture \[ \text{SiH}_4(1-x) + \text{CH}_4(x) \] has been varied
from 0.2 to 0.8. For the p-type a-SiC:H films medium r.f. power was used and the substrate temperature was 523 K. The films were prepared with different diborane concentrations in two different mixtures of silane and methane with \( x = 0.35 \) and 0.65. The thicknesses of the films were measured by a stylus type instrument (Planer Products, UK) and were in the range 300-400 nm.

The dark conductivity and photoconductivity of the films were measured using gap cell geometry under a vacuum \( \sim 10^{-5} \) Torr. Electric field applied to the Al electrodes was 700 V/cm and photoconductivity was studied under white light of intensity 20 mW/cm² from a tungsten lamp. Spectral response of the film was studied with the help of a monochromator and the intensities of radiation at different wavelengths were measured by a calibrated silicon photodiode. The intensity dependence of photoconductivity was measured by using a radiation of wavelength 560 nm from the monochromator and using neutral density filters. The absorption coefficient of the film materials was studied by a Cary 17D double beam spectrophotometer.

7.3. Results and discussion :

7.3.1. Dark Conductivity :

The room temperature (300 K) dark conductivity \( \sigma_D \) of a-SiC:H films prepared at medium r.f. power and substrate temperature of 523 K have been plotted in Fig. 1 as function of methane concentration \( x \). It is seen from the Figure that up to \( x = 0.35 \) the decrease in \( \sigma_D \) with the increase of \( x \) is very slow and this
Fig. 1. Variation of dark conductivity ($\sigma_D$), photocconductivity ($\sigma_{ph}$) and optical band gap ($E_g$) with carbon concentration ($x$) for carbonated a-Si:H films.
Fig. 2. Dark conductivity ($\sigma_D$) as a function of $1/T$ for carbonated a-Si:H films. Curves 1, 2, 3, 4, 5 correspond to $x = 0, 0.20, 0.35, 0.50$ and 0.65 respectively.
decrease is much faster with further increase in \( x \). From infrared vibration spectroscopy other workers have previously reported that the following changes take place in a-SiC:H films compared to those for a-Si:H films, viz: (1) hydrogen concentration increases as the concentration of \( \text{CH}_4 \) increases (2) structural changes are produced by the introduction of Si-C, C-C and C-H bonds in addition to Si-H, Si-H\(_2\) etc. bonds (3) E.S.R. studies have shown that the density of dangling bonds increases steeply with the increase of carbon concentration.

For a-SiC:H films the decrease in the conductivity with increase in \( \text{CH}_4 \) concentration is probably due to the structural changes which reduce conductivity. The steeper variation of \( \sigma_D \) for \( x > 0.35 \) (Figure 1) may be due to the dominating influence of Si-C structure at higher concentrations of \( \text{CH}_4 \).

The variation of \( \log \sigma_D \) with \( 10^3/T \) for the a-SiC:H films deposited with various concentrations of methane has been shown in Fig. 2. Each of the plots shows only one slope over the whole temperature range of our measurements. The activation energy \( \Delta E \) as obtained from these plots increases from 0.73 to 0.94 eV as \( x \) increases from 0 to 0.65 (Table 1). The conductivity prefactor \( \sigma_0 \) varies from \( 10^4 \) to \( 10^2 \) as \( x \) increases. This corroborates the fact that with increasing carbon concentration defect states in a-SiC:H film increases. The comparatively large activation energy and single slope of \( \log \sigma_D \) vs \( 10^3/T \) plot shows that for a-SiC:H films the transport mechanism is probably by conduction in the extended states.
### Table 1: Dark and photoconductivities, activation energies and band gaps of carbonated a-Si:H films deposited under various conditions.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Activation energy (eV)</th>
<th>Conductivity prefactor ($a_0$) (S/m)</th>
<th>Band gap ($E_g$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High 100</td>
<td>0.86</td>
<td>$3.20 \times 10^{-9}$</td>
<td>3.20</td>
</tr>
<tr>
<td>Medium 200</td>
<td>0.87</td>
<td>$1.45 \times 10^{-9}$</td>
<td>1.45</td>
</tr>
<tr>
<td>Low 300</td>
<td>0.88</td>
<td>$4.00 \times 10^{-10}$</td>
<td>4.00</td>
</tr>
<tr>
<td>High 400</td>
<td>0.88</td>
<td>$2.81 \times 10^{-9}$</td>
<td>2.81</td>
</tr>
<tr>
<td>Medium 500</td>
<td>0.89</td>
<td>$6.56 \times 10^{-10}$</td>
<td>6.56</td>
</tr>
</tbody>
</table>

