STRUCTURAL AND ELECTRICAL CHARACTERISATIONS OF AMORPHOUS SILICON CARBIDE FILMS

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# Table Of Contents

Acknowledgements i  
List Of Figures vi  
List Of Tables xii  
List Of Symbols xiv  
Summary xvi  

**Chapter 1**  
**Introduction**  
1.1 Background 1  
1.2 R.F. Sputtering Process: A Viable Alternative 3  
1.3 Research Objectives 4  
1.4 Organisation of Thesis 5  

**Chapter 2**  
**Literature Survey**  
2.1 Amorphous Silicon Carbide 7  
2.1.1 The Role of Carbon 9  
2.1.2 The Role of Hydrogen 10  
2.1.3 Chemical Ordering 12  
2.2 Structural Properties 13  
2.2.1 Infrared Spectroscopy 13  
2.2.1.1 Shift in Bonding Peaks 17  
2.2.1.2 Annealing Effects 20  
2.2.2 X-Ray Photoelectron Spectroscopy 24  
2.2.2.1 Chemical Bonding States 25  
2.3 Optical Properties 26  
2.3.1 Optical Gap 27  
2.3.2 Refractive Index 31  
2.3.3 Photoluminescence 35  
2.4 Electrical Properties 37
Chapter 3  Theoretical Background  

3.1 Radio Frequency (R.F.) Sputtering Technique  
3.2 Fourier Transform Infrared (FTIR) Spectroscopy  
   3.2.1 Principle of FTIR  
3.3 X-Ray Photoelectron Spectroscopy  
   3.3.1 Principle of XPS  
   3.3.2 Quantitative XPS Analysis  
3.4 Conduction Mechanism in Dielectrics  
   3.4.1 Ohmic Conduction  
   3.4.2 Frenkel-Poole Emission  
   3.4.3 Schottky Emission  
   3.4.4 Tunnelling  
3.5 Temperature Dependence of D.C. Conductivity  
3.6 Capacitance-Voltage Measurements  
3.7 Interface Trap Density $D_H$ by Conductance Method  
   3.7.1 Correction for Series Resistance ($R_S$)  
   3.7.2 Correction for Dielectric Capacitance ($C_I$)  
   3.7.3 Interface Trap Density in Silicon Bandgap  

Chapter 4  Sample Preparation  

4.1 Sample Preparation and Cleaning  
4.2 Film Deposition by R.F. Sputtering  
4.3 Annealing  
   4.3.1 Furnace Annealing  
   4.3.2 Rapid Thermal Anneal (RTA)  
4.4 Thickness Measurement  
4.5 Metallisation  
4.6 Fourier Transform Infrared (FTIR) Spectrophotometer Measurement  
4.7 X-ray Photoelectron Spectroscopy  
4.8 Electrical Measurements
4.8.1 Current vs Voltage Measurements 92
4.8.2 Capacitance and Conductance Measurements 92
4.8.3 Noise Measurements 92

Chapter 5 Infrared Spectroscopy Results 94
5.1 Infrared Spectroscopy Results of As-Deposited Films 94
   5.1.1 Rfh Samples 97
   5.1.2 Rfp Samples 103
5.2 Infrared Spectroscopy Results of Annealed Films 105
   5.2.1 Rfh Samples 105
   5.2.2 Rfp Samples 116
5.3 Conclusions 123

Chapter 6 X-Ray Photoelectron Spectroscopy 128
6.1 XPS Results of As Deposited Samples 128
   6.1.1 Rfh Samples 129
   6.1.2 Rfp Samples 132
6.2 XPS Results of Annealed Samples 134
   6.2.1 Rfh Samples 134
   6.2.2 Rfp Samples 138
6.3 Conclusions 139

Chapter 7 Electrical Characterisation Results 142
7.1 Current–Voltage Characteristics of As Deposited Films 142
   7.1.1 Rfh Samples 146
      7.1.1.1 Temperature Dependence of Conductivity 150
      7.1.1.2 Conduction Mechanism 156
   7.1.2 Rfp Samples 165
      7.1.2.1 Temperature Dependence of Conductivity 169
      7.1.2.2 Conduction Mechanism 173
7.2 Capacitance-Voltage Measurement of As-Deposited Films 181
List Of Figures

2.1 Typical IR Spectra of a-Si$_{1-x}$C$_x$:H Films.  

2.2 Assignment of wavenumbers to Si-C modes with changing back bonding.  

2.3 Tauc plot for a-Si$_{1-x}$C$_x$:H films reported by Sussman and Ogden [64]. The films were prepared by the glow discharge of SiH$_4$ and C$_2$H$_4$ at 400$^\circ$C, rf power 15-25W and pressure 0.2 to 0.5 mbar. The values of x are labeled beside the curves.  

2.4 The $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot for r.f. sputtered a-Si$_{1-x}$C$_x$:H films prepared under different hydrogen partial pressures (rfh05: $P_\text{H}$=0.15 Pa; rfh10: $P_\text{H}$=0.30 Pa; rfh20: $P_\text{H}$=0.60 Pa).  

2.5 Optical gap for a-Si$_{1-x}$C$_x$:H films sputtered with a polycrystalline SiC target at an ambient of Ar + H$_2$ at different hydrogen partial pressure ($P_\text{H}$). (●)[81], (○) [8] and (×) [23].  

2.6 Refractive index of a-Si$_{1-x}$C$_x$:H films plotted against the precursor gas flow rate of [77] and [78] respectively.  

2.7 Refractive index of a-Si$_{1-x}$C$_x$:H films plotted against the precursor gas flow rate of [77] and [78] respectively.  

2.8 Refractive index ($n_0$) as a function of x for a-Si$_{1-x}$C$_x$:H films deposited with SiH$_4$+CH$_4$ and SiH$_4$+C$_2$H$_2$ gas mixtures. (SiH$_4$+CH$_4$: (Δ) [91], (○) [98], (+) [32]; SiH$_4$+C$_2$H$_2$: (×) [4], (●)[99])  

2.9 Refractive index ($n_0$) of a-Si$_{1-x}$C$_x$:H films as a function r.f. power and hydrogen partial pressures.  

2.10 Photoluminescence spectra for a-Si$_{1-x}$C$_x$:H films reported by Sussman and Ogden [64] (solid lines) and Engemann et al. [90] (dashed lines).  

3.1 Schematic representation of the various experimental aspects of sputtering.  

3.2 Fourier Transform infrared spectrometer schematic.  

3.3 Typical widescan XPS spectrum of r.f. sputtered a-Si$_{1-x}$C$_x$:H film.  

3.4 Frenkel-Poole emission of trapped electrons.  

3.5 Lowering of potential barrier by image forces in Schottky emission.  

3.6 Tunneling models for heterojunction.
3.7 Equivalent circuit of MIS capacitor in strong accumulation.

3.8 Equivalent circuit for conductance measurement (a) MIS capacitor with interface state time constant, (b) simplified circuit of (a), (c) measured circuit.

3.9 Band-bending diagram of p-type silicon showing how the position of the Fermi level at the silicon surface is related to band bending.

3.10 Band-bending diagram of p-type silicon showing how the position of the Fermi level at the silicon surface is related to band bending.

4.1 Schematic diagram of the r.f. sputtering system.

4.2 Schematic diagram of the rapid thermal processing system.

4.3 The temperature-time profiles of the rapid thermal annealing process at 600 and 800 °C used in this work.

4.4 A schematic diagram of the experimental set-up for the electrical measurements.

5.1(a) Infrared spectra of rfsputtered amorphous silicon carbide films prepared with different hydrogen pressures.

5.1(b) Infrared spectra of rfsputtered amorphous silicon carbide films prepared with different chamber pressures.

5.2(a) Infrared spectra of rfh0 series of samples, with annealing temperatures of 400-800°C.

5.2(b) Infrared spectra of rfh5 series of samples, with annealing temperatures of 400-800°C.

5.2(c) Infrared spectra of rfh10 series of samples, with annealing temperatures of 400-800°C.

5.2(d) Infrared spectra of rfh15 series of samples, with annealing temperatures of 400-800°C.

5.3(a) Infrared spectra of rfp08 series of samples, with annealing temperatures of 400-800°C.

5.3(b) Infrared spectra of rfp15 series of samples, with annealing temperatures of 400-800°C.
5.3(c) Infrared spectra of rfp20 series of samples, with annealing temperatures of 400-800° C.

5.3(d) Infrared spectra of rfp25 series of samples, with annealing temperatures of 400-800° C.

6.1 Typical widescan XPS spectrum of r.f. sputtered a-Si\textsubscript{1-x}C\textsubscript{x}:H film.

6.2 Typical narrow scans of the Si2p and Cls peaks of the r.f. sputtered a-Si\textsubscript{1-x}C\textsubscript{x}:H films.

7.1(a) Current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different hydrogen partial pressures.

7.1(b) Current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different sputtering pressures.

7.2 Log scale current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different hydrogen partial pressures.

7.3 Log scale current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different hydrogen partial pressures for forward and reverse bias.

7.4(a) Current versus voltage characteristics of rfh0 sample as a function of ambient temperature.

7.4(b) Current versus voltage characteristics of rfh5 sample as a function of ambient temperature.

7.4(c) Current versus voltage characteristics of rfh10 sample as a function of ambient temperature.

7.5 Log conductivity versus (1000/T) plot of samples rfh0, rfh5 and rfh10.

7.6 A multitunneling capture-emission model for the SiC:H/ c-Si heterojunction.

7.7(a) Log current versus voltage characteristics of rfh0 sample as a function of ambient temperature.

7.7(b) Log current versus voltage characteristics of rfh5 sample as a function of ambient temperature.

7.7(c) Log current versus voltage characteristics of rfh10 sample as a function of ambient temperature.

7.8 Log $I_S$ against (1000/T) plot for rf samples.
7.9 Log $I_S/T^2$ against $(1000/T)$ plot for rfh samples. 163
7.10 Log $I_0$ against $(1000/T)$ plot for rfh samples. 164
7.11 Log scale current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different chamber pressures. 167
7.12(a) Current versus voltage characteristics of rfp08 sample as a function of ambient temperature. 169
7.12(b) Current versus voltage characteristics of rfp15 sample as a function of ambient temperature. 170
7.12(c) Current versus voltage characteristics of rfp15 sample as a function of ambient temperature. 171
7.13 Log conductivity versus $(1000/T)$ plot of samples rfp08, rfp15 and rfp25. 172
7.14(a) Log current versus voltage characteristics of rfp08 sample as a function of ambient temperature. 175
7.14(b) Log current versus voltage characteristics of rfp15 sample as a function of ambient temperature. 176
7.14(c) Log current versus voltage characteristics of rfp25 sample as a function of ambient temperature. 177
7.15 Log $I_S$ against $(1000/T)$ plot for rfp samples. 178
7.16 Log $I_S/T^2$ against $(1000/T)$ plot for rfp samples. 179
7.17 Log $I_0$ against $(1000/T)$ plot for rfp samples. 180
7.18 The capacitance-voltage characteristic of rfh5 sample. 183
7.19 The capacitance-voltage characteristic of rfp15 sample. 184
7.20 The $G_p/\omega$ as a function of frequency at different applied biases for rfh5 sample. 187
7.21 Interface trap density as a function of energy level in the silicon band gap for samples prepared under different hydrogen partial pressures. 188
7.22 The $G_p/\omega$ as a function of frequency at different applied biases for rfp20 sample. 190
7.23 Interface trap density as a function of energy level in the silicon band gap for samples prepared under different chamber pressures. 191
7.24(a) Current versus voltage characteristics of rfh0 sample annealed at temperatures 400, 600 and 800°C.

7.24(b) Current versus voltage characteristics of rfh5 sample annealed at temperatures 400 and 600°C.

7.24(c) Current versus voltage characteristics of rfh10 sample annealed at temperatures 400 and 600°C.

7.25(a) Log current versus voltage characteristics of rfh0 sample annealed at temperatures 400, 600 and 800°C.

7.25(b) Log current versus voltage characteristics of rfh5 sample annealed at temperatures 400 and 600°C.

7.25(c) Log current versus voltage characteristics of rfh10 sample annealed at temperatures 400 and 600°C.

7.26(a) Log current versus voltage characteristics of rfh0 sample RTA at temperatures 600 and 800°C.

7.26(b) Log current versus voltage characteristics of rfh5 sample RTA at temperature 600°C.

7.26(c) Log current versus voltage characteristics of rfh10 sample RTA at temperature 600°C.

7.27 Current versus voltage characteristics of rfh04 sample as a function of ambient temperature.

7.28(a) Log conductivity versus (1000/T) plot of sample rfh0 annealed at temperatures 400, 600 and 800 °C.

7.28(b) Log conductivity versus (1000/T) plot of sample rfh5 annealed at temperatures 400 and 600 °C.

7.28(c) Log conductivity versus (1000/T) plot of sample rfh10 annealed at temperatures 400 and 600 °C.

7.29(a) Log conductivity versus (1000/T) plot of sample rfh0 RTA at temperatures 600 and 800 °C.

7.29(b) Log conductivity versus (1000/T) plot of sample rfh5 RTA at temperature 600 °C.

7.29(c) Log conductivity versus (1000/T) plot of sample rfh10 RTA at temperature 600 °C.

7.30(a) Current versus voltage characteristics of rfp08 sample annealed at
temperatures 400, 600 and 800 °C.

7.30(b) Current versus voltage characteristics of rfp15 sample annealed at temperatures 400, 600 and 800 °C.

7.30(c) Current versus voltage characteristics of rfp25 sample annealed at temperatures 400 and 600 °C.

7.31(a) Log current versus voltage characteristics of rfp08 sample annealed at temperatures 400, 600 and 800 °C.

7.31(b) Log current versus voltage characteristics of rfp15 sample annealed at temperatures 400 and 600 °C.

7.31(c) Log current versus voltage characteristics of rfp25 sample annealed at temperatures 400 and 600 °C.

7.32 Current versus voltage characteristics of rfp154 sample as a function of ambient temperature.

7.33(a) Log conductivity versus (1000/T) plot of sample rfp08 annealed at temperatures 400, 600 and 800 °C.

7.33(b) Log conductivity versus (1000/T) plot of sample rfp15 annealed at temperatures 400, 600 and 800 °C.

7.33(c) Log conductivity versus (1000/T) plot of sample rfp25 annealed at temperatures 400 and 600 °C.

7.34 The capacitance-voltage characteristics of rfh5 sample after annealing.

7.35 The capacitance-voltage characteristics of rfp20 sample after annealing.

7.36 Interface trap density as a function of energy level in the silicon band gap for rfh0 sample after annealing.

7.37 Interface trap density as a function of energy level in the silicon band gap for rfh5 sample after annealing.

7.38 Interface trap density as a function of energy level in the silicon band gap for rfh10 sample after annealing.

7.39 Interface trap density as a function of energy level in the silicon band gap for rfp08 sample after annealing.

7.40 Interface trap density as a function of energy level in the silicon band gap for rfp15 sample after annealing.

7.41 Interface trap density as a function of energy level in the silicon band gap for rfp25 sample after annealing.
List Of Tables

2.1 Summary of Si-C, Si-H$_n$ and C-H$_n$ vibrations and their corresponding frequency. 15

2.2 Calculated stretching frequency of Si-H$_n$ with changing back bonding. 18

4.1 Preparation and annealing conditions of the r.f. sputtered $a$-Si$_{1-x}$C$_x$:H samples used in this work. 86

4.2 Thickness of the r.f. sputtered $a$-Si$_{1-x}$C$_x$:H samples prepared under different P$_H$ and P$_S$. 89

5.1 Peak position of Si-C, Si-H and C-H stretching modes of as-prepared rfh films. 98

5.2 Density of Si-C bonds (N$_{Si-C}$), Si-H bonds (N$_{Si-H}$) and C-H bonds (N$_{C-H}$) of as-prepared rfh films. 101

5.3 Peak position of Si-C and Si-H stretching modes of as-prepared rfp Films. 103

5.4 Density of Si-C bonds (N$_{Si-C}$) and Si-H bonds (N$_{Si-H}$) of as-prepared rfp films. 103

5.5 Density of Si-C bonds (N$_{Si-C}$), Si-H bonds (N$_{Si-H}$) and C-H bonds (N$_{C-H}$) calculated from the IR spectra of the as-prepared and annealed rfh samples. 114

5.6 Peak position of Si-C, Si-H and C-H absorption band of the as-prepared and annealed rfh samples. 115

5.7 Density of Si-C bonds (N$_{Si-C}$) and Si-H bonds (N$_{Si-H}$) calculated from the IR spectra of the as-prepared and annealed rfp samples. 121

5.8 Peak position of Si-C and Si-H absorption band of the as-prepared and annealed rfp samples. 122

6.1 Binding energy and stoichiometry of r.f. sputtered P$_H$ samples. 131

6.2 Film composition of P$_H$ samples. 132

6.3 Binding energy and stoichiometry of r.f. sputtered P$_S$ samples. 133

6.4 Film composition of P$_S$ samples. 133

6.5 Binding energy and stoichiometry of annealed and as-prepared r.f. sputtered P$_H$ samples. 135
6.6 Film composition of annealed and as-prepared \( \text{P}_\text{H} \) samples.

6.7 Binding energy and stoichiometry of furnace annealed and as-prepared r.f. sputtered \( \text{P}_\text{S} \) samples.

6.8 Film composition of furnace annealed and as-prepared \( \text{P}_\text{S} \) samples.

7.1 D.C. Conductivity, saturation current \((I_S)\), and ideality factor and rectifying ratio of as-prepared rfh films

7.2 Density of Si-H bonds, d.c. conductivity and activation energy of as-prepared rfh films.

7.3 Density of Si-H bonds and the activation energy \( \Delta E_{AS} \) and \( \Delta E_{AF} \) and barrier height \( \Phi_B \) of as-prepared rfh films.

7.4 D.C. Conductivity, saturation current \((I_S)\), and ideality factor of as-prepared rfp films.

7.5 D.C. conductivity and activation energy of as-prepared rfp films.

7.6 Activation energy \( \Delta E_{AS} \) and \( \Delta E_{AF} \) and barrier height \( \Phi_B \) of as-prepared rfp films.

7.7 Density of Si-H bonds, dielectric constant and interface trap density of as-prepared rfh films.

7.8 Dielectric constant and interface trap density of as-prepared rfp films.

7.9 D.C. Conductivity, saturation current \((I_S)\), and ideality factor of as-prepared and annealed rfh films.

7.10 Density of Si-H bonds, d.c. conductivity and activation energy of as-prepared and annealed rfh films.

7.11 D.C. Conductivity, saturation current \((I_S)\), and ideality factor of as-prepared and annealed rfp films.

7.12 D.C. Conductivity and activation energy of as-prepared and annealed rfh films.

7.13 Thermal properties relevant to the adherence of SiC films to Si

7.14 Density of Si-H bonds, dielectric constant and interface trap density of as-prepared and annealed rfh films.

7.15 Dielectric constant and interface trap density of as-prepared and annealed rfp films.
List Of Symbols

$E_B$  Binding energy (eV)

$V_S$  Substrate floating potential

$\alpha(\omega)$  Absorption coefficient

$\omega$  Wavelength

$A$  Inverse absorption cross section constant

$h\nu$  Photon energy

$E_K$  Kinetic energy of the electron

$W$  Spectrometer work function

$I$  Number of photoelectrons per second in a specific spectra peak

$n$  Number of atoms of the element per cm$^3$ of the sample

$f$  X-ray flux in photons per cm$^2$-sec

$\sigma$  Photoelectric cross-section for the atomic orbital of interest in cm$^2$

$\theta$  Angular efficiency factor for the instrument arrangement based on the angle between the photon path and detected electron

$\lambda$  Mean free path of the photoelectrons

$A$  Area of the sample

$T$  Detection efficiency for electrons emitted from the sample

$A_X$  Area under the peak of element X

$S_X$  Sensitivity factor

$E_a$  Activation energy

$\varepsilon_d$  Dynamic dielectric constant

$\Phi_B$  Depth of the trap potential well

$\varepsilon_s$  Static permittivity
\( C_a \)  Accumulation layer capacitance
\( R_S \)  Series resistance
\( C_i \)  Dielectric capacitance
\( C_C \)  Corrected capacitance
\( G_C \)  Corrected conductance
\( C_{it} \)  Interface trap capacitance
\( E_C \)  Conduction band edge
\( E_T \)  Trap energy
\( I_S \)  Saturation current
\( n \)  Ideality factor
\( q \)  Electron charge
\( k \)  Boltzmann’s constant
\( T \)  Temperature
\( \psi_s \)  Surface band bending
\( V_G \)  Applied bias
\( V_{FB} \)  Flatband voltage
Summary

Amorphous silicon carbide (a-SiC) films have received a considerable amount of interest recently due to their potential applications in the electronics and optical devices. In this research, amorphous silicon carbide films were prepared using the r.f. sputtering technique by varying the hydrogen partial pressure ($P_{H}$) and chamber pressure ($P_{S}$). The structural properties of the films were characterised by the infrared (IR) and x-ray photoelectron (XPS) spectroscopy techniques. Electrical evaluation of the film quality was obtained from current (I-V), capacitance (C-V) and conductance (G-V) versus voltage measurements.

The infrared (IR) results of the as-prepared films show that as $P_{H}$ or $P_{S}$ increases, more hydrogen is incorporated into the film to form Si-H and C-H bonds. On the other hand, there will be less silicon and carbon available to form Si-C bonds. The stoichiometry of the as-prepared films was studied using x-ray photoelectron spectroscopy (XPS) and it was found to be dependent on the composition of the target and not so much on the preparation conditions. Annealing of the films show an increase in the Si-C bonds and a decrease in the hydrogenated bonds. For the unhydrogenated film, as annealing temperature increases, more silicon and carbon dangling bonds will combine to form more Si-C bonds. For the hydrogenated films, the increase in the Si-C bonds is more likely due to the formation of Si-C bonds from the dissociation of the Si-H and C-H bonds.

The d.c. conductivity $\sigma$ of the as-prepared films were found to be in the range of $2.76 \times 10^{-6}$ to $3.86 \times 10^{-8} \, \Omega^{-1} \text{cm}^{-1}$ and it decreases as $P_{H}$ or $P_{S}$ increases. Annealing causes a
reduction in the conductivity of the film. The activation energy $E_a$ was found to increase as $P_H$ or $P_S$ increases. Unlike the d.c. conductivity, the activation energy do not always decrease after annealing especially at higher temperatures. The current conduction mechanism in the sputtered films at low field region was found to be either thermionic emission over a potential barrier or a combination of the multi-tunneling capture emission model (MTCE) and thermionic emission over a potential barrier. At high field region, the I-V curve deviates from linearity due to the series resistance associated with the contacts. Annealing of the films also causes a change in the transport mechanism. The interface trap density $D_{it}$ of the as-prepared films were found to be in the range of $45 \times 10^{11}$ to $4.5 \times 10^{11} \text{eV}^{-1}\text{cm}^{-2}$. $D_{it}$ decreases with either an increase in $P_H$ or $P_S$. The decrease in $D_{it}$ was found to be closely related to the increase in the number of Si-H and C-H bonds. Annealing will cause a reduction in $D_{it}$ except for films with higher hydrogen content (10%). It was found that RTA is not as effective as furnace annealing in reducing $D_{it}$. 
Chapter One

Introduction

1.1 Background

Amorphous hydrogenated silicon carbide (a-Si$_{1-x}$C$_x$:H) was first prepared by Anderson and Spear in 1977 by the glow discharge technique [1]. Since then, amorphous hydrogenated silicon carbide films continue to be of considerable current interest both fundamentally, in regard to understanding the effect of the film microstructure on film properties, and also technologically, in regard to its applications as electronic and optoelectronics devices.

a-Si$_{1-x}$C$_x$:H films are extensively studied both as a typical material of an amorphous system with variable disorder and microstructures, and for potential applications such as solar cells, thin film transistors, photoreceptors, and graphic devices. This is due to the fact that the optical gap of the films can be controlled by changing the compositional ratio of its constituent elements, namely carbon and hydrogen, which can be controlled by appropriately choosing the experimental deposition conditions and techniques. Furthermore, amorphous silicon carbide films are chemically and mechanically stronger and more durable in terms of temperature resistance than a-Si films. As such, a-SiC films can be applied in silicon micromachining and biological devices [2]. In addition, recent studies have been focusing on the use of silicon carbide membranes as x-ray masks due to the high Young modulus and good optical and x-ray transparencies of this material [3]. Moreover, since it has been established that a-SiC film can be used as a wide-bandgap window material, the combination of this feature
with the good electronic properties of crystalline Si would mean that an a-SiC/crystalline Si (c-Si) heterostructure would give a higher conversion efficiency than that of a c-Si homostructure provided that a good amorphous/crystalline junction could be fabricated [4].

As the structural, optical and electrical properties of a-Si$_{1-x}$C$_x$:H films can be controlled by changing the percentage of carbon and hydrogen, several techniques have been employed to prepare a-Si$_{1-x}$C$_x$:H films. These techniques include glow discharge, chemical vapor deposition, photochemical vapor deposition and sputtering processes. Among the different techniques, plasma-enhanced chemical vapour deposition (PECVD) is the most widely used due to its ability to produce high quality thin films. However, new applications have highlighted the unsuitability of the PECVD films. For example, the inherent high hydrogen content in PECVD films (and therefore high compressive stress) makes it necessary for the films to be annealed to reduce stress for x-ray masks. This, coupled with the demands of present microelectronics industry for low temperature and ecologically safe technologies, has led to a renewed interest in techniques such as radio frequency (r.f.) sputtering and more recently, electron cyclotron resonance deposition technique [5].

Even in the sputtering processes, there are various methods. Physical sputtering of a polycrystalline SiC target always yields unhydrogenated materials, which are nearly at stoichiometric ratio of 0.5. Co-sputtering from silicon and graphite targets allows the silicon to carbon ratio of the deposited film to vary. Sputtering in the presence of reactive gases including H$_2$, SiH$_4$ and CH$_4$ makes it possible to incorporate various amounts of hydrogen into the films and to control the silicon to carbon ratio.
1.2 R.F. Sputtering Process: A Viable Alternative

R.F. sputtering process has been used for the deposition of dielectric thin films such as tantalum oxide and silicon carbide, for many different device applications. The technique is based on the bombardment of a material target with ionised gas molecules from a r.f. plasma maintained at low pressure, primarily leading to atoms or molecules ejection and electron emission from the target surface. Atoms or molecules are then deposited onto the substrate while the electrons play a number of complex roles including sustaining the plasma and regenerating the electrons emitted from the target surface.

The sputtering process offers the following advantages:

(i) It is intrinsically a low temperature process. R.F. sputtered films are typically deposited at temperatures of 200 °C or less [6,7] while PECVD films require temperatures greater than 250 °C.

(ii) It is versatile in that different target materials can be co-sputtered together and this would lead to different materials being incorporated into the deposited films. Hydrogenated films can be easily obtained by adding a small amount of hydrogen in the sputtering gas and therefore offers the flexibility of depositing both hydrogenated and unhydrogenated films [8].

(iii) It is ecologically safe or environmental friendly [7]. R.F. sputtering eliminates the use of toxic and flammable gases such as silane and methane. Usually, the main sputtering gases are argon and hydrogen, which can be released into the atmosphere without treatment.

(iv) Deposition rate can be precisely controlled.
The main drawbacks of the sputtering process are the complexity of the process mechanism and the poor film quality. Fortunately, by proper characterisation of the process parameters and performing a post deposition anneal on the sputtered films, it is possible to produce films that display good structural and electrical characteristics.

1.3 Research Objectives

Extensive research has been done on the structural and optical properties of a-Si_{1-x}C_{x}:H films. However, work done on the electrical characterization of r.f. sputtered a-Si_{1-x}C_{x}:H films is relatively few. Therefore the objective of this project is to focus on the electrical characterisation of a-SiC:H films prepared by rf sputtering technique. Firstly, the deposition conditions of rf sputtered a-SiC:H films were investigated. The effects of the chamber pressure and hydrogen partial pressure during the sputtering process were considered. Secondly, to investigate the properties of the a-SiC:H / c-Si interface as well as the electrical properties of the metal - a-SiC:H - c-Si (MIS) structure. The effects of conventional furnace and rapid thermal annealing (RTA) on the rf sputtered a-SiC:H-Si system were also studied and it formed a major aspect of this investigation. Infrared (IR) spectroscopy was performed on the samples to aid in the explanation of the electrical results. Current, capacitance and conductance versus voltage measurements, including noise measurements, were performed on the MIS structures to determine the film properties and that of the a-SiC:H-Si interface.
1.4 Organisation of Thesis

Following this introductory chapter, a literature survey on the r.f. sputtered a-Si$_{1-x}$C$_x$:H films will be presented in Chapter 2. The next chapter presents the relevant theoretical background for this work. It discusses the principles of r.f. sputtering and outlines the various structural and electrical characterisation methods used in this project. The experimental setup, sample preparation conditions and the annealing conditions will be reviewed in Chapter 4. The structural and electrical results of the present investigation and a discussion and interpretation of these results will be presented in Chapters 5, 6 and 7 respectively. Also presented in these three chapters will be the effects of furnace and rapid thermal annealing on the films. A preliminary investigation of the noise measurements is presented in Chapter 8. Finally, Chapter 9 will conclude the investigation and recommend a number of relevant research areas for further study.
References


Chapter Two

Review of Amorphous Silicon Carbide System

Amorphous hydrogenated silicon carbide (a-Si$_{1-x}$C$_x$:H) was first prepared by Anderson and Spear in 1977 by the glow discharge technique [1]. Since then, much effort has been spent on understanding the properties of this material as well as its application in electronic and optoelectronic devices. It should be pointed out that majority of the work done is on films prepared by the glow discharge or plasma enhanced chemical vapour deposition (PECVD). Relatively few works are on the r.f. sputtered films. In this review chapter, emphasis will be on published results of r.f. sputtered amorphous hydrogenated (a-Si$_{1-x}$C$_x$:H) and non-hydrogenated (a-Si$_{1-x}$C$_x$) silicon carbide films. Due to the relatively few reports on r.f. sputtered films, we will, whenever necessary, draw on the conclusions for the PECVD or reactive sputtered films. An overview of the development of this material over the past decades will be presented first. This will be followed by a discussion on the structural and electrical characteristics of the amorphous film.

2.1 Amorphous Silicon Carbide

Amorphous silicon carbide is a tetrahedrally bonded binary compound. It exhibits useful properties such as chemical resistance, high thermal stability and mechanical hardness. Amorphous silicon carbide films have been prepared by various methods, such as the glow discharge technique [1,2,3], plasma CVD [4,5], reactive sputtering [6], r.f. sputtering [7,8], and more recently, the electron cyclotron resonance (ECR) CVD [9]. The structural and electrical properties of these films depend on the
deposition methods and preparation conditions. These conditions include the source gases, the r.f. power, the chamber pressure and the substrate temperature.

In general, the structural, electrical and optical properties of the a-Si$_{1-x}$C$_x$:H films are primarily controlled by the ratio of silicon to carbon and the degree of hydrogenation in the film [10]. The carbon content influences the formation of graphite-like C-C bonds in the film. In carbon-rich a-Si$_{1-x}$C$_x$:H film, the high carbon content leads to films that are porous and have a reduced band gap. The incorporation of hydrogen into the film, on the other hand, serves to minimise the dangling bonds and promotes a more coordinated amorphous network. The carbon content and degree of hydrogenation in the film are usually varied using the glow discharge or PECVD techniques. For r.f. sputtering, the ratio of carbon to silicon can be adjusted by co-sputtering from silicon and carbon targets of different dimensions. Alternatively, sputtering in reactive gases like CH$_4$, SiH$_4$ and H$_2$ can also vary the carbon content. In addition, hydrogen too can be incorporated into the film in this manner. To obtain near stoichiometric films, a polycrystalline SiC target is used during r.f. sputtering. As highlighted earlier, the film properties are closely related to the preparation techniques and conditions. Therefore, a survey of the films prepared by different techniques and conditions is necessary for the in depth structural and electrical study of the r.f. sputtered amorphous silicon carbide films.

The next section will highlight the importance of carbon and hydrogen have on the properties of the amorphous silicon carbide films. Each element will be considered individually although there are instances where both are closely dependent on each other.
2.1.1 The Role of Carbon

Carbon has the distinct property of modifying the random network of amorphous silicon when being incorporated. This has led to the possibility of distinguishing three ranges of alloys, which differ in carbon content [11]. At relatively low carbon content, the carbon is incorporated in the random network of amorphous silicon. The carbon is incorporated by various CHₙ (n = 1,2,3) species [12,13] so that the carbon atoms adopt many bridging and network-terminating configurations. Hence, the carbon disturbance of the Si network is minimised. When the contents of the components are approximately equal, we are dealing with amorphous hydrogenated silicon carbide proper, which may be slightly supersaturated with carbon. Morell et al. [14] observed that as stoichiometry is approached, the formation of Si-C bonds dominates allowing a considerable degree of chemical order to take place. At high carbon concentration, various structural modifications can arise. They depend on the method used to introduce the carbon and conditions for the energy excitation of the carbon atoms and molecules incident on the surface of the growing layer. In the latter case, the structure may vary from graphite to diamond, including intermediate carbide modifications and a possible polymerization of hydrogenous carbon complexes. Liu et al. [9] observed sp³-bonding configuration in the C-C bonds for films with high carbon incorporation.

Zhang et al. [15] showed that the stress of the films changes from compressive to tensile stress by the addition of carbon. The introduction of higher relative electronegativity carbon (2.5) into lower relative electronegativity of silicon (1.8) will lead to the strengthening of the interaction among atoms in the film and make the film more compact. As a result, the compressive stress is weakened due to the film contracting.
The optical band gap and refractive index of the film are functions of the carbon content. Anderson and Spear et al. [1] showed that the optical gap increases from about 1.6 eV to 2.9 eV as carbon content increases to $x = 0.7$. After which, the optical gap decreases with further increase in carbon content. Shimada et al. [16] also observed that same trend for their reactive sputtered films except that the maximum optical gap occurs at $x = 0.4$. However, Saraie et al. [17] reported that the optical band gap does not show a maximum in contrast with the results of those mentioned. Instead, the band gap increases more steeply with $x$ from $x \approx 0.75$. This is attributed to a change in structure from tetrahedral amorphous to polymer-like amorphous brought about by the high hydrogen content.