*Note: The table contains data for various conditions of substrate temperature, with corresponding activation energies, conductivity prefactors, and band gaps.*
Fig. 3. Variation of dark conductivity ($\sigma_D$), photoconductivity ($\sigma_{ph}$) and optical band gap ($E_g$) with the substrate temperature ($T_D$) for carbonated a-Si:H films with $x = 0.35$. 
Fig. 4. Dark conductivity as a function of $1/T$ for a-SiC$_x$H films (with $x = 0.35$) deposited at different substrate temperatures ($T_D$). Curves 1, 2, 3 and 4 correspond to $T_D = 423$ K, 473 K, 523 K and 573 K respectively.
In Fig. 3 effect of variation of substrate temperature on the a-SiC\(_x\)H sample (x = 0.35) are shown. log \(\sigma_D\) vs \(10^{3/2}\) plots for these samples are given in Fig. 4. Values of room temperature conductivity and activation energy for these samples are given in Table 1. Lower conductivity and higher activation energy for the low temperature deposited samples can be explained by the presence of larger number of defect states. Increase of defect states with lowering of substrate temperature is also reflected in the photoconductivity data which we will discuss later.

Changes in conductivity and activation energy of a-SiC\(_x\)H films (with x = 0.35) observed with the change of r.f. power is however opposite to that observed in the case of intrinsic and P-doped a-Si:H films (Chapter 4). In this case activation energy decreases with increase of r.f. power. This could be due to smaller proportion of carbon to silicon atoms in the network at higher powers resulting in a less number of localized states in the pseudogap.

The variation of \(\sigma_D\) at room temperature with diborane concentration for p-type a-SiC\(_x\)H films prepared with x = 0.35 and 0.65 has been shown in Fig. 5. It is seen that for the films prepared with x = 0.35 (curve 1, Fig. 5), with the initial diborane concentration of 0.1%, \(\sigma_D\) is lower than that of the undoped film. However \(\sigma_D\) increases monotonically with further increase in diborane doping. For the a-SiC\(_x\)H films (curve 2, Fig. 5) prepared with x = 0.65, however there is no initial lowering of \(\sigma_D\) but a monotonic increase over the entire range of diborane.
Fig. 5. Variation of dark conductivity ($\sigma_D$) and band gap ($E_g$) with diborane concentration for carbonated a-Si:H films. $\sigma_D^1$ and $E_g^1$ correspond to $x = 0.35$; $\sigma_D^2$ and $E_g^2$ correspond to $x = 0.65$. 

$E_g$ (eV)
Fig. 6. Dark conductivity ($\sigma_D$) as a function of $1/T$ for boron doped carbonated a-Si:H films ($x = 0.35$). Curves 1, 2, 3, 4 and 5 correspond to $B_2H_6/(SiH_4 + CH_4)$ ratios of 0.0, $5 \times 10^{-4}$, $1 \times 10^{-3}$, $1 \times 10^{-2}$ and $2 \times 10^{-2}$ respectively.
Fig. 7. Dark conductivity ($\sigma_0$) as a function of $1/T$ for boron doped carbonated a-Si:H films ($x = 0.65$). Curves 1, 2, 3, 4, 5 correspond to $\text{B}_2\text{H}_6 / (\text{SiH}_4 + \text{CH}_4)$ ratios of 0.0, $1 \times 10^{-3}$, $3 \times 10^{-3}$, $1 \times 10^{-2}$ and $2 \times 10^{-2}$ respectively.
concentrations. For $x = 0.35$, the lowering of $\sigma_p$ for a-SiC:H films with initial diborane doping up to 0.1\% may be due to the possibility of n-type nature of undoped a-SiC:H films. Enomoto, Nishiwaki, Watanabe, Nakashima, Tsuda, Ohinose and Kuwano (1982) have also observed a similar minimum in $\sigma_p$ vs diborane concentration plot for p-type a-SiC:H film prepared with $x = 0.3$. Thus the minimum in the $\sigma_p$ vs diborane concentration plot may be due to the compensation effect. As described earlier, for a-SiC:H films prepared with $x = 0.65$ there is no minimum in $\sigma_p$ vs diborane concentration plot. This change of behaviour may be explained as due to the change of a-SiC:H films from n-type to p-type when $x$ is sufficiently higher than 0.35.