2.1.2 The Role of Hydrogen

Generally the presence of hydrogen in the plasma and the incorporation of hydrogen into the films during deposition are responsible for the passivation of the dangling bonds in the films, leading to changes in the optical and electrical properties [9]. Hydrogen also prevents the formation of graphite-like C-C bonds in the films, which can lead to porous film properties and reduced band gap. The presence of hydrogen favours the formation of a tetrahedral network and thus enhances the chemical order in the material, thus producing a more coordinated amorphous network [18]. Finocchi et al. [19], through the analyses of the different bonding configurations, revealed that hydrogenated carbon forms tetrahedral units, whereas carbon not bonded to hydrogen gives rise to sites with bonding intermediate between sp$^2$ and sp$^3$. 
Beyer et al. [20] reported that hydrogen induces voids in a-Si$_{1-x}$C$_x$:H films. This is due to the fact that hydrogen-terminated bonds do not participate in the amorphous network. Therefore, for a certain hydrogen density, the network will lose its connectiveness and result in the formation of voids. This is also supported by Arce et al. [21]. However, Hicks et al. [12] and Baker et al. [22] suggested that the comparatively large fraction of incorporated hydrogen is not itself the primary reason for the formation of a defect network. The improvements in the electronic properties of the hydrogenated samples were attributed to a much denser network structure with fewer voids.

Girginoudi et al. [23] observed that the optical band gap of their sputtered film increases as the hydrogen partial pressure increases from 0.0 to 1.2 mTorr. For hydrogen pressures greater than 1.2 mTorr the optical band gap is almost constant due to the hydrogen saturation effects. The increase in hydrogen content in the film increases the optical gap [24,16].

For silicon-rich films, the incorporation of hydrogen was shown to encourage chemical clustering that promotes Si-Si nearest-neighbour pair against heteratomic Si-C bonding in the local silicon environment [13]. As carbon content increases to near stoichiometric i.e. $x = 0.5$, a significant tendency towards chemical ordering was observed [25]. Finocchi et al. [19] also noted that the degree of chemical ordering of hydrogenated network is higher than a pure network.

For carbon-rich films, the presence of a sizeable amount of hydrogen in the films prevents $sp^2$ bonding and promotes tetrahedral carbon coordination ($sp^3$) and chemical
ordering. This is due to the preferential binding of hydrogen to carbon atom as the C-H binding energy is higher than the Si-H binding energy. Ray et al. [26] reported that at higher carbon concentration, depending on the substrate temperature, the probability of hydrogen bonded to silicon decreases whereas the preferential bonding of hydrogen and silicon with carbon takes place.

2.1.3 Chemical Ordering

There has been much debate as to the degree of chemical ordering in amorphous silicon carbide films. Complete chemical ordering refers to the situation where carbon atoms have only silicon nearest neighbours in silicon-rich and where silicon atoms have only carbon nearest neighbours in carbon-rich alloys. Thus, completely chemically ordered films contain the maximum possible number of Si-C bonds. If the Si-C bonds are randomly dispersed throughout the film, then the chemical ordering is said to be homogeneous. If, however, the Si-C bonds are clustered, then in addition to chemical ordering there is also phase separation. According to Morimoto et al. [27], chemical ordering means that Si-C and Si-Si bonds are randomly distributed for $x < 0.5$, and Si-C and C-C bonds are randomly distributed for $x > 0.5$. If there exist no preferential chemical bonding between silicon and carbon atoms, then the alloys are said to be chemically disordered.

From the literature survey, there exist some discrepancies over the chemical ordering of the amorphous silicon carbide films. Finocchi et al. [19] showed that the Si-C films is a complex network composing of homonuclear and heteronuclear bonds whereas others characterise the structure as highly ordered, with a pre-dominance of Si-C bonds [28]. Some argued that the Si-C films have a moderate degree of chemical ordering.
[13]. In fact, different degrees of chemical ordering ranging from near random [29] to near complete have been proposed in particular studies of a-Si_{1-x}C_{x}:H. Thus, it can be seen that different approaches have been adopted to describe the nature of chemical ordering in the films. One which describes silicon carbide films as a tetrahedral network where carbon and silicon atoms are randomly distributed to one which exhibits a tendency towards chemical ordering. However, it should be agreed upon that the structure of the films is highly dependent on the deposition techniques and conditions. And therefore, films prepared by different techniques will be different structurally in some way or another.

### 2.2 Structural Properties

In this section, a review of the structural characteristics, namely the infrared and x-ray spectroscopy results will be presented. The infrared measurement is one of the most important tool in analysing the chemical bonding of the molecular units in a-Si_{1-x}C_{x}:H films and therefore it comes as no surprise that it is one of the most frequently used technique to study the structure of the films.

#### 2.2.1 Infrared Spectroscopy

There are three main infrared active vibrational modes in a-Si_{1-x}C_{x}:H films. These includes: a strong stretching mode at ~800 cm\(^{-1}\) corresponding to the partly ionic Si-C bond, a stretching mode at ~2000 cm\(^{-1}\) relating to the Si-H\(_n\) bond, and a stretching mode at ~3000 cm\(^{-1}\) assigned to the C-H bond [30]. Due to the enormous number of references available, the various bond peak frequencies quoted by various researchers over the years are listed in Table 2.1 for easy referencing. A typical IR a spectrum of an a-Si\(_{1-x}C_x\) film is presented in Figure 2.1.
It can be seen in Table 2.1 that Weider et al. [29] assigned the SiC bonds to the 670 cm\(^{-1}\) line in the absorption spectrum. The carbon admixture was identified on the basis of the 606 cm\(^{-1}\) line in the absorption of crystalline silicon. The bond at 780 cm\(^{-1}\) was attributed to the Si-CH\(_3\) wagging mode. Other authors disputed this allocation with the strongest argument being the observation of 780 cm\(^{-1}\) bond in hydrogen-free β-SiC [31,35]. Besides, the results of annealed films showed that the peak at 780 cm\(^{-1}\) either remained relatively constant or increased in intensity. This would not be the case if the bond were assigned to the hydrogenated bond Si-CH\(_3\) as the intensity would reduce once hydrogen effusion occurs during annealing.

Also from Table 2.1, it can be seen that the interpretation of the bond peaks is complicated by the overlapping of the different bonds in the same frequency range, and the difference of peak position with varying degree of hydrogenation. For instance, the broad peak seen over the range of 600 to 1000 cm\(^{-1}\) consists of Si-H wagging (640 cm\(^{-1}\)), Si-C stretching (780 cm\(^{-1}\)) and C-H\(_n\) wagging mode (1000 cm\(^{-1}\)) [25]. The allocation of bonds is thus not straight forward, and careful consideration must be given to the deposition techniques used. Films prepared by glow discharge or using hydrocarbon source gases tend to have more “complicated” infrared spectra due to the high degree of hydrogenation as well as the overlapping of the different bonds within the same frequency range. Effects of other processes such as annealing which will lead to hydrogen effusion of Si-CH\(_3\) bond [46] must also be taken into consideration.
Table 2.1 Summary of Si-C, Si-H<sub>n</sub> and C-H<sub>n</sub> Vibrations and their corresponding frequency.

<table>
<thead>
<tr>
<th>Vibrating Unit</th>
<th>Vibration Mode</th>
<th>Frequency (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-C</td>
<td>Stretching</td>
<td>670</td>
<td>29</td>
</tr>
<tr>
<td>Si-C</td>
<td>Stretching</td>
<td>780 - 800</td>
<td>8,31,32,33,34,35,36</td>
</tr>
<tr>
<td>Si-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Wagging</td>
<td>700 - 800</td>
<td>9,35,29,37,38,39</td>
</tr>
<tr>
<td>Si-H</td>
<td>Stretching</td>
<td>2000</td>
<td>35,40,41</td>
</tr>
<tr>
<td></td>
<td>Bending/Wagging</td>
<td>630-640</td>
<td>30,41,42</td>
</tr>
<tr>
<td>Si-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Stretching</td>
<td>2090</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Bending (Doublet)</td>
<td>845</td>
<td>40,42</td>
</tr>
<tr>
<td></td>
<td>Bending (Doublet)</td>
<td>890</td>
<td>40,42</td>
</tr>
<tr>
<td></td>
<td>Bending/Wagging</td>
<td>630</td>
<td>30,41</td>
</tr>
<tr>
<td>C-H&lt;sub&gt;n&lt;/sub&gt; (n=1,2,3)</td>
<td>Stretching</td>
<td>2860 - 3000</td>
<td>30</td>
</tr>
<tr>
<td>C-H</td>
<td>Stretching (sym)</td>
<td>2915 - 2920</td>
<td>9,43,44</td>
</tr>
<tr>
<td>C-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Stretching (sym)</td>
<td>2850</td>
<td>44,45</td>
</tr>
<tr>
<td>C-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Stretching (asym)</td>
<td>2890 - 2925</td>
<td>30,43</td>
</tr>
<tr>
<td>C-H&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Stretching (sym)</td>
<td>2870 - 2880</td>
<td>43,44</td>
</tr>
<tr>
<td>C-H&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Stretching (asym)</td>
<td>2940 - 2960</td>
<td>30,43,44</td>
</tr>
<tr>
<td>C-H&lt;sub&gt;n&lt;/sub&gt;</td>
<td>Bending</td>
<td>1450 - 1470</td>
<td>35,40,45</td>
</tr>
<tr>
<td>C-H&lt;sub&gt;n&lt;/sub&gt;</td>
<td>Rocking/Wagging</td>
<td>1000-1100</td>
<td>30,35,40,45</td>
</tr>
</tbody>
</table>
Figure 2.1 Typical IR Spectra of a-Si$_{1-x}$C$_x$H Films
2.2.1.1 Shift in Bonding Peaks

From the literature review, it was noticed that for the Si-C and the Si-H bonds, there exists a range of frequency where the particular bond was observed, i.e. shifting of the bond frequency. The vibration frequency of an IR active bond can “shift” due to the inductive effects of the nearest neighbouring atoms. This is different for different chemical environments. Due to the network bonding configuration information that can be derived from these shifts in the vibration frequency, a great deal of research has been directed towards interpreting the features in the IR spectra.

A theory developed by Lucovsky [47] explains the shift of the Si-H stretching mode from 2000 cm\(^{-1}\) in a-Si due to impurities. Back bonding of atoms other than Si to the vibrating Si increases the frequency proportionally to a modified electronegativity. In this case back bonding by C increases the frequency by placing a slight positive charge on the Si (1.8) by the electronegative C (2.5). As hydrogen has an intermediate negativity of 2.1, the polarity (and frequency) of the Si-H is increased. Lucovsky has also shown that the mass of the back bonded atom is of little importance since the amplitude of its vibration is low. Here the shift is due both to C back bonding and multiple hydrides, which also appear in the 800 to 950 cm\(^{-1}\) region. Morimoto et al. [27] reported that the absorption at 2000 cm\(^{-1}\) could be the Si-H stretching mode of SiH without nearest neighbour C atoms and the absorption at 2090 cm\(^{-1}\) could be attributed either to Si-H stretching mode of SiH\(_2\) or to the shift of the SiH stretching mode due to the presence of nearest-neighbour C atoms. Weider et al. [29] attributed the shift of the 2000 cm\(^{-1}\) peak to a higher wave number with an increase in the carbon content in the film. Catherine and Turban [48] and Tawada et al. [38] used the relation obtained by Lucovsky and obtained the configurations obtained in Table 2.2.
Table 2.2  Calculated stretching frequency of Si-H\(_{n}\) with changing back bonding.

<table>
<thead>
<tr>
<th>Monohydride (Si-H)</th>
<th>Dihydride (Si-H(_{2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(\text{Si-Si-H})</td>
<td>Si(\text{Si-Si-H})</td>
</tr>
<tr>
<td>2013 cm(^{-1})</td>
<td>2092 cm(^{-1})</td>
</tr>
<tr>
<td>Si(\text{C-Si-H})</td>
<td>Si(\text{C-Si-H})</td>
</tr>
<tr>
<td>2054 cm(^{-1})</td>
<td>2119 cm(^{-1})</td>
</tr>
<tr>
<td>Si(\text{C-Si-H})</td>
<td>Si(\text{C-Si-H})</td>
</tr>
<tr>
<td>2095 cm(^{-1})</td>
<td>2149 cm(^{-1})</td>
</tr>
<tr>
<td>Si(\text{C-Si-H})</td>
<td>Si(\text{C-Si-H})</td>
</tr>
<tr>
<td>2135 cm(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

The C-H stretching mode peaks do not show any shape or position change with deposition parameter. The application of inductive shift theory to the Si-C stretching mode was first proposed by Mohr \textit{et al.} [49]. In this work, the shape of the Si-C stretching mode varies widely. In the IR spectra the various Si-C stretching modes observed between 650 and 780 cm\(^{-1}\) are explained by back bonding variations. Using the model devised by Lucovsky by analogy to the Si-H and C-H bonds, the back bonding of C to Si is expected to raise the wavenumber, while backbonding of C to C is expected to have little effect. The fitting of the fine structure of the four sub-peaks between 650 and 780 cm\(^{-1}\) [49] is shown in Figure 2.2.

If back bonding on C is significant, Si bonding would raise the frequency, so in general chemical ordering increases the frequency. It should be noted that crystalline SiC shows a SiC stretching mode just below 800 cm\(^{-1}\).
Figure 2.2 Assignment of wavenumbers to Si-C modes with changing back bonding

However, it must be noted that this shift in the bond frequency of the Si-H stretching mode may not be exclusively related to the ligand effect arising from the electronegativity difference between the silicon and the backbonded atoms. Other possible effects includes:

- a solid state effect caused by the kind of environment or embedding into a dielectric medium [40,47,50] and
- structural inhomogeneities, such as voids [50,51]

Both Lucovsky [47] and Weider et al. [29] attributed the frequency shift entirely to inductive effects. If no nucleations or preferential chemical order are present, these models predict a linear behaviour of the shifting as a function of carbon content. For the latter effect proposed by Wagner and Beyer [50], the Si-H stretching mode at 2000 cm$^{-1}$ is related to an isolated monohydride in the amorphous bulk while the peak at 2080 – 2100 cm$^{-1}$ may be due to Si-H or Si-H$_2$ in the inner surface of voids or free volumes [51]. Petrich et al. [52] reported that the absorption peak near 2000 cm$^{-1}$, due to stretching mode of isolated Si-H, appears in only the low-carbon content films. Prior to its disappearance, the position of the 2000 cm$^{-1}$ absorption shifts to a higher wave number with increasing carbon content, due to the back bonding of the silicon
atoms to carbon. The 2080 cm\(^{-1}\) absorption due to the stretching mode of clustered Si-H also shifts to higher wave number, but the increase may, in part, be due to a change in the local dielectric constant owing to a transition from small well-ordered clusters to large ill-defined groups of hydrogen atoms.

### 2.2.1.2 Annealing Effects

Annealing has become a common process in IC fabrication. Therefore, it is necessary to study the effects of annealing on the semiconductor film. Generally, annealing is performed after ion implantation to repair the damages done due to the ion bombardment. In the study of amorphous silicon carbide, annealing will be responsible for the rearrangement of the amorphous structure and the subsequent reduction of dangling bonds and voids. The concentration of hydrogen in the films also varies due to the release of this element during the annealing process [53].

From the infrared spectra, Khakani et al. [25] observed interesting features associated with the hydrogenated bands. The areas under the Si-H and C-H stretching bands decrease as the film is annealed up to 850 °C. For temperatures higher than 650 °C, the Si-CH\(_n\) wagging and the Si-H rocking or wagging vibration mode areas decrease while the Si-C stretching band area increases. The broadening of the Si-C absorption band at 850°C can be explained by the increase in the number of Si-C bonds resulting in an enhancement of the bond angle distortion in the amorphous network [54]. These observations clearly point out that when the temperature was increased from 300 to 850°C, both breaking of hydrogenated bonds resulting in a decrease of hydrogenated band areas and an increase of the Si-C band area occur.
The Si-H bond density ($N_{Si-H}$) continuously decreases for annealing temperature higher than 450 or 500°C, depending on the film thickness. The Si-C bond density ($N_{Si-C}$) starts to increase at 450 or 500°C and shows a linear increase with increasing temperatures. An increase of about 40% of $N_{Si-C}$ together with a decrease of about 55% of hydrogenated bonds ($N_{Si-H} + N_{C-H}$) are observed when annealing temperature is varied from 300 to 850°C.

The annealing behaviour of C-H bonds differs from that of Si-C and Si-H related bonds. First, the C-H bond area increases with increasing temperature to a maximum at 550°C. Then, with a further increase of annealing temperature the number of C-H bonds also decreases. Friessnegg et al. [10] observed that hydrogen evolved under annealing in a two-step process, which first involves the breaking of Si-H bonds and then, in a second step, of C-H bonds. The single-bond energy difference between Si-H (70.4 kcal mol$^{-1}$) and C-H (98.9 kcal mol$^{-1}$) bond [17] explains this behaviour. During dehydrogenation of Si-H bonds, some hydrogen atoms could saturate carbon dangling bonds, thus forming new C-H oscillators at temperatures below 600°C [31]. In a recent paper, Gomez et al. [55] have shown that rapid thermal annealing can lead to nearly complete dehydrogenation of a-SiC:H fabricated by electron cyclotron resonance chemical vapour deposition (ECR-CVD).