It is possible that with $x = 0.65$, the SiO structure may predominate over the a-Si:H structure. It may be mentioned that Mogals and Kingery (1968) found that non-crystalline silicon carbide films were p-type.

Temperature dependence of the dark conductivity of the p-type a-SiC:H films with $x = 0.35$ and $x = 0.65$ at different diborane concentrations are shown in Figs. 6 and 7 respectively. From Fig. 6 we see that for p-type a-SiC:H films (with $x = 0.35$) activation energy remains almost constant upto 0.1\% $B_2H_6$ concentration. With higher concentrations of $B_2H_6$ [curves 4 and 5, Fig. 6] activation energy decreases and the transport is more like activated hopping process at lower temperatures. The p-type a-SiC:H films with $x = 0.65$ show (Fig. 7) a continuous decrease of activation energy with increase of $B_2H_6$ concentration. In this case also at higher dopant concentration a decrease of slope occurs at lower temperatures.
7.3.2. Photoconductivity

In Fig. 1, the room temperature photoconductivity ($\sigma_{ph}$) of a-SiC:H films prepared at 523 K and medium r.f. power has been plotted against methane concentration. It is seen that $\sigma_{ph}$ decreases slowly with the increase of $x$ up to $x \approx 0.2$ and then decreases steeply with the further increase of $x$. In fact $\sigma_{ph}$ decreases from $1 \times 10^{-4} \text{ cm}^{-1}$ to $3.2 \times 10^{-10} \text{ cm}^{-1}$ as $x$ increases from 0 to 0.65 and at $x = 0.8$, $\sigma_{ph}$ is negligibly small. Similar decrease of $\sigma_{ph}$ of the order of $10^4$ with increase of $x$ has been reported by Tawada et al. (1982 b) and Morimoto et al. (1982). The decrease in $\sigma_{ph}$ with increase of $x$ may be explained as due to the increase of number of recombination centers with increase of $x$ which is corroborated by the increase of dangling bond density with the increase of $x$.

The variation of log $\sigma_{ph}$ with $10^3/T$ has been shown in Fig. 8 for a-SiC:H prepared with different concentrations of methane. For the uncarbonated and lightly carbonated a-Si:H films log $\sigma_{ph}$ vs $10^3/T$ plots show a plateau at higher temperature. The behaviour is similar to that observed [S. Ray, Chaudhuri, Batabyal and Barua (1985) ; Anderson and Spear (1977)] for undoped and lightly phosphorus doped a-Si:H films. For the highly carbonated films,
Fig. 8. Photoconductivity ($\sigma_{ph}$) as a function of $1/T$ for carbonated a-Si:H films. Curves 1, 2, 3, 4, 5 correspond to $x = 0, 0.20, 0.35, 0.50$ and 0.65 respectively.
Fig. 9. Photoconductivity ($\alpha_{ph}$) as a function of intensity ($I$) at room temperature for carbonated a-Si:H films. Curves 1, 2, 3 correspond to $x = 0.20, 0.35, 0.50$ respectively.
as seen in Fig. 8, the slope of $\log \sigma_{ph}$ vs $10^3/T$ plots become steeper in the higher temperature range. Similar types of plots have been obtained by Anderson and Spear (1977) for lightly boron doped a-Si:H films. These results tend to support the idea that a-SiC:H films are n-type when the concentration of carbon is low and at higher carbon concentration they become p-type.

Exact interpretation of $\log \sigma_{ph}$ vs $10^3/T$ plots for a-SiC:H films depends on the electron transport path, positions of quasi-Fermi levels and recombination mechanism. Anderson and Spear (1977) explained the transition of recombination mechanism from monomolecular to bimolecular process on the basis of known density of state distribution. But as the distribution for a-SiC:H films is not yet known, the interpretation of the observed data is at present difficult.

The photoconductivities of a-SiC:H films have also been measured at different intensities of illumination. The variation of $\sigma_{ph}$ with the illumination intensity $I$ has been shown in Fig. 9. The values of $\gamma$ have been calculated from the relation $\sigma_{ph} \propto I^\gamma$. There is a single value of $\gamma$ over the intensity range of our measurements. As seen in Fig. 9, $\gamma$ increases from 0.78 to 0.84 as $x$ increases from 0.2 to 0.5. These values of $\gamma$ probably indicate a continuous exponential or quasi-exponential distribution of traps [Zansucchi, Wronski and Carlson (1977)].

The variation of $\sigma_{ph}$ with substrate temperature $T_D$ has been shown in Fig. 3. $\sigma_{ph}$ increases as $T_D$ is increased from 423 K to
Fig. 10. Photoconductivity ($\sigma_{ph}$) as a function of $1/T$ for boron doped carbonated a-Si:H films. Curves 1, 2, 3, 4 correspond to $x = 0.35$ and $B_2H_6/(SiH_4+CH_4)$ ratio 0.0, $1 \times 10^{-3}$, $1 \times 10^{-2}$, $2 \times 10^{-2}$ respectively. Curves 5, 6, 7 correspond to $x = 0.65$ and $B_2H_6/(SiH_4+CH_4)$ ratio 0.0, $1 \times 10^{-3}$, $1 \times 10^{-2}$ respectively.
523 K and then it tends to saturate with further increase of $T_D$. This clearly shows a decrease in density of defect states with increase of substrate temperature.

$\log \sigma_{ph}$ vs. $10^3/T$ plots for p-type a-SiC:H films prepared with $x = 0.35$ and 0.65 have been given in Fig. 10. It is seen that for $x = 0.35$, $\sigma_{ph}$ decreases with initial diborane doping of 0.1% and starts increasing with the further increases of dopant concentration (curves 3 and 4 of Fig. 10). This behaviour is similar to that observed for uncarbonated a-Si:H films (Chapter 5, Figs. 5 and 6). For a-SiC:H films with $x = 0.65$, even with low doping of 0.1% diborane, $\sigma_{ph}$ is higher than the value for undoped films (curves 5, 6, 7 of Fig. 10). The increase of $\sigma_{ph}$ with diborane doping has also been observed by Tawada et al (1982 b) and it has been suggested that boron acts also as dangling bond passivator in a-SiC:H films. It is likely that passivation is more effective for a-SiC:H film prepared with $x = 0.65$ than that prepared with $x = 0.35$. This may be responsible for the monotonic increase of $\sigma_{ph}$ with the increase of diborane concentration for a-SiC:H films prepared with $x = 0.65$.

7.3.3. Optical absorption and band gap :

The absorption coefficient $\alpha$ of a-SiC:H films have been determined from the transmittance and reflectance data for a-SiC:H films prepared with different values of $x$. The optical band gap $E_g$ has been calculated from the expression

$$ (\alpha h \nu)^{1/2} = \gamma B (h \nu - E_g) $$

..... (1)
Fig. 11. Plots of \((ah\nu)^{\frac{1}{2}}\) against photon energy \((h\nu)\) for carbonated a-Si:H films. Curves 1, 2, 3, 4, 5 correspond to \(x = 0.20, 0.35, 0.50, 0.65, 0.80\) respectively.
where B is a constant. The plots of \((\alpha h\nu)^{1/2} vs.\) photon energy \(\nu\) for films with different carbon concentrations have been shown in Fig. 11. The values of \(E_g\) for a-SiC:H films have been given in Table 1. The value of \(\sqrt{B}\) varies from \(1 \times 10^3\) to \(5.1 \times 10^2\) \((eV/cm)^{-1}\) as \(x\) increases from 0.2 to 0.8. Sussmann and Ogden (1981) obtained similar variation of \(\sqrt{B}\) with the increase in carbon concentration. They also defined \(B^{-1}\) as the edge width parameter. Therefore the increase of \(B^{-1}\) with the increase of \(x\) may be interpreted as an indication of the widening of the localized tail states.

It may also be seen from Fig. 11 that the absorption edge shifts to higher photon energy and the optical band gap increases with increasing carbon concentration. The maximum value of \(E_g\) obtained by us is 2.6 eV at \(x = 0.8\). Using ethylene as the carbon source, Sussmann and Ogden (1981) and Anderson and Spear (1977) obtained a peak in \(E_g vs x\) plots at an intermediate value of \(x\). Tawada et al (1982 b) obtained a monotonic increase of \(E_g\) with increase of \(x\) with both methane and ethylene as the carbon source. We have obtained monotonic increase of \(E_g\) with \(x\) using methane as carbon source.