The concomitant breaking of C-H bonds with compressive to tensile stress transition and the significant decrease of all the hydrogenated bands at high annealing temperatures suggest that the hydrogenated bonds (Si-H and C-H) decrease is correlated to the compressive stress relaxation. Low compressive stress is associated with low hydrogenated bond densities. As the annealing temperature is increased, both
C-H and Si-H hydrogenated bonds dissociate leading to additional Si-C formation. Thus the strengthening of the interaction among Si and C atoms in the film, due to their respective electronegativities lead to film contracting [15]. Accordingly, the film enrichment in Si-C bond results in a tensile stress thought to be produced by subsequent structural rearrangement and shrinkage of the disordered material.

As discussed above, when annealing temperature is increased, the C-H and Si-H bonds dissociate leading to additional Si-C bond formation. The hydrogen atoms resulting from this breaking of hydrogenated bonds can either combine to form hydrogen molecules which are expected to diffuse towards the interfaces during the annealing, or be trapped in the Si or C dangling bonds to form new hydrogenated bonds. These two mechanisms may occur simultaneously.

The Si-C bond density linearly increases with the annealing temperature in the 500-850°C range, as shown by IR quantitative analysis. Moreover, the studied a-SiC:H films remain amorphous even at 850°C annealing temperature, in agreement with the work reported by Derst et al. [56]. This suggests that the observed chemical environment variations are mainly due to the local environment rearrangements resulting in additional Si-C bond formation. The polycrystallization of a-SiC:H PECVD films is known to start at annealing temperatures as high as 1100°C [56]. At such high temperatures, the corresponding tensile stress is very high and can result in a film delamination, depending on the film thickness. Friessnegg et al. [10] reported that after annealing at 800°C, most of the free hydrogen has outdiffused and further annealing up to 900°C resulted in cracked films, most likely due to the high stress in the films at these temperatures. Zhang et al. [15] observed that the surface cracks
when heated to 500 °C and higher. After annealing at 600 °C, the film peels off in flakes from the substrate.

Annealing of the layers achieves a gain of Si-C bonds at both temperatures but most at 1000°C. The increase of the silicon carbide signals lead to the conclusion that no deposited silicon is lost by the annealing; leaving behind a Si-C enriched composition. This means that deposited chemically imperfect silicon carbide is transformed to a more perfect one.

Annealing can also be used to confirm the bonding at 2000 and 2100 cm\(^{-1}\). Eberhardt \textit{et al.} [46] observed that the SiH\(_n\) related mode decreases upon annealing but the peak position does not change. This is an indication that the shift of the 2000 cm\(^{-1}\) mode to 2080 cm\(^{-1}\) is not caused from dihydrides or hydrogen in voids, but from Si-C-H groups. Mohr \textit{et al.} [49] also observed that after 400°C anneal, the size, shape and position of the peaks changes little except for the region from 800 cm\(^{-1}\) to 950 cm\(^{-1}\) where the SiH\(_2\) bending modes are noticeably reduced. The stability of the C related peaks indicates that the chemical disorder and the amount of higher hydrides of C are not reduced. The reduction in SiH\(_2\) without a large shift in the Si-H stretching peak helps to confirm the validity of the idea that the Si-H peak shift is more due to C back bonding rather than SiH\(_n\).
2.2.2 X-Ray Photoelectron Spectroscopy

One of the most widespread uses of XPS is to detect the chemical composition and bonding state of silicon carbide prepared at different carbon/silicon contents. According to many authors, the binding energy spectra of amorphous silicon and carbon were used as standards and they relate the shift of silicon peak (Si2p) and carbon peak (C1s) of silicon carbide films at different compositions to deduce the transition of their chemical states [12,34,57,58].

According to Lee [58], the XPS data showed that the Si2p binding energy and the full width at half maximum (FWHM) increases from 99.1 eV and 1.5 eV, respectively for amorphous silicon to 101.1 eV and 2.7 eV for the carbon-rich film (x=0.98). The C1s peak also demonstrated an increase in the full width and FWHM from 283.0 eV and 1 eV for the silicon-rich film (x=0.057) to 284.3 eV and 1.6 eV for amorphous carbon. Stoichiometric film has a Si2p and C1s binding energies of 100.5 eV and 283.3 eV, respectively [57].

The increase in the Si2p binding energy as x increases was also observed by Hicks et al. [12]. They associated this increase to the fact that Si-Si bonds dominate in the silicon rich films and the Si-C bonds in stoichiometric films. Katayama et al. [34] calculated the effective charge (q) using the electronegativity difference of the atoms for SiC and correlated the charge of 1 to the Si2p binding energy of 100.5 eV. Gat et al. [57] extrapolated from this finding and suggested that silicon atoms that exhibit this binding energy range are mainly bonded in the H-Si-C$_3$ or Si-C$_4$ unit configurations.
While Si2p exhibits a smooth increase in energy as x increases, the C1s binding energy has a kink at about x ≈ 0.5-0.6 [12,30,34,57]. In conjunction with the optical studies, it has been accepted that there is a change of carbon bonding configurations from fourfold (sp3) to threefold (sp2) in the carbon–rich region. Furthermore, the incorporation of hydrogen has led to a chemical shift of 1.0 eV, which is much larger than the value estimated using the electronegativity difference between carbon and hydrogen. This means that a large effective charge change has occurred, which may be due to the change in the co-ordination number of the carbon atoms.

2.2.2.1 Chemical Bonding States

XPS, which can scan over a narrow range of energy, enables the accurate determination of line energies for the identification of chemical states and environment in the film. In binary materials and alloys, each of the elemental narrow scan consists of an envelope of various bonding configurations which can be identified by curve fitting the spectrum obtained.

For the silicon carbide system, two major window scans are usually examined, namely the silicon (Si2p) and the carbon (C1s) peaks. In general, the Si 2p peak has been deconvoluted into the Si-Si, Si-C and SiOx bonds, and the major components of the C1s peak are C-Si, C-C, C-H and C-Ox bonds. It is important to note that different authors have assigned different ranges of binding energy to the same bonds. For example, Tabata et al. [43,59] assigned the Si-C(Si-C4) bond based on the Si2p binding energy of ß-SiC which is 99.5 eV. Khakani et al. [25], however, obtained a binding energy of 100.6 eV for their ß-SiC. This large difference would affect the accuracy of the chemical states determined.
Furthermore, the peak decomposition is not unique and is dependent on assumptions such as the number of peak fit, peak positions, intensities and profiles etc. and this could lead to differences in results. This is compounded by the fact that surface contamination and inhomogeneities in the material can contribute to the broadening of the carbon and silicon core levels, causing a shift in the core level and complicating the curve fitting procedure [60]. Nevertheless, XPS is still regarded as an effective tool used in the investigation of the chemical structure of silicon carbide. Together with other spectroscopic measurements such as the infrared or Raman spectroscopy, more accurate results could be obtained.

2.3 Optical Properties

With regards to the optical properties of semiconductors, the optical absorption edge is an important parameter that needs to be determined. In crystalline semiconductors, this is easily defined experimentally and the sharp rise in the optical absorption at a characteristic energy suggests the concept of an optical gap. Experimental and theoretical examinations of the absorption edge of crystalline semiconductors led to the distinction between two kinds of optical transition between the filled valance band and the unoccupied conduction band, namely the direct and indirect transition [61,62].

However, the absorption edge of amorphous semiconductors is difficult to define experimentally. During the early days of research on the optical properties of amorphous semiconductors, it was observed that there was often a wide variation in the sharpness of the absorption edge for the same material (a-Si:H and a-Ge) but prepared by different methods. The sharpness of the absorption edge is estimated by
the Urbach energy ($E_u$). For amorphous silicon alloys, the optical gap ($E_{opt}$) and the refractive index ($n$) is dependent mostly on film composition and the Urbach energy is strongly dependent on the disorder of the alloy materials. The degree of disorder in amorphous semiconductors is sometimes measured by the edge-width parameter $B$.

### 2.3.1 Optical Gap

Using Tauc’s model, the optical band gap of a-Si$_{1-x}$C$_x$:H films can be obtained by fitting the absorption data to the expression [64]

$$\alpha(hv) = B(hv - E_{opt})^2$$  \hspace{1cm} (2.1)

where $h$ is the Planck’s constant, $v$ is the frequency and $B$ is the edge-width parameter. The values of $E_{opt}$ and $B$ can then be obtained from the $(\alpha hv)^{1/2}$ versus $hv$ plot. Tauc’s method has shown to give a good estimate of $E_{opt}$ because the error in the matrix element is more or less cancelled by the error in the density of states at the band edges.

Figure 2.3 shows typical Tauc plots for a series of PECVD a-Si$_{1-x}$C$_x$:H films with different carbon contents [64]. It was observed that $E_{opt}$ increases as the carbon content in the film increases. Research shows that the values of $E_{opt}$ for amorphous silicon carbide films vary between 1.8 to 3.5 eV. Morimoto et al. [65] and Tran [66] also reported that $E_{opt}$ increases almost linearly as $x$ increases. However, Anderson and Spear [1] and Sussman and Ogden [64] showed that $E_{opt}$ initially increases but reaches a maximum at $x$=0.4 or 0.65 and reduces thereafter. Bullot and Schmidt [67] suggested that the maximum in $E_{opt}$ could be due to (i) the maximum number of Si-C bonds or (ii) the $(\text{sp}^3)C - (\text{sp}^3)C$ bonds in the a-Si$_{1-x}$C$_x$:H films. It was considered that the volume density of the C-C bonds in carbon-rich a-Si$_{1-x}$C$_x$:H films is low due to the formation of the graphitic domain and therefore the latter assertion can be ignored.
From the literature survey, it is obvious that $B$ of a-Si$_{1-x}$C$_x$:H films obtained reduces as $x$ increases. Several authors have tried to interpret the slope of the linear part of the Tauc plot in terms of disorder [68][69][70][71]. Sussman et al. [64] reported a large a decrease in the edge width parameter, $B$, due to a pronounced widening of the localised tail states as the carbon concentration is increased. This widening of the localised band tail states, in turn, is indicative of the increased disorder in the film [72]. Bullot et al. [73] claimed that this property of $B$ increase with $x$ is a genuine property of SiC alloys as no such variation was observed in a-Si$_x$Ge$_{1-x}$:H alloys. Saito et al. [68] proposed that the decrease in $B$ is due to the graphitisation and/or to the change in bonding configuration of carbon caused by an increase in C-H$_n$ bonds.
Della Sala et al. [69] and Skumanich et al. [74] reported that B remains fairly constant until an x value of around 40%, beyond which it decreases. They claimed that in the silicon rich films the addition of carbon only results in an increase in the Urbach energy without appreciably changing the density of gap states. As the x value increases beyond 40% the mean free path reduces considerably, thus, decreasing the B value and increasing the disorder. It is, however, more or less agreed upon that B is a fundamental property related to the disorder in the film irrespective of the x value, a decrease in B indicating a rapid increase of defects in the films.

There are significantly less published works with regards to sputtered films. Figure 2.4 shows a typical Tauc plot for films prepared by sputtering a polycrystalline SiC target in an Ar + H2 ambient. It was observed that the slope of the \((\alpha h\nu)^{1/2}\) versus \(h\nu\) plot, \(B\), increases as \(P_H\) increases. This shows that by increasing the hydrogen content in the films, it reduces the disorder of the films and thus increases the \(E_{opt}\) of the films. \(E_{opt}\) obtained from several authors [7,23,75] are plotted in Figure 2.5 as a function of the partial pressure (\(P_H\)) in the sputtering gas. The value of \(E_{opt}\) of Choi et al. [81] increases from 1.5 to 2.15 eV as \(P_H\) increases from 0.15 to 0.6 Pa. Dutta et al. [7] also reported an increase in \(E_{opt}\) from 1.39 to 1.51 eV as \(P_H\) increases from 0.04 to 0.66 Pa. The \(E_{opt}\) values of Dutta et al. are considerable lower than that of Choi et al. Girginoudi and Thanailakis [23] reported an increase of \(E_{opt}\) from 1.35 to 2.3 eV as \(P_H\) increases from 0 to 1.6 Pa, and remain fairly constant at approximately 2.3 eV with further increase in \(P_H\). The difference in the value of \(E_{opt}\) could be due to the different preparation conditions employed by the three groups of workers. The target
composition of Girginoudi and Thanailakis is 66 wt. % of Si and 34-wt. % of C, and
50-wt. % of Si and 50-wt. % of C for Choi et al. and Dutta et al.

Figure 2.4 The $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot for r.f. sputtered a-Si$_{1-x}$C$_x$:H films prepared under different hydrogen partial pressures (rfh05: $P_H=0.15$ Pa; rfh10: $P_H=0.30$ Pa; rfh20: $P_H=0.60$ Pa).

Figure 2.5 Optical gap for a-Si$_{1-x}$C$_x$:H films sputtered with a polycrystalline SiC target at an ambient of Ar + H$_2$ at different hydrogen partial pressure ($P_H$). (●)[81], (○) [8] and (x) [23].
Recently, phosphorus doped a-Si$_{1-x}$C$_x$:H films has been prepared by placing a disc (1 cm in diameter) of triphenylphosphine at the central region of a silicon target (15 cm in diameter) [75]. The sputtering was carried out in an Ar+H$_2$ ambient. It was shown that both the electrical and optical properties changed significantly with triphenylphosphine doping. $E_{opt}$ reduces from 1.8 eV for the undoped films to 1.61 eV for the doped films. Note that Demichelis et al. [39] have also observed a reduction in $E_{opt}$ in their phosphorus doped PECVD a-Si$_{1-x}$C$_x$:H films.

### 2.3.2 Refractive Index

Another important optical parameter of a-Si$_{1-x}$C$_x$:H films is the refractive index ($n_o$). The refractive index may be measured by application of basic thin film optics without any assumption on the band structure. Thus, it is perhaps the most fundamental optical parameter of a solid [76]. The most elegant method for determining the refractive index of a thin film is spectroscopic ellipsometry [20]. The refractive index may be used as a parameter to judge the quality of a-Si$_{1-x}$C$_x$ as it is closely related to the porosity and microstructural defects in the deposited films.

Refractive index of a-Si$_{1-x}$C$_x$:H films is a strong function of the carbon content in the film. It remains rather insensitive to the changes in the deposition parameters and independent of the hydrocarbon source as long as the silicon to carbon ratio remains the same [76,77]. The refractive index, thus, provides a convenient means to estimate the carbon content in the film because it solely depends on the $x$ (carbon content) value [76].

The refractive index of a-Si$_{1-x}$C$_x$:H film falls as the carbon content in the film increases [77, 78]. As shown in Figures 2.6 and 2.7, $n$, the refractive index, falls from a value of
3.8 linearly up to about 30 atomic % of C, beyond which it saturates at about 1.8 [77, 78]. Catherine et al. [79] reported a similar variation of refractive index with concentration. Choi et al. [4] also observe a decrease in refractive index from 2 down to 1.7 as $x$ (carbon content in the film) increases from 0.3 to 0.6. This has been attributed to the reduction in the Si-C bonds and the decrease in the density of the films as the carbon content increases [80].

Figure 2.6 and 2.7  Refractive index of a-Si$_{1-x}$C$_x$:H films plotted against the precursor gas flow rate of [77] and [78] respectively.
The refractive index for a-Si$_{1-x}$C$_x$H films, prepared with SiH$_4$ + CH$_4$ and SiH$_4$ + C$_2$H$_2$ gas mixtures, as a function of x is shown in Figure 2.8. It can be seen that for most of the films, $n_o$ varies quite significantly for $x < 0.5$. For $x > 0.5$, $n_o$ lies in the range from 1.8 to 1.9. The refractive index results of sputtered films prepared by Choi et al. [81] at different P$_H$ values and rf power are shown in Figure 2.9. It was observed that $n_o$ increases from 2.8 to 3.0 as P$_H$ increases from 0.15 to 0.6 Pa. There is, however, a marked increase in $n_o$ as P$_H$ reaches 0.6 Pa. Also, by increasing r.f. power from 100 to 600 W, $n_o$ was observed to increase from 1.85 to 3.1.
Bullot and Schmidt [67] suggested that $n_0$ might be a reliable parameter for the determination of the carbon content for silicon-rich a-Si$_{1-x}$C$_x$:H films. This is based on their hypothesis that $n_0$ is independent of hydrocarbon and is insensitive to changes in the deposition parameters, which is not true in reality. The lack of proper refractive index information on a-Si$_{1-x}$C$_x$:H films may therefore be the difficulty in obtaining consistent results for these films. However, Pascual et al. [82] have used spectroscopic ellipsometry in the optical characterisation of the a-Si$_{1-x}$C$_x$:H/c-Si structures. It showed that all the samples consist of a substrate, a homogeneous layer and a porous overlayer that is the effective medium mixture of the same material and 40\% of voids with thickness values ranging from 4 nm to 12 nm. The spectra of the refractive index of the layer vary as x increases.

Figure 2.9 Refractive index ($n_0$) of a-Si$_{1-x}$C$_x$:H films as a function r.f. power and hydrogen partial pressures.
2.3.3 Photoluminescence

The reports on the photoluminescence (PL) studies on a-Si$_{1-x}$C$_x$:H films were almost all on films prepared by the PECVD technique. The PL studies were performed on films prepared using SiH$_4$ + C$_2$H$_4$ [17,64,83-84], SiH$_4$ + CH$_4$ [84,85], SiH$_4$ + C$_8$H$_{10}$ [86,87] and hexamethyldisilane and tetrakis(trimethylsilyl)silane [88]. For sputtered films, there is only one earlier paper on the reactive sputtered a-Si$_{1-x}$C$_x$:H film [89]. Thus, the review for the PL studies is mainly on the PECVD films.

Engemann et al. [90] reported a PL spectrum of a-Si$_{1-x}$C$_x$:H films (0 < x < 0.57) that consists of two main bands. The band at 1.35 eV dominates in Si-rich samples (x < 0.35). As x increases, the other band begins to dominate over the 1.35 eV band. Tsai et al. [85] also reported a two-band feature in the PL spectra of their a-Si$_{1-x}$C$_x$:H films. The rest of the studies revealed a broad spectrum. Typical results as reported by Sussman and Ogden [64] are presented in Figure 2.10. The peak of the spectrum broadens and shifts to higher energy as x increases. The PL results of Engemann et al. (dashed line) are also included in this figure. The difference between the spectra of Engemann et al. and the subsequent PL studies has been attributed to the presence of carbon and silicon-rich clusters in the former samples.
Figure 2.10  Photoluminescence spectra for a-Si$_{1-x}$C$_x$:H films reported by Sussman and Ogden [64] (solid lines) and Engemann et al. [90] (dashed lines). 

The PL spectra of a-Si$_{1-x}$C$_x$:H films prepared with hexamethyldisilane and tetrakis(trimethylsilyl)silane at different substrate temperatures show a single broad
peak. The peak shifts from 1.7 eV to 2.6 eV with increasing Si/C and/or substrate temperature. Wróbel et al. also reported a linear increase in the PL peak and $E_{\text{opt}}$ as the Si/C increases. Carius et al. [83] and Siebert et al. [84] investigated the photoluminescence efficiency of a-Si$_{1-x}$C$_x$:H films by the steady state and time-resolved photoluminescence methods. When compared to a-Si:H films, it was found that the radiative lifetime for a-Si$_{1-x}$C$_x$:H films is much reduced. This reduction in lifetime can be due to (i) the tail states are broader in a-Si$_{1-x}$C$_x$:H, the faster thermalization may reduce the influence of carrier diffusion or (ii) the stronger Coulombic interaction between recombining carriers that enforces stronger localisation.

2.4 Electrical Properties

Very few reports on the electrical properties of amorphous silicon carbide are available. Most of the literature is on the structural and optical aspects of the film. In this section, recent work done on the electrical properties of a-Si$_{1-x}$C$_x$:H films will be presented. The d.c. conductivity will be looked into first, followed by the d.c. transport mechanism. The property of the SiC/Si interface will be examined using the capacitance or conductance versus voltage results.

The D.C. conductivities of the PECVD films prepared by Akita et al. [3] are in the range of $10^{-13}$ to $10^{-9}$ Ω$^{-1}$cm$^{-1}$. Dutta et al. [7] reported a higher conductivity for their sputtered films which are in the range of $10^{-8}$-$10^{-4}$ Ω$^{-1}$cm$^{-1}$ and the D.C. conductivity decreases with hydrogen concentration in the films. It is generally true that the PECVD a-Si$_{1-x}$C$_x$:H films exhibit a much lower conductivity than the sputtered films. The higher conductivity of the sputtered films has been attributed to the higher density
of gap states associated with this material. The temperature dependence of the electrical conductivity of r.f. sputtered films at various hydrogen concentrations was reported. Activation energy derived from the slope of the high temperature conductivity was found to increase with an increase in hydrogen concentration. The conductivity at low temperature was found to be shared by hops between localised sites in addition to the hops between the nearest sites. Annealing lowered the D.C. conductivity and increased the activation energy gap.

Magafas et al. [93] reported that the I-V characteristics of a-SiC/c-Si(p) heterojunctions exhibit a low turn-on voltage and a high reverse breakdown voltage (about 140 V). It was found that a model of an abrupt anisotype crystalline heterojunction is valid for the a-SiC/c-Si(p) structure. This model, for forward bias voltage lower than the critical value $V_T$, predicts that at low temperatures ($<250$ K) recombination is the dominant transport mechanism, whereas at temperatures ($>250$ K) recombination-diffusion becomes the dominant transport mechanism. For higher voltages ($V > V_T$), the tunneling process dominates.

Rahman and Furukawa [94] fabricated a-Si$_{1-x}$C$_x$:H/c-Si heterostructure in an inductively-coupled PECVD system. The heterostructure showed good rectifying properties with an ideal factor $n = 1.31$ over a large voltage range. From the current versus voltage measurements at 195 to 445K, the current in the junction is dominated by thermal injection component at higher temperatures and by tunneling and recombination at lower temperatures. The saturation current is $4.5 \times 10^{-9}$ A/cm$^2$ when the high voltage slope is extrapolated to zero volts. The reverse characteristic shows that the reverse current increases slowly in a linear fashion and is about $10^{-7}$ A/cm$^2$ at 1
V reverse bias. The rectification ratio at 1 V stands at 8 orders. These values are quite promising for an amorphous/crystalline heterostructure.

The characteristics of the a-SiC:H/Si interface is critical to the performance and reliability of silicon-based heterostructure devices. Harjono et al. [92] carried out C-V measurement on their Al/undoped a-SiC:H/p-Si MIS structure. The high frequency capacitance method developed by Terman was used to extract the density of interface traps (Dit) of the a-Si\textsubscript{1-x}C\textsubscript{x}:H/c-Si interface. The interface trap density in the midgap was $10^{11} \text{eV}^{-1}\text{cm}^{-2}$.

The drift mobility is also another area of interest in a-Si\textsubscript{1-x}C\textsubscript{x}:H films. Previously, the time-of-flight measurements have been applied to obtain the excess carrier drift mobility and the band tail density of states in a-Si:H films. Only recently has it been successfully applied to a-Si\textsubscript{1-x}C\textsubscript{x}:H films [95,96]. Bayley et al. [96] prepared the films in the low power regime (0.113 W/cm\textsuperscript{2}) of the PECVD process with $x < 0.1$. Transient photocurrents were observed in the time-of-flight measurement. The transit times were calculated using the method proposed by Marshall et al. [97]. It was found that the low temperature transport was characterised by anomalous dispersion. The mobility obtained at higher temperatures was in the range 1 to 10 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}. It was discovered that increasing the carbon incorporation in the film causes an increase in the band tail density of state extending deeper into the mobility gap.
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Chapter Three

Theoretical Background

This chapter introduces some of the basic concepts that have been used in this research work. The principle of radio frequency (r.f.) sputtering will be highlighted as will the theory of the techniques used to characterise the structure of the amorphous silicon carbide film and the electrical properties of the Al-\textit{\textit{a}}-SiC:H-Si system.

3.1 Radio Frequency (R.F.) Sputtering Technique

It was discovered that when a solid is subjected to bombardment by high energy atomic particles (usually ions), it is possible for individual atom or molecule to acquire enough energy via the collision processes to escape from the surface. The ejected atoms or molecules can then form a new layer on the substrate surface. This means of ejection of atoms or molecules from a surface, known as sputtering, will be the fundamental process involved in the deposition of films in this research.

Figure 3.1 is a schematic representation of the sputtering process [1]. From this figure, it can be seen that a voltage is applied between two electrodes spaced some distance apart in a chamber filled with gas at low pressure (~mTorr). The target is mounted on the cathode and the substrate is placed on the bottom (anode) electrode. No current is flowing in this configuration as there are no charge carriers (electrons or ions) in the gas. However, at sufficiently high negative potential, electrons can be emitted from the cathode via thermionic emission. Under this high electrical field, these electrons
Figure 3.1 Schematic representation of the various experimental aspects of sputtering

accelerate towards the anode at high velocities. A majority of these electrons collide with the gas atoms before reaching the anode. In such a collision, the free electron will give up energy to an orbital electron of the gas atom. If this energy is greater than the ionisation potential, the orbital electron will separate from the atom, becoming a free electron and leaves behind a free ion. The second free electron encounters the same electric field and reacts in the same manner as the first free electron. This in turn leads to a cascade of free electrons and ions and an equilibrium condition is reached almost
instantaneously. This equilibrium discharge condition is known as the glow discharge [2].

The free ions, being positively charged, are accelerated towards the cathode and strike the polycrystalline silicon carbide target surface at high energies. The Si and C atoms from the target gain sufficient momentum from the ion bombardment and begin to sputter down onto the substrate placed below in a random fashion. The Si atoms react with the C atoms predominantly on the substrate surface, since collisions between Si and C atoms in the plasma is less probable. At the substrate surface, the sputtered species with a mean energy of about 10 eV synthesised with each other to form SiC. The substrate temperature will decide whether the SiC deposited is crystalline or amorphous in nature [3,4]. During the ion bombardment process, the secondary electrons ejected from the target react in the same manner as the other free primary electrons and assist in maintaining the discharge. During the sputtering process, the primary and secondary electrons will be repelled from the negative cathode, and some will be attracted to the positive anode. This will induce a negative potential at the anode with respect to ground. However, a negative cathode-anode bias still prevails for sputtering to occur.

Although the negative voltage applied to the target is necessary to initialise sputtering, it is the r.f. power that is necessary to sustain the sputtering action. This is due to the buildup of a surface charge of positive ions on the front side of the insulator target, which will prevent any further ion bombardment. This is the reason why D.C. sputtering cannot be applied to insulators as SiC. This problem can be overcome by applying a high frequency potential to a metal electrode behind the insulator target. The positive charge that accumulates on the surface during the negative or sputter
portion of each cycle is neutralised by the plasma electrons in the positive part of the cycle. It has been found that by using a r.f. generator operating at a frequency of a megacycle per second or more, the rate of reversal would be high enough for sputtering of insulators at a practical rate [2].

Argon gas is usually used for sputtering because of its inertness and its high atomic weight. Dopant such as hydrogen can be incorporated into the films during sputtering by introducing them in the sputtering ambient. The deposition of hydrogen may occur by direct sputtering of hydrogen incorporated in the outer layer of the target, by elastic backscattering from the target, or by adsorption and reaction directly at the growing film surface. The sputter deposition is generally a more physical than chemical process. It was found that in sputtering of a-Si:H and crystalline SiC, the film appears to grow via a simple kinetic process of incorporation of monoatomic species [4,5,6]. The sputtering process has several variable parameters such as the type of gas, pressure, input power, electrode spacing and substrate temperature. Because of the very complex interactions among these parameters, it is extremely difficult to study the sputtering process in quantitative details from a theoretical approach. Hence, the practical sputtering conditions are often obtained through experiments [7].

A major issue related to sputtering is the effect of bombardment of ions and atoms has on the microstructure of the underlying substrate. Positive ions such as Ar\(^+\) will be extracted from the plasma by the substrate bias (which is always somewhat negative with respect to the plasma) and will arrive at the substrate with energy \(\approx eV_S\), where \(V_S\) is the substrate floating potential. Because of the higher mass of Ar\(^+\) ions, the arriving Ar\(^+\) ions will have enough energy to [5,8]
a) resputter the growing film – preferentially resputtering the weakly bonded surface species,
b) become implanted to a shallow depth in the surface,
c) cause atomic rearrangement in the near surface,
d) increase the mobility of film surface adatoms through momentum transfer.

One important factor governing the film properties is the sputtering or chamber pressure, which affects the bombardment processes. The chamber pressure is inversely related to the substrate floating potential $V_S$. Ross and Messier [5,8] pointed out that a-Si:H sputtered at low-pressure lead to a minimisation of microstructural defects. At low pressure (~0.5 – 1.5 Pa), $V_S$ becomes more negative, and this gives rise to other bombardment phenomena. In particular, the cathode (target) potential becomes more negative and the electron and ion mean-free paths, which vary inversely with pressure, increase. This will lead to the following possible bombardment processes:

a) high energy inert gas atoms reflected from the target with increased energy and longer mean-free path [9]
b) secondary electrons emitted from the target with higher energy due to the cathode potential and longer mean-free path. This will enhance the surface charge of the substrate, leading to further energetic ion implantation [5]
c) high energy secondary neutral and ion sputtered species.

During r.f. sputtering, electrons may arrive at the substrate with very high energies [10], up to a maximum potential of the r.f. supply or up to 2 keV in many cases. The range of high energy electrons is about 500 Å, great enough to produce damage that might not anneal at deposition temperature [11]. Argon atoms or ions can also reach the substrate at up to 200 eV energy [12]. The range of these low energy Ar$^+$ ions or
atoms is small, possibly around 100 Å but this is sufficient to penetrate below the surface and disarrange lattice atoms after they have been incorporated in the deposited film [11].

The increased bombardment of the films by Ar\(^{+}\) increases the probability of Ar incorporation in the film. Due to the higher atomic mass of Ar, back reflection from the substrate may be also minimal. Given these considerations, it is thus reasonable to expect a certain degree of incorporation of Ar in the films. This is supported by the observations of Kudoyarova et al. [13] in that their sputtered SiC film that contained a considerable amount of trapped Ar as determined by Rutherford Backscattering (RBS) analysis. The Ar content in the sputtered film was observed to be dependent on the operating parameters of the sputtering process. Incorporating hydrogen or increasing the substrate temperature can reduce the Ar incorporation [14].

From above, it can be seen that sputtering is a process that involves physical bombardment. The bombardment of ions and atoms, which is essential to the reduction of microstructural heterogeneity in sputtered material, may at the same time create atomic-scale electronically active defects [5]. The deleterious effects of such bombardment indicate that post deposition annealing is necessary for sputtered films in order to obtain better quality film.
3.2  Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy is a non-destructive chemical analysis method that is particularly sensitive to the asymmetrical bonding in semiconductor materials such as silicon carbide. Over the years, it has become an integral technique for the study of amorphous silicon carbide, with constants being developed that allow the calculation of the bond densities directly from the IR spectrum [15]. In this work, infrared spectroscopy is used to study the microscopic environment of the sputtered a-SiC:H films.

3.2.1  Principle of FTIR

In infrared spectroscopy, the molecules are radiated with electromagnetic energies that cover a whole range of infrared frequencies. However, the molecules only absorb energy at a certain frequency which coincides with their natural vibrational frequency. When there is a change in the dipole moments during the vibration of the molecules, the mode of vibration is said to be infrared active. Molecular vibrations which can cause a change in the dipole moments include stretching, rocking, wagging, bending and twisting of an asymmetrical nature. Symmetrical bonds cannot be detected by this method, as they do not possess any dipole moment. An absorption peak can be observed in an infrared spectrum that identifies the vibrational mode of each molecule. The position of the peaks depends on the dipole moments or the relative electronegativity of the two bonded atoms. The intensity of the absorption band is proportional to the concentration of the molecules present [16].
The basic component of Fourier transform spectrometers is the Michealson interferometer shown in simplified form in Figure 3.2. Light from an infrared source is incident on a beam splitter, which creates two separate optical paths by reflecting 50% of the incident light and transmitting the remaining 50%. Travelling through different optical lengths, the light intensity reaching the detector is the sum of the beams. The detector output – interferogram, I(x) – thus consists of a series of maxima and minima due to constructive and destructive interference of the two light beams respectively. The spectral response is then calculated from the interferogram using Fourier transformation

$$B(f) = \int_{-\infty}^{\infty} I(x) \cos(2\pi fx) \, dx \quad (3.1)$$

Signal processing can then be performed using computers, such as background subtraction and weighting or apodisation schemes to reduce irregularities in the interferogram.
From the infrared spectrum obtained, the position and the area of the absorption band provide important information about the chemical structure and bonding characteristics of the film. Changes in the bond density calculated from the area under the absorption peak enable us to study the effects of annealing as well as the different preparation conditions on the sputtered films. The density of the Si-C, Si-H and C-H bonds, can be estimated from the Si-C, Si-H and C-H absorption peak respectively as

\[ N_{\text{Si-C}, \text{Si-H}, \text{C-H}} = A \int \alpha(\omega) \frac{d\omega}{\omega} \]  

(3.2)

where \( \alpha(\omega) \) is the absorption coefficient, \( \omega \) is the wavelength and \( A \) is the inverse absorption cross section constant. By comparing the bond density via other independent methods, e.g. nuclear magnetic resonance, the constant is taken to be 2.13x10^{19} \text{ cm}^{-2} [15] for the Si-C stretching mode. For Si-H and C-H bonds, \( A \) is taken to be 1.40x10^{20} \text{ cm}^{-2} [15,17] and 1.35x10^{21} \text{ cm}^{-2} [15,18] respectively.

### 3.3 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), or more commonly known as Electron Spectroscopy for Chemical Analysis (ESCA), is an analytical tool that is widely used for investigating the chemical composition of solid surfaces. In this work, it is used to provide information of the chemical structure of the sputtered a-Si_{1-x}C_{x}:H films.

#### 3.3.1 Principle of XPS

XPS is one of the techniques used in electron spectroscopy, which is primarily concerned with the emission and energy analysis of electrons (generally 20 – 2000
Basically, the technique requires a source of primary radiation and an electron analyser and a detector, all contained within an ultra-high vacuum chamber.

A primary X-ray source of 1 to 2 keV is used as an irradiation source to excite the atoms at the surface of the sample, causing electrons to be emitted by the photoelectric effect. The binding energy (\(E_B\)) of the photoelectrons is given by [27]

\[
E_B = h\nu - E_K - W
\]

(3.3)

where \(h\nu\) is the photon energy, \(E_K\) is the kinetic energy of the electron and \(W\) is the spectrometer work function. The energy of the emitted photoelectrons is analysed by the electron spectrometer and the data presented as a photoelectron spectrum. The photoelectron spectrum is basically a plot of the number of emitted electrons per energy level versus electron energy. The spectrum is usually observed as a series of peaks on a continuous background, which exhibits step-like increases on the high binding energy side of each significant peak. A typical wide scan spectrum for the silicon carbide system is shown in Figure 3.3.