As the substrate temperature increase from 423 K to 473 K band gap decreases from 1.95 to 1.80 eV (Fig. 3) which is probably due to the dominant effect of decrease of hydrogen content with the increase of \(T_D\). As \(T_D\) increases further \(E_g\) increases to 1.85 eV which may be due to the dominating influence of improvement of
Fig. 12. Plots of \((\alpha h \gamma)^{1/2}\) against photon energy \((h \gamma)\) for B-doped carbonated a-Si:H films \((x = 0.65)\) curves 1, 2, 3, 4 and 5 correspond to \(B_2H_6/(SiH_4 + CH_4)\) ratios of 0.0, \(1 \times 10^{-3}\), \(3 \times 10^{-3}\), \(1 \times 10^{-2}\) and \(2 \times 10^{-2}\) respectively.
amorphous net work at higher $T_p$, 

In Fig. 12 (oh)) vs. $h \nu$ plots for the p-type a-SiC:H films ($x = 0.65$) are shown together with that for the corresponding undoped sample. Optical band gap decreases from 2.14 eV to 1.76 eV as B$_2$H$_6$ concentration increases from 0% to 2%. A slight decrease of slope also occurs with increase of doping. This implies the presence of an acceptor band near the valence band tail.

In the case of p-type a-SiC:H samples with $x = 0.35$ the change in band gap [plotted in Fig. 5] also shows a saturation towards 1.76 eV at high doping level [2% B$_2$H$_6$].

7.3.4. Spectral response:

The photocurrent $(i_{ph})$ of undoped a-SiC:H films have been measured at room temperature with incident photon energies in the range 1.4 to 3.0 eV. The films have been prepared under different deposition conditions. From these data the number of photogenerated carriers flowing in the circuit per incident photon has been calculated as function of photon energy $(h \nu)$ for each specimen. Using the absorption coefficient $(\alpha)$ and spectral response data of a film the product $\eta \mu \tau$ has been calculated [Zansucchi, Wronski and Carlson (1977)] where $\eta$ is generation efficiency of carriers, $\mu$ is the mobility and $\tau$ the lifetime of carriers. The values of $\eta \mu \tau$ as function of $h \nu$ for a-SiC:H films prepared with different methane concentrations have been plotted in Fig. 13. It is seen that $\eta \mu \tau$ decreases rapidly with the increase of $x$. Above the band gap energy $\eta \mu \tau$ for a-SiH film
Fig. 15. The product of photoconductivity lifetime ($\eta$), mobility ($\mu$) and quantum efficiency ($\tau$) as a function of photon energy ($h\nu$). Curves 1, 2, 3 correspond to $x = 0.20$, 0.35, 0.50 respectively at $T_D = 523$ K. Curves 4, 5, 6 correspond to $T_D = 423$ K, 473 K and 553 K respectively at $x = 0.35$. 
is $8 \times 10^{-6} \text{ cm}^2/\text{V}$ [Chaudhuri, Ray and Barua (1984)] whereas it is $1.6 \times 10^{-9} \text{ cm}^2/\text{V}$ for a-Si:C:H film with $x = 0.5$. This decrease in $\eta_{\mu t}$ also indicates an increase of recombination centres due to the increase in defect states with increase in $x$. Similar variations of $\eta_{\mu t}$ with $x$ has been obtained by Morimoto, Miura, Kumeda and Shimizu (1982). Variation of $\eta_{\mu t}$ with substrate temperature for films with $x = 0.35$ has also been shown in Fig. 13. At $T_D = 423 \, \text{K}$, the $\eta_{\mu t}$ is very low and it increases with increase in substrate temperature and almost saturates above 523 K.

7.4. Conclusions:

The results of studies reported above for undoped and p-type a-Si:C:H films show that the properties are dependent in a complicated way on the various deposition conditions specially on methane and diborane concentrations and substrate temperatures. It appears that as carbon concentration increases the SiC structure starts predominating over the a-Si:H structure resulting in different behaviour in respect of dark conductivity, photoconductivity etc. The dark conductivity, photoconductivity, the $\eta_{\mu t}$ product, all tend to saturate above the substrate temperature of 523 K which indicates that due to higher surface mobility of the atoms during deposition the films deposited at and above 523 K may have an improved void free amorphous network.