The well define peaks are due to electrons that have not lost energy in emerging from the sample. Electrons that have lost energy form the raised background at binding energies higher than the peak. The continuous background is due to the random and multiple energy loss processes. The peaks in the spectrum reflect the discrete binding energies of the electrons present in the solid according to Equation 3.3. The peak position (\(E_B\)) is unique for each element and can therefore be used to identify the elements present in the material being studied. Besides elemental identification, the energy of the photoelectrons in the inner shells or the valence band is influenced by the chemical bonding of the atoms. A change in the chemical composition or bonding...
Figure 3.3  Typical widescan XPS spectrum of r.f. sputtered a-Si$_{1-x}$C$_x$:H film.

...gives rise to core level peaks with different $E_B$. The resulting $E_B$ difference is known as the ‘chemical shift’ and has become a useful tool in obtaining information on the chemical states of a given film.

3.3.2 Quantitative XPS Analysis

The photoelectron spectrum is basically a plot of the number of emitted electrons per energy level versus electron energy. Since each element has a unique elemental spectrum, the spectra peaks from a mixture are approximately the sum of the elemental peaks from the individual constituents. Hence, it is possible to determine the relative concentrations of the various constituents of the compound by utilising the peak area and peak height sensitivity factors.
For films that are homogeneous, the number of photoelectrons per second in a specific spectra peak is given by

\[ I = n f \theta \sigma \lambda y A T \]  

(3.4)

where \( n \) is the number of atoms of the element per cm\(^3\) of the sample, \( f \) is the x-ray flux in photons per cm\(^2\)-sec, \( \sigma \) is the photoelectric cross-section for the atomic orbital of interest in cm\(^2\), \( \theta \) is an angular efficiency factor for the instrument arrangement based on the angle between the photon path and detected electron, \( y \) is the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, \( \lambda \) is the mean free path of the photoelectrons in the sample, \( A \) is the area of the sample, and \( T \) is the detection efficiency for electrons emitted from the sample. Equation (3.4) can also be expressed as

\[ n = I/ f \theta \sigma \lambda y A T \]  

(3.5)

The denominator in Equation (3.5) can be defined as the atomic sensitivity factor, \( S \). Consider a strong line from two elements, then the ration of the atomic number of the atoms in the two elements can be written as

\[ \frac{n_1}{n_2} = \frac{I_1/S_1}{I_2/S_2} \]  

(3.6)

As the ratio of each of the two quantities \( \sigma_1/\sigma_2 \) and \( \lambda_1/\lambda_2 \) remain fairly constant for different materials, it is possible to develop a set of relative values of \( S \) for all of the elements for any spectrometer [28].

63
A general expression for determining the elemental composition of the film can then be written as

\[
\%X = \frac{A_x / S_x}{\sum_{i=1}^{N} A_i / S_i}
\]  

(3.7)

where \(X\) is the element, \(A_x\) is the area under the peak of element \(X\) and \(S_x\) is the sensitivity factor. The values of \(S\) are based on empirical data, which have been corrected for the transmission function of the spectrometer. The sensitivity factor for carbon, oxygen, silicon and nitrogen is 0.31, 0.72, 0.37 and 0.49, respectively, for the spectrometer used in this work [28].

### 3.4 Conduction Mechanisms in Dielectrics

In an ideal MIS structure, the conductance of the insulating film is assumed to be zero. This is a consequence of the large energy band gap. In practice, however, insulating films are generally amorphous and the usual model of sharply defined energy bands cannot be readily applied; rather, fuzzy tails arise both at the top of the valence band and bottom of the conduction band. These extend into the gap and overlap to form a continuous electron state distribution. When this happens insulators assume semiconductor-like properties. Therefore, real insulators show carrier conduction when the temperature and electric field is sufficiently high. The identification of the dominant transport mechanism is the key to understanding the relationships between the material parameters of the insulator and contacts, and the resulting current-voltage characteristics. The various conduction mechanisms are discussed below [19].
3.4.1 Ohmic Conduction

If the insulator is of high quality and electrons are thermally generated, the current is carried by electrons jumping from one isolated state to the next. This behaviour, which occurs at low field and high temperature, is ohmic and is exponentially dependent on temperature, i.e.

\[ J = E \exp(-\Delta E_a / kT) \]  

where \( E_a \) is the activation energy. The plot of \( J \) against \( V \) can be fitted with a straight line. The conductivity can be found from the gradient of the plot.

3.4.2 Frenkel-Poole emission

Frenkel-Poole emission is due to field-enhanced thermal excitation of trapped electrons into the conduction band. This mechanism dominates at high temperature and high fields and is shown in Figure 3.4 [19]. The current is given by

\[ I = A V \exp\left[ -q (\Phi_B - \sqrt{qV / \pi \varepsilon \varepsilon_d}) / kT \right] \]  

where \( A \) is a constant, \( d \) is the dielectric thickness. \( \varepsilon_d \) is the dynamic dielectric constant, which can be obtained from the slope of a \( \ln I \) versus \( \sqrt{V} \) plot as

\[ \varepsilon_d = q \frac{\text{slope}(\ln I \text{ vs } \sqrt{V})}{d \pi \varepsilon \varepsilon_d} \]  

\( \Phi_B \) is the depth of the trap potential well and can be calculated from the Arrhenius plot of \( \ln I \) versus \( 1/T \) for a constant electric field \( E \) as

\[ \Phi_B = \frac{k \text{slope (lnI vs 1/T)}}{q} + \sqrt{qE / \pi \varepsilon \varepsilon_d} \]
3.4.3 Schottky emission

Schottky barrier is formed at the metal-semiconductor interface due to the difference in the work functions $q(\Phi_m - \Phi_s)$ of the metal and semiconductor. This barrier hinders the flow of current across the interface. When an electric field is applied, the potential barrier for charge carrier emission is lowered due to the presence of an image force as shown in Figure 3.5 [19]. This thermionic emission across the metal insulator interface is responsible for current conduction at high field. The current flow for this process is

$$I = AT^2 \exp\left[-\frac{q(\Phi_n - \sqrt{qV / 4\pi\varepsilon_d}}{kT}\right]$$ (3-12)

where $A$ is the effective Richardson constant, $\Phi_n$ is the barrier height, $V$ the applied voltage and $\varepsilon_d$ is the dynamic permittivity. The dynamic permittivity can be obtained from the plot of $\log I$ against $\sqrt{V}$ while the barrier height can be calculated from the plot of $\ln I/T^2$ versus $1/T$. 

---

Figure 3.4  Frenkel-Poole emission of trapped electrons.
In order to identify the dominant mode of conduction, the dynamics permittivity ($\varepsilon_d$) calculated based on Frenkel-Poole (Eq. 3-10) and Schottky (Eq. 3-12) relations are compared with the static permittivity ($\varepsilon_s$) obtained from the C-V data measured at 1MHz. The dynamics and static permittivities should be of comparable magnitude. The difference in the temperature dependence of their current density can also be used as a test for the dominant mechanism.

### 3.4.4 Tunneling

A variety of models for junction transport based on tunneling process have been proposed by several authors [20,21], which are schematically shown in Figure 3.6. The simplest tunneling model consists of tunneling of carriers through the spike – shaped barrier in the conduction band. According to Riben et al. [20], predominant tunnel flux takes place at an energy close to the peak of the barrier, within an energy difference of about 0.1 eV for crystalline heterojunction, which is indicated by path A in the figure. In the present heterojunction, however, tunneling process at an energy
range far below the barrier peak, indicated by path B in the figure, is quite possible because the localised states are quasi-continuously distributed within the gap of a-SiC:H spatially as well as energetically.

Figure 3.6 Tunneling models for heterojunction.

A second model is based on tunneling process of carriers, which has originally been presented for excess current in tunnel diode [22]. As has been discussed by Riben et al. [20,23], tunneling current by one-step tunneling (path C or D in the figure) is always smaller than that by multitunneling (path E in the figure).

3.4.5 Space-Charge-Limited Conduction

This bulk mechanism occurs because the rate of carrier injection from the contact exceeds the rate at which charge can be transported through the film. A space-charge cloud develops that discourages further charge injection and leads to nonlinear conduction effects. At low levels of carrier injection Ohm’s law is obeyed. If traps are present, the SCL current will be reduced because carriers are removed by empty traps.
3.5 Temperature Dependence of D.C. Conductivity

The d.c. conductivity is measured from the ohmic region of the I-V characteristics. At temperature higher than the room temperature, conductivity can be approximated by the general expression

\[ \sigma = \sigma_0 \exp(-\Delta E/kT) \]  \hspace{1cm} (3-13)

where \( \Delta E \) is the activation energy gap.

The conductivity at low temperature is presumably shared by hops between localised sites \( \sigma_{\text{hop}} \) in addition to the hops between the nearest sites \( \sigma_{\text{ext}} \). The \( \sigma_{\text{hop}} \) is calculated as the difference between the measured conductivity at low temperatures and the extrapolated straight-line fit of high temperature region. According to Mott [24]

\[ \sigma_{\text{hop}} = \frac{\sigma_o}{\sqrt{T}} \exp\left[-\left(\frac{T_o}{T}\right)^{-1/4}\right] \]  \hspace{1cm} (3-14)

where \( \sigma_o^2 = (3/4\pi\alpha k)N(E_F)\nu_{\text{ph}}q^2 \) and \( T_o = 18.1\alpha^3/kN(E_F) \), \( q \) is the electronic charge, \( \nu_{\text{ph}} \) is the characteristics phonon frequency obtained from Debye temperature (\( \nu_{\text{ph}} = 2.7 \times 10^{13} \) s\(^{-1} \) for SiC), \( k \) is the Boltzmann constant, \( \alpha \) is the inverse rate of fall-off of the wave function of a localised state and \( N(E_F) \) is the density of states at the Fermi level. \( T_o \) and \( \sigma_o \) are determined from the plot of \( \ln(\sigma_{\text{hop}}T^{1/2}) \) against \( (T^{1/4}) \).
3.6 Capacitance-Voltage Measurements

The principle C-V characteristics are shown in Figure 3.7. The curves can be characterised by 3 regions namely the accumulation, depletion and inversion region.

![Figure 3.7](image)

Figure 3.7 The C-V behaviour for three different conditions: (a) low frequency; (b) high frequency and (c) deep depletion.

Curve (a) represents the low frequency behaviour where the frequency is sufficiently low that the minority carriers are in thermal equilibrium with the small-signal AC voltage. For the minority carriers to be in equilibrium with the small-signal AC voltage and to contribute to the capacitance, the measurement frequency period $1/f$ must be less than the minority carrier generation time. Curve (b) represents the high frequency behaviour where the minority carriers are in equilibrium with the slowly varying ramp voltage, but these minority carriers cannot vary with the more rapidly varying small-signal AC voltage. The minority carriers pin the band bending so that the depletion width becomes fixed at its maximum and independent of gate bias. Therefore the capacitance remains constant as gate bias increases to beyond the
threshold voltage. Curve (c) depicts the condition deep depletion. In deep depletion, the gate bias ramp is too rapid to allow the inversion layer to form by thermal generation. Therefore, as the gate bias exceeds the threshold voltage, the absence of the inversion charge requires the space charge in the semiconductor to exceed the maximum depletion width. This increase in the depletion width provides more negative charge due to the ionized acceptors in order to balance the larger positive gate charge. Further increases in the gate bias could lead to avalanche breakdown.

### 3.8 Interface Trap Density $D_{it}$ by Conductance Method

The conductance method proposed by Nicollian and Goetzberger[25] can be used to determine the interface trap density $D_{it}$. It is based on the measurement of a equivalent parallel conductance $G_p/\omega$ of an MIS capacitor as a function of bias and frequency. The conductance, representing the loss mechanism due to interface trap capture and emission of carriers, is a measure of the interface trap density. However, correction has to be made for both the series resistance and dielectric capacitance before the correct $G_p/\omega$ is obtained.

#### 3.7.1 Correction for Series Resistance ($R_s$)

The equivalent circuit of a MIS capacitor in strong accumulation consists of an accumulation layer capacitance $C_a$ in parallel with interfacial trap admittance $Y_{it}$ as in Figure 3.7(a). The large $C_a$ shunting $Y_{it}$ results in a simplified circuit in Figure 3.7(b). This can be further simplified to the circuit in Figure 3.7(c) as $C_a >> C_i$. The series resistance ($R_s$) in the equivalent circuit (Figure 3.7(c)) causes a frequency dependent capacitance in accumulation and a much lesser extent in depletion. The capacitance
and conductance measurements, particularly at high frequencies, will be affected by the series resistance [26].

Figure 3.8 Equivalent circuit of MIS capacitor in strong accumulation.

The MIS capacitor is biased into strong accumulation to correct for series resistance. In strong accumulation, the admittance $Y_{ma}$ across the terminal can be expressed in terms of the measured capacitance $C_{ma}$ and conductance $G_{ma}$ as

$$Y_{ma} = G_{ma} + i\omega C_{ma}$$  \hspace{1cm} (3-15)

The series resistance $R_s$ and dielectric capacitance $C_i$ can be obtained in terms of the measured parameters in accumulation as

$$R_s = \frac{G_{ma}}{G_{ma}^2 + \omega^2 C_{ma}^2}$$  \hspace{1cm} (3-16)

$$C_i = C_{ma} \left[ 1 + \left( \frac{G_{ma}}{\omega C_{ma}} \right)^2 \right]$$  \hspace{1cm} (3-17)
The corrected capacitance, $C_c$ and conductance, $G_c$ at any frequency are

$$C_c = \frac{(G_{pm}^2 + \omega^2 C_{pm}^2) C_{pm}}{a^2 + \omega^2 C_{pm}^2}$$  \hspace{1cm} (3-18)$$

and

$$G_c = \frac{(G_{pm}^2 + \omega^2 C_{pm}^2) a}{a^2 + \omega^2 C_{pm}^2}$$  \hspace{1cm} (3-19)$$

respectively, where $a = G_{pm}^{-1}(G_{pm}^2 + \omega^2 C_{pm}^2) R_S$ and $C_{pm}$ and $G_{pm}$ are the measured capacitance and conductance across the terminal of the MIS capacitor. After correction for $R_S$, the conductance peak can be obtained and $C_i$ can be found from Equation (3.17).

3.7.2 Correction for Dielectric Capacitance ($C_i$)

An equivalent circuit for the conductance method is shown in Figure 3.8. The measured admittance across the capacitor terminal A-A in Figure 3.8(c) is $Y_m = G_{pm} + i\omega C_{pm}$. The $C_i$ value obtained is used to correct for the dielectric capacitance included in $Y_m$ to obtain $Y_p = G_p + i\omega C_p$ in Figure 3.8(b). This is done by converting $Y_m$ into an impedance, subtracting $1/i\omega C_i$, and converting back to an admittance to yield for the real part

$$\frac{G_p}{\omega} = \frac{\omega C_i^2 G_{pm}}{G_{pm}^2 + \omega^2 (C_{ox} - C_{pm})^2}$$  \hspace{1cm} (3-20)$$
3.7.3 Interface trap density in silicon bandgap

The equivalent circuit for the conductance method is shown in Figure 3.8 [27]

![Circuit Diagram](image)

Figure 3.9    Equivalent circuit for conductance measurement (a) MIS capacitor with interface state time constant, (b) simplified circuit of (a), (c) measured circuit

It consists of the dielectric capacitance $C_i$, the semiconductor capacitance $C_s$ and the interface trap capacitance $C_{it}$. The lossy process of interface carriers capture and emission is represented by $G_{it}$. The circuit in Figure 3.8(a) can be simplified to that in Figure 3.8(b), which

$$C_p = C_i + \frac{C_{it}}{1 + (\omega \tau_{it})^2}$$

and

$$\frac{G_{it}}{\omega} = \frac{q \omega \tau_{it} D_{it}}{1 + (\omega \tau_{it})^2} \quad (3-21)$$
where \( C_{it} = qD_{it} \) with \( D_{it} \) = interfacial trap level density and \( \tau_{it} = R_{it}C_{it} \) is the interface trap time constant. Equation (3-21) is valid for interface traps with single energy level in the bandgap. However in a real interface, there exits a continuum of interface trap energy and surface potential fluctuation, which result in a time constant dispersion. The normalised conductance is thus modified as [27]

\[
\frac{G}{\omega} = \frac{qD_{it}}{2\omega\tau_{it}} \ln\left(1 + \omega^2\tau_{it}^{-2}\right)
\]  

(3-22)

From (3-22), for a maximum \( G/\omega \), \( \omega = 2/\tau_{it} \) and \( D_{it} = 2.5G_{p}/q\omega \). Hence, \( D_{it} \) can be determined from the maximum \( G/\omega \) and \( \tau_{it} \) from \( \omega_p \) at the conductance peak location on the \( \omega \)-axis. An approximate expression giving the interface trap density in terms of the measured maximum conductance.

\[
D_{it} = \left(\frac{G_{p}}{\omega}\right)_{\text{max}} \frac{2.5}{Aq}
\]  

(3-23)

The relation between the band bending and energy in the bandgap for p-type substrate is shown schematically in Figure 3.9 [25]. The interface trap density as a function of the energy level in the silicon bandgap can be calculated from the relation

\[
\frac{E_I - E_C}{q} = \frac{E_{\delta}}{2q} + \psi_s - \phi_B
\]  

(3-24)

The surface band bending \( \psi_s \) is related to the applied bias \( V_G \) by the expression

\[
V_G = V_{FB} + \varphi_s + \frac{\sqrt{2qN_{s}e_{s}\phi}}{C_{ox}}
\]  

(3-25)
Figure 3.10  Band-bending diagram of p-type silicon showing how the position of the Fermi level at the silicon surface is related to band bending.
References


Chapter Four

Sample Preparation

This chapter deals with the experimental procedures involved in the preparation of the Al-a-SiC:H-Si structure used in this study. The experimental methods used in the structural characterisation of the sputtered films are described. This is followed by an outline of the experimental set-up used in the electrical measurements.

4.1 Sample Preparation and Cleaning

The samples used throughout this work were fabricated on boron doped (P-type) Czochralski silicon wafers of 50 mm in diameter. The silicon wafers were 8-12 Ω cm in resistivity and (100) in orientation. Prior to the deposition of films, the wafers were cleaned thoroughly to remove any surface contamination due to handling. Standard RCA cleaning was used to remove the contamination. RCA cleaning involved three steps:

(1) RCA I Solution Cleaning

This solution comprises of deionised water (H₂O), hydrogen peroxide (H₂O₂) and ammonia hydroxide (NH₄OH) mixed in a volume ratio of 5:1:1. The solution was heated to a temperature of 80 – 90 °C. The wafers were then immersed into the heated solution for 10 – 15 minutes. This was followed by a 15 minutes rinse in deionised water after which organic contaminants are removed from the surface of the wafers.

(2) RCA II Solution Cleaning
This solution comprises of deionised water (H\textsubscript{2}O), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and hydrochloric acid (HCl) mixed in a volume ratio of 6:1:1. The solution was heated to a temperature of 80 – 90 °C. The wafers were then immersed into the solution for 10 – 15 minutes and rinsed in deionised water for 15 minutes. This step removes the inorganic contaminants from the surface of the wafers.

(3) Hydrofluoric Acid Dip
The last step in the cleaning process involved dipping the wafers in a 10% hydrofluoric acid for about 10 seconds. This is to remove the native oxide layer on the wafer surface. The wafers are then rinsed in de-ionized water for 15 minutes and finally blown dry with nitrogen.

4.2 Film Deposition by RF Sputtering
An Anelva SPH-210H machine was used for the deposition of the amorphous silicon carbide films. The schematic diagram of the r.f. Magnetron-sputtering system is shown in figure 4.1. The system comprises of a diode structure housed in a low-pressure chamber with the target holder as the cathode and the substrate as the anode. A combination of mechanical and oil diffusion pumps are utilised to evacuate the chamber. Liquid nitrogen is used as a cold trap for the system. The sputtering gas is released into the chamber via a variable conductance valve. A 1kW, 13.6 MHz r.f. generator is used to create a plasma of ionising gas and to accelerate these ions towards the target for sputtering to occur. A matching network is employed to minimise the reflected power loss due to the impedance mismatch. The target used is a 99.99% pure polycrystalline silicon carbide disk, 100mm in diameter and 10mm thick. The substrate is mounted onto the substrate holder of 80 mm in diameter and can be heated to a
maximum temperature of 300 °C. Most of the power in the plasma is dissipated in the form of heat in the target. To avoid excessive heating, the target is attached to a water-cooled system to remove excessive heat generated during sputtering.

Prior to sputtering, the pressure of the system was first pumped down to about 10⁻⁶ torr before the argon or the argon plus hydrogen sputtering gas was introduced into the chamber. The substrate was heated to the desired temperature. When the pressure reached about 7x10⁻⁴ torr and the gas flow had stabilised, the main valve was slowly opened to raise the chamber or sputtering pressure, \( P_S \), to the required value. When the pressure and substrate temperature has stabilised, the r.f. generator was turned on and set to the desired power. Pre-sputtering was carried out for about 10 minutes, with a shutter over the substrate, to remove contaminants from the surface of the target. The shutter was then moved away for the sputtering to take place.

In this work, three sets of samples were prepared and the experimental conditions are shown in table 4.1. The first set of samples (rfh series) was prepared by varying the hydrogen content in the sputtering gas from 0% to 15%. As the chamber pressure (\( P_S \)) was kept constant at 3.0 Pa, the hydrogen partial pressure (\( P_{H} \)) was varied between 0 and 0.45 Pa. The second set (rfp series) was deposited by varying \( P_S \) from 0.8 to 3.0 Pa with the hydrogen content in the sputtering gas fixed at 5%. 
The substrate holder was heated to 250°C. The r.f. power was set to the required value with the target holder as the cathode and the substrate as the anode. Pre-sputtering was carried out for 10 minutes and the actual sputtering lasted for 30 minutes.

4.3 Annealing

4.3.1 Furnace Annealing

Furnace annealing of the films was carried out using the “Mini-brute” Thermco model MB71 furnace (bench model). Annealing was done in nitrogen ambient for 15 minutes at 400, 600 and 800°C. A Thermco Ana-lock controller series 201 was incorporated into the furnace to control the three different temperature zones in the furnace, the front, center and back zones. The temperature at each zone can be set to a temperature
range of 300 to 1200 °C. Nitrogen flow was maintained at a constant rate of 1.5 lt./min.

4.3.2 Rapid Thermal Annealing

RTA was carried out in an A.S.T. Electronik SHS 10 system with nitrogen gas being used to create an inert ambient. The schematic diagram of the rapid thermal processing system is shown in figure 4.2. The system chamber consists of a quartz jacket with halogen lamps arranged on the top and bottom serving as heat sources. The samples were placed on a 4-in. silicon wafer holder and the substrate temperature read through a pyrometer placed directly below the wafer. The pyrometer was constantly calibrated with a thermocouple and had an absolute temperature accuracy of ±4 °C. A closed –loop temperature controller system was used to monitor the temperature profile requested from the computer. These profiles or so-called recipes can be stored and can be called up for future use thus ensuring consistent wafer-to-wafer process repeatability. The system has a recommended temperature range of 400 to 1100 °C. The chamber is cooled by enclosed circulating water and thus referred to as a cold wall chamber. In this work, the films were annealed at 600 and 800°C for 60s. The temperature-time profile used for treating the samples is shown in figure 4.3. Details of the experimental conditions are shown in table 4.1.
Figure 4.2  Schematic diagram of the rapid thermal processing system

Figure 4.3  The temperature-time profiles of the rapid thermal annealing process at 600 and 800 °C used in this work.
Table 4.1. Preparation and annealing conditions of the r.f. sputtered $a$-Si$_{1-x}$C$_x$:H samples used in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_s$ (Pa)</th>
<th>$Ar$</th>
<th>$H_2$</th>
<th>$T_s$ ($^\circ$C)</th>
<th>r.f. (W)</th>
<th>Annealing</th>
<th>Furnace</th>
<th>RTA</th>
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<td>3.00</td>
<td>0.00</td>
<td>0.00</td>
<td>250</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>0.00</td>
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<td>200</td>
<td>400</td>
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<td>-</td>
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<td>0.00</td>
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<td>600</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>600</td>
<td>-</td>
</tr>
<tr>
<td>rfh08A</td>
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<td>0.00</td>
<td>0.00</td>
<td>250</td>
<td>200</td>
<td>-</td>
<td>800</td>
<td>-</td>
</tr>
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<td>RTA (°C)</td>
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<td>250</td>
<td>200</td>
<td></td>
<td>800</td>
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</tr>
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</table>
4.4 Thickness Measurement

The thickness of the deposited samples was measured using the Tencor Alphastep 500 surface profiler. Before sputtering, a small rectangular step was created by placing a strip of silicon on the wafer. After sputtering, the strip of silicon was removed and a horizontal scan across the step using the Alphastep would provide the thickness of the film sputtered. The thickness was used mainly in the electrical characterisation.

4.4.1 Rfh Samples

From Table 4.2, it was observed that there is an increase in the sputtered thickness as the hydrogen partial pressure ($P_{H}$) increases from 0 to 0.30 Pa. Since the chemical reaction occurs mainly at the silicon substrate, any change in the thickness is most likely due to the change in the Ar partial pressure as the total chamber or sputter pressure is kept constant at 3.0 Pa. Therefore, as $P_{H}$ increases, the Ar partial pressure decreases, leading to a decrease in the Ar ion density in the plasma which result in a greater mean free path of Si and C species. The increase in the hydrogen atoms with increasing $P_{H}$ may not have much effect on the mean free path of the species because of its relatively small atomic mass. However, there may be a point where the decrease in the Ar partial pressure will reduce the number of species sputtered from the target. This will cause the sputtered thickness to saturate with increasing $P_{H}$.

4.4.2 Rfp Samples

The thicknesses of samples sputtered under different $P_{S}$ are shown in Table 4.2. It was observed that there is not a significant increase or decrease in the thickness as $P_{S}$ increases. At low sputter pressures, the low Ar ion density and high re-sputtering effects would have a dampening effect on the thickness. However, this may be
balanced by the increase deposition due to the higher mean free path of the species in the plasma, thus resulting in a relatively constant sputtered thickness.

Table 4.2  Thickness of the r.f. sputtered $\alpha$-Si$_{1-x}$C$_x$:H samples prepared under different $P_{H}$ and $P_S$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thickness (Å)</th>
<th>Samples</th>
<th>Thickness (Å)</th>
</tr>
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<tbody>
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<td>6630</td>
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<tr>
<td>rfh10</td>
<td>8095</td>
<td>rfp25</td>
<td>6615</td>
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</tbody>
</table>

4.5 Metallisation

For the fabrication of the MIS structure, aluminum contacts were deposited on the front and back of the samples using the Anelva VI-43N evaporation system, which deposits metal by electron beam evaporation in a vacuum chamber. The required vacuum level is achieved through 2 levels of pumping. First, the sorption pump reduces the chamber pressure from atmospheric level to about $10^{-4}$ Torr. An ion pump then takes over and brings the pressure down to about $10^{-7}$ Torr. When the pressure goes below $2\times10^{-5}$ Torr, the main valve to the chamber may be opened slowly; taking care to ensure that at any one time, the pressure does not exceed $2\times10^{-5}$ Torr. Otherwise, it is very likely that the system will trip. This is done until the main valve is fully opened. As the sorption and ion pump are both oil free, there is no problem of oil contamination in the system.

When a pressure of $10^{-7}$ Torr is achieved, electron beam evaporation of the material can proceed. A 4 kV electron beam gun ejects high-energy electrons, which are
diffracted by an electro-magnetic field and bombard onto the high purity metal ingots placed below the substrate. Electron bombardment caused the metal to vaporise. The high vacuum ensures that the substrate above is maintained at a lower temperature allowing for deposition of the aluminum by condensation. The growth rate and the thickness of the deposited aluminum can be measured by the Inficon XTM film monitor, which is incorporated into the system.

In this work, the aluminum dots with area of approximately $1 \times 10^{-2}$ cm$^2$ and thickness of 0.6-0.8 µm was deposited on the SiC surface. The aluminum back contact was 0.4-0.5 µm thick.

### 4.5 Fourier Transform Infrared (FTIR) Spectrophotometer Measurement

The chemical structure of the r.f. sputtered a-Si$_{1-x}$C$_x$:H film was investigated using the FTIR spectroscopy. The infrared experiments were carried out using a Nicolet Magna-IR 850 FTIR spectrophotometer. This system employs a Michaelson interferometer with Happ-Genzel apodization. The samples were placed normal to the infrared beam and the transmittance spectra were measured at room temperature. To ensure accurate and well-resolved recordings, each sample was scanned 20 times with a spectral resolution of 2 cm$^{-1}$. Smoothing was applied to remove noisy components from the spectra. For transmission studies in the 400 – 4000 cm$^{-1}$ frequency range, a bare silicon wafer from the same crystal as the sample was placed in the background beam to eliminate lattice absorption bands. Baseline correction was also performed on the spectra obtained.
4.7 X-ray Photoelectron Spectroscopy

The XPS measurement was carried out using a VG ESCA LAB/SIMS LAB II spectrometer with a MgKα (1253.6 eV) source. The spectrometer was operated in the analyser mode, set at 20 eV with the X-ray source running at 120 W. Samples were cut into 10 mm² pieces and introduced into the chamber. The pressure was brought down to 10⁻¹⁰ Torr before measurement commenced. All spectra were acquired at room temperature and the detection angle of the photoemitted electrons was set to 75° with respect to the surface. For the annealed samples, the samples were etched in 5% hydrofluoric acid for 5 mins and sputter etched with 2.5 keV Ar⁺ ions for 15 mins to remove the surface oxide. All the spectra of the samples were fitted with Gaussian functions and the background was removed by the Shirley subtraction method.

4.8 Electrical Measurements

The quality of the r.f. sputtered a-Si₁₋ₓCₓ:H films are evaluated through the results obtained from the electrical measurements. All measurements were carried out on the Al- a-Si₁₋ₓCₓ:H-Si structure. A schematic diagram of the experimental set-up is shown in figure 4.4. The measuring instruments consist of a HP 4155A-semiconductor parameter analyser for I-V measurement and a HP 4192 impedance analyser for C-V measurement controlled by a personal computer through an IEEE 488-interface bus. The sample was placed in an enclosed probe station which shields the sample from light and external electrical noises. A vacuum system was used to hold the sample in close contact with a copper base plate, which was connected, to the measuring instrument. The probe, which is capable of contacting any one of the aluminum dots
on the sample, form the other connection lead. During measurements, the sample was flushed continuously with dry nitrogen to prevent humidity and contamination.

4.8.1 I-V Measurements

The I-V characteristics were obtained using the HP 4155A semiconductor parameter analyser. The I-V characteristics of all our films were measured with the applied voltage swept from -5 to 5 V in steps of 0.01 V. For the temperature dependence experiments, a temperature controller (MMR KT20) was used to vary the sample temperature in a vacuum enclosure.

4.8.2 Capacitance and Conductance Measurements

The C-V and G-V measurements were carried out with the voltage swept from 0 to -5 V and then back from -5 to 5V in steps of 0.1 V. For the C-f and G-f experiments with a fixed bias, the frequency was swept from 100 Hz to 10 MHz with bias varied from depletion to weak inversion region. Note that these measurements were carried out using the "parallel capacitance and conductance" configuration of the HP4192 impedance analyser.

4.8.3 Noise Measurements

The noise measurements were carried out at room temperature using a HP3567A dynamic signal analyzer. The Al-a-SiC-Si structures were placed in a well-shielded probe-box and the noise characteristics of the samples were measured in the constant-voltage mode using a HP4155A as the voltage source. The current from the sample was fed to a low current preamplifier (Stanford Research Systems SR750) and then amplified by a low noise amplifier (SR560). The spectrum analyzer measured the
temporal current fluctuations and a noise spectrum was taken after 40 averages. The background noise spectrum was found to be $10^{-11}$-$10^{-13}$ V$^2$/Hz for a frequency range of 1-10$^4$ Hz. The noise results were obtained with the negative bias applied to the top aluminum contact, i.e. with the silicon surface in accumulation.

Figure 4.4 A schematic diagram of the experimental set-up for the electrical measurements.
Chapter Five

Infrared Spectroscopy Results

Infrared (IR) spectroscopy is a useful tool to obtain important information on the chemical bonding of the molecular units in an amorphous solid. For $a$-$Si_{1-x}C_x$:H, the IR technique is non-destructive and provides information on hydrogen content as well as the other bonding configurations like silicon-carbon, silicon-hydrogen and carbon-hydrogen bonds. In this chapter, the infrared results of the $a$-SiC:H films prepared under different deposition conditions will be investigated. The results of the as-deposited films will be presented first, followed by the results of the furnace and rapid thermal annealed films.

5.1 Infrared Spectroscopy Results of As-Deposited Films

The infrared spectra of the rfh and rfp series of samples are shown in Figures 5.1 (a) and (b), respectively. The spectra show modes of vibration that characterise $a$-$Si_{1-x}C_x$:H films, i.e. the Si-C stretching mode at about 780 cm$^{-1}$ and the Si-H and Si-H$n$ stretching mode at about 2100 cm$^{-1}$. The C-H$n$ stretching mode at 2900 cm$^{-1}$ is absent in most of our films except for films prepared with higher $P_H$ values. The position and the area of the absorption band provide important information about the chemical structure and bonding characteristics of the film. Changes in the bond density calculated from the area under the absorption peak enable us to study the effects of annealing as well as the different preparation conditions on the sputtered films. All these results will be discussed in this chapter.
Fig. 5.1(a) Infrared spectra of rf sputtered amorphous silicon carbide films prepared with different hydrogen partial pressures.
Fig. 5.1(b) Infrared spectra of rf sputtered amorphous silicon carbide films prepared with different chamber pressures.
5.1.1 Rfh Samples

The infrared spectrum of the rfh samples is shown in Figure 5.1(a). From this figure, it can be seen that the infrared spectrum for the unhydrogenated sample, rfh00, exhibits only one broad dominant mode of vibration centered at ~780 cm\(^{-1}\). It was observed that for the hydrogenated samples (rfh5, rfh10 and rfh15), the most dominant mode of vibration is also the Si-C stretching mode at ~780 cm\(^{-1}\). This indicates the dominant role of Si-C bonds in the structure of the film. The broad absorption band is indicative of the amorphous nature of the silicon carbide films.\[1,2\] With the addition of hydrogen through increasing the hydrogen partial pressure (P\(_{H}\)), an additional absorption band, the Si-H/Si-H\(_2\) stretching mode, begins to appear at ~2100 cm\(^{-1}\). As P\(_{H}\) increases, it was observed that the intensity of the Si-H stretching mode enhances. For higher P\(_{H}\) values of 0.3 and 0.45 Pa, the C-H wagging/rocking mode at ~1000 cm\(^{-1}\) and stretching mode at ~2900 cm\(^{-1}\) can be observed. For the C-H absorption band, it is too small to be easily identified but this does not imply that there are very little C-H bonds. This is mainly due to the relatively low oscillator strength of the C-H stretching vibrations, which is further reduced by a third to a quarter when Si-C bonds are present \[3,6\]. This reduction stems from the transfer of electronic charges from Si to C, which results in a more electronegative C, which weakens the polarity of the C-H bond. The oscillator strength of the C-H stretching mode is smaller than that of the Si-H stretching mode and this is consistent with the facts that the electronegativity difference is larger for Si-H bonds and that the Si-H bond length is also larger. \[4\]

The positions of the vibrational peaks of the rfh samples are shown in Table 5.1. For the unhydrogenated sample, rfh00, the absorption peak at 785 cm\(^{-1}\) was assigned to the Si-C stretching mode. It was noted that as P\(_{H}\) increases, the Si-C peak position shifts slightly to a lower wavenumber from 785 to 773 cm\(^{-1}\). This assignment was
reasonable as the fundamental lattice vibration of SiC was reported to be at 800 cm\(^{-1}\). [1,5] However, both Wieder et al.[6] and Eberhardt et al.[7] reported that the absorption band at 770 ~780 cm\(^{-1}\) is due to Si-CH\(_3\) vibration. It is very unlikely that the absorption band at around 780 cm\(^{-1}\) is related to H as the absorption band was observed for films with and without hydrogen and with similar intensity. [2,8] Moreover, there is no observable Si-CH\(_n\) bending modes in the absorption band between 1200 and 1500 cm\(^{-1}\). Furthermore, the highest hydrogen content of the sputtering gas is only 15\% and therefore the probability of -CH\(_3\) incorporation is low. In general, the incorporation of methyl (CH\(_3\)) group in a-Si\(_{1-x}\)C\(_x\):H films is enhanced when hydrocarbon gases like methane or ethylene is used. [8,9] Also, the effusion of hydrogen during annealing will cause the area of the absorption band to decrease if it is hydrogenated. [7] However, the area increases after annealing (see section 5.2.1) and thus supports the assignment of the band at 780 cm\(^{-1}\) as the Si-C stretching mode.

Table 5.1  Peak position of Si-C, Si-H and C-H stretching modes of as-prepared rfh films.

<table>
<thead>
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<th>Si-H Stretching Mode (cm(^{-1}))</th>
<th>C-H Stretching Mode (cm(^{-1}))</th>
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</thead>
<tbody>
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</table>

The next major absorption band in the hydrogenated samples that is of interest is situated at wavenumber ~ 2100 cm\(^{-1}\). This band can be attributed to the stretching vibrations of the Si-H\(_2\) and/or Si-H bonds backbonded to carbon or silicon atoms.
or mono- or dihydride in a cluster environment (e.g. voids). The following section will discuss the most likely source of this absorption band.

The presence of the Si-H\textsubscript{2} stretching mode would usually require the existence of the Si-H\textsubscript{2} bending mode at 885 cm\textsuperscript{-1}. From the spectra of our hydrogenated samples, it was observed that there is no occurrence of such a mode. This suggests that the vibration mode at \sim 2100 cm\textsuperscript{-1} is not due to Si-H\textsubscript{2} bonds. However, according to Morimoto \textit{et al.} \cite{Morimoto}, for carbon (x) content greater than 0.3, they have difficulty in observing the Si-H\textsubscript{2} bending mode due to the strong Si-C absorption band at 780 cm\textsuperscript{-1}. Katayama \textit{et al.} \cite{Katayama} noted that the Si-H\textsubscript{2} bending mode disappears when carbon is added and this suggests that the chance of two hydrogen atoms bonding simultaneously to one silicon atom becomes scarce in the presence of carbon atoms in their reactive sputtered a-SiC:H films.

Finally, the other most likely source of this absorption mode may be due to presence of hydrogenated silicon bonds in the inner surface of voids or free volumes. According to Koropecki \textit{et al.}\cite{Koropecki, Eberhardt} and Eberhardt \textit{et al.}\cite{Eberhardt}, the existence of voids is closely linked to the post-deposition oxidation of the air-exposed amorphous silicon carbide films. This was established by the strong Si-O absorption band at 1000 cm\textsuperscript{-1}. The presence of voids is usually associated with silicon and carbon hydrogen complexes (C-H\textsubscript{n} and Si-CH\textsubscript{n} bonds) in methane-based amorphous silicon carbide films. These bonds are responsible for the open void structure, allowing post-deposition oxygen diffusion into the film as well as absorption of water.\cite{Eberhardt} As our as-deposited samples do not exhibit the level of oxidation seen in the literature,\cite{Eberhardt} it is reasonable to expect that the voids content in our samples are negligible. This conclusion is further
supported by the annealing results of the samples (see Section 5.2.1) in that no significant shift of the peak is observed for these samples. If the hydrogenated bonds are present in voids, annealing will cause hydrogen to effuse out and thereby leading to a decrease in these modes.[11] As such, the Si-H stretching mode at 2000 cm\(^{-1}\) (which corresponds to isolated hydrogen bonding) should be observed as hydrogen effuses from Si-H/Si-H\(_2\) clusters. It was observed that the Si-H stretching mode decreases upon annealing; the peak position however has minimal change. This is an indication that the band at \(~ 2100\) cm\(^{-1}\) is not caused from dihydrides or hydrogen in voids but from Si-C-H groups.

As discussed above, the band at \(~ 2100\) cm\(^{-1}\) is not caused by Si-H\(_2\) bonds or hydrogen in voids but only by Si-H bonds back bonded to C atoms which shift the Si-H peak toward a higher wavenumber. This shift can be related to the electronegativity of the carbon substituent. [10] This is reasonable as the probability of C-Si-H bonds is high, given the dominance of the Si-C bonds. Also, Eberhardt et al. [7] observed that the peak at 2000 cm\(^{-1}\) decreases rapidly upon adding small amount of carbon, indicating a strong increase of C-Si-H groups.

The only other observable band left in the spectra of the hydrogenated samples (P\(_H > 0.3\) Pa) is the C-H absorption band at \(~ 2900\) cm\(^{-1}\). Due mainly to the relatively low oscillator strength of C-H stretching vibrations, the C-H absorption band is generally small and as such, difficulties are encountered in the identification of the various C-H species. This observation was shared by Rynders et al.[17]. In view of the low hydrogen dilution content, the absorption band at \(~ 2900\) cm\(^{-1}\) is assigned to C-H stretching mode.
Table 5.2 Density of Si-C bonds ($N_{\text{Si-C}}$), Si-H bonds ($N_{\text{Si-H}}$) and C-H bonds ($N_{\text{C-H}}$) of as-prepared rfh films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_{\text{H}}$(Pa)</th>
<th>$N_{\text{Si-C}}$ ($x 10^{21}$ cm$^{-3}$)</th>
<th>$N_{\text{Si-H}}$ ($x 10^{21}$ cm$^{-3}$)</th>
<th>$N_{\text{C-H}}$ ($x 10^{21}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh00</td>
<td>0</td>
<td>4.68</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>rfh05</td>
<td>0.15</td>
<td>4.26</td>
<td>0.93</td>
<td>-</td>
</tr>
<tr>
<td>rfh10</td>
<td>0.30</td>
<td>4.05</td>
<td>1.10</td>
<td>1.45</td>
</tr>
<tr>
<td>rfh15</td>
<td>0.45</td>
<td>2.88</td>
<td>2.22</td>
<td>4.28</td>
</tr>
</tbody>
</table>

The densities of the bonds are determined using equation (3.2) and are listed in Table 5.2 above. Note that increasing $P_{\text{H}}$ from 0 to 0.45 Pa has the effect of decreasing $N_{\text{Si-C}}$ from 4.68 (rfh00) to 2.88x$10^{21}$ cm$^{-3}$ (rfh15) and increasing $N_{\text{Si-H}}$ from 0 to 2.22 x $10^{21}$ cm$^{-3}$. Note that the C-H bonds were detected only for samples with higher hydrogen incorporation, namely rfh10 and rfh15. It was also noted that $N_{\text{C-H}}$ is larger than $N_{\text{Si-H}}$ for the rfh10 and rfh15 samples. This can be attributed to the fact that hydrogen may have an affinity for carbon over silicon based on the bond energies of the C-H bond (4.31 eV) and Si-H bond (3.34 eV). Morimoto et al. [2] also observed a preferential attachment of H atom to C atom for their sputtered $a$-$\text{Si}_{1-x} \text{C}_x$:H films.

The results shown above suggested that as $P_{\text{H}}$ increases, more hydrogen is incorporated into the film to form Si-H bonds and C-H bonds. Banerjee et al. [18] also observed that the incorporation of hydrogen in the films increases with increasing partial pressure of hydrogen. As a result, there will be less Si and C atoms available to form Si-C bonds. This will lead to a decrease in $N_{\text{Si-C}}$ in the hydrogenated samples. From Figure 5.1(a), the dominant Si-C stretching mode suggests a significant degree of chemical ordering in the rfh samples. The appearance of such a strong peak has been
related to a chemically ordered material. [19] However, as $P_H$ increases, the reduction in the Si-C bonds due to formation of the Si-H and C-H bonds will reduce the chemical ordering of the films. Furthermore, from Table 5.1, the Si-C peak position decreases as $P_H$ increases indicating that the chemical ordering has decreased although the reduction in the peak position is not as significant as those mentioned in the literature. [10] Therefore, it can be deduced that the reduction in chemical ordering is small. From the results shown above, it can be concluded that hydrogen incorporation in the films increases as $P_H$ increases and this leads to a lesser degree of chemical ordering in the films.
5.1.2 Rfp Samples

The IR spectra of the $a$-$\text{Si}_{1-x}\text{C}_x$:H films sputtered under different chamber pressures, $P_s$, are shown in Figure 5.1(b). The dominant mode of vibration is the Si-C stretching mode. It was observed that the Si-C absorption peak intensity decreases as $P_s$ increases from 0.8 to 3.0 Pa. The Si-H stretching mode can only be observed for sample rfp30 and no C-H stretching band can be seen.

**Table 5.3** Peak position of Si-C and Si-H stretching modes of as-prepared rfh films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_H$(Pa)</th>
<th>Si-C Stretching Mode (cm$^{-1}$)</th>
<th>Si-H Stretching Mode (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>0.8</td>
<td>787</td>
<td>-</td>
</tr>
<tr>
<td>rfp15</td>
<td>1.5</td>
<td>783</td>
<td>-</td>
</tr>
<tr>
<td>rfp20</td>
<td>2.0</td>
<td>780</td>
<td>-</td>
</tr>
<tr>
<td>rfp30</td>
<td>3.0</td>
<td>778</td>
<td>2103</td>
</tr>
</tbody>
</table>

**Table 5.4** Density of Si-C bonds ($N_{\text{Si-C}}$) and Si-H bonds ($N_{\text{Si-H}}$) of as-prepared rfp films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_S$(Pa)</th>
<th>$N_{\text{Si-C}}$ (x 10$^{21}$ cm$^{-3}$)</th>
<th>$N_{\text{Si-H}}$ (x 10$^{21}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>0.8</td>
<td>6.12</td>
<td>-</td>
</tr>
<tr>
<td>rfp15</td>
<td>0.15</td>
<td>5.81</td>
<td>-</td>
</tr>
<tr>
<td>rfp20</td>
<td>0.20</td>
<td>5.63</td>
<td>-</td>
</tr>
<tr>
<td>rfp30</td>
<td>0.30</td>
<td>4.26</td>
<td>0.93</td>
</tr>
</tbody>
</table>

From Table 5.4 above, it shows that $N_{\text{Si-C}}$ decreases as the pressure increases from 0.8 to 3.0 Pa. The Si-H stretching mode can only be observed for the rfh30 sample. This suggests that increasing chamber pressure facilitates hydrogen incorporation in the
sputtered films, and only for pressures above 2.0 Pa can Si-H bonds be detected by the IR technique. The absence of Si-H bonds at lower chamber pressure may be due to the re-sputtering effects.

Ross and Messier [19] observed an inverse relationship between the chamber pressure and the substrate bias, i.e. a low $P_S$ would mean a large negative potential. This negative potential would attract the $\text{Ar}^+$ ions to the substrate, thus bombarding it and causing the weaker Si-H bonds to break. This could explain the absence or in this case the undetectable Si-H stretching mode at low pressures. As the chamber pressure increases, the increase in the number of gas particles would cause more collisions between themselves. This would reduce the mean free path of the gas particles and as a result could also reduce the number and energy of the $\text{Ar}^+$ ions bombarding the target. Thus, less Si and C atoms would be available to form the Si-C bonds and this could explain the lower $N_{\text{Si-C}}$ obtained. As $P_S$ increases, the substrate bias would be less negative and therefore there would be less attraction of the $\text{Ar}^+$ ions to the substrate. This could explain the higher Si-H bonds as $P_S$ increases.

From Tables 5.3 and 5.4, the Si-C peak position and $N_{\text{Si-C}}$ decreases as the chamber pressure was increased from 0.8 to 3.0 Pa respectively. The reduction in the Si-C bonds will reduce the chemical ordering in the film. The shift in the peak position, however, is not very significant, similar to that in section 5.1.2. Hence, from the IR results, it can be concluded that low chamber pressure does not favour hydrogen incorporation in the sputtered films.
5.2 Infrared Spectroscopy Results of Annealed Films

In this section, the rfh and rfp samples were subjected to furnace and rapid thermal annealing (RTA). The furnace annealing was carried out at 400, 600 and 800 °C for 15 minutes while RTA was performed at 600 and 800 °C for 60s. It was observed that changes to the surface of the hydrogenated films occurred when annealed at higher temperatures. Micro-cracks were observed after annealing at 800 °C and this could be due to the modification of the stress in the films after annealing. Friessnegg *et al.* [20] also observed that annealing up to 900°C resulted in cracked films, most likely due to the high stress in the films at these temperatures [21]. Zhang *et al.* [22] noticed that when their films were heated to 500°C and higher, the surface cracks under the observation of the microscope, which may be due to both hydrogen evolution and increase of original tensile stress.

5.2.1 Rfh Samples

The IR absorption spectra for the annealed rfh samples are shown in Figures 5.2(a)-(d). It can be seen that the intensity of the Si-C absorption band increases with annealing temperature for all the samples. For the hydrogenated samples, the intensity of the Si-H and C-H absorption bands reduces with annealing. [20,21] The bond densities (i.e. N_{Si-C}, N_{Si-H} and N_{C-H}) of the annealed rfh samples are listed in Table 5.5. For the rfh00 samples, N_{Si-C} increases from 4.68×10^{21} to 6.64×10^{21} cm^{-3} (8.98×10^{21} cm^{-3}) when furnace annealed (RTA) at 800 °C. An increase in the value of N_{Si-C} can also be observed for the hydrogenated samples after annealing. It is interesting to note that while N_{Si-C} of RTA hydrogenated samples are generally less than those of furnace annealed samples, the opposite was observed for unhydrogenated samples, i.e., N_{Si-C} of
Fig. 5.2(a) Infrared spectra of rfh0 series of samples, with annealing temperatures of 400-800°C.
Fig. 5.2(b) Infrared spectra of rfh5 series of samples, with annealing temperatures of 400-800 °C.
Fig. 5.2(c) Infrared spectra of rfh10 series of samples with annealing temperatures of 400-800 °C.
Fig. 5.2(d) Infrared spectra of rfh15 series of samples with annealing temperatures of 400-800 °C.
RTA sample is greater than the furnace annealed sample. The $N_{\text{Si-H}}$ and $N_{\text{C-H}}$ were observed to decrease after annealing. An interesting observation to note was that while $N_{\text{Si-H}}$ decreases after annealing at each particular temperature, $N_{\text{C-H}}$ actually increases before decreasing after annealing at 400 °C. One possible explanation could be that Si-H bonds tend to break at a lower temperature as compared with C-H bonds due to the smaller Si-H single bond energy (70.4 kcal/mol or 3.1 eV) compared to C-H (98.8 kcal/mol or 3.5 eV). Friessnegg et. al. [20] and DellaMea et al. [24] also confirmed that the evolution of H from the a-Si$_x$C$_{1-x}$:H films is a two step process which, first, involves the breaking of Si-H bonds and second, of the C-H bonds. The hydrogen released from the breaking of the Si-H bonds would then passivate the C dangling bonds, thereby increasing $N_{\text{C-H}}$. Ray et al. [25] & Schliwinski et al.[26] also observed a similar increase in $N_{\text{C-H}}$ after annealing at 350 °C.

The increase in $N_{\text{Si-C}}$ of the annealed samples could be due to the formation of Si-C bonds from either of the following events:

1. The recombination of existing Si and C dangling bonds in the film.
2. The recombination of the Si and C dangling bonds formed from the dissociation of Si-H and C-H bonds due to annealing.

For the unhydrogenated samples, namely rfh00, the increase in $N_{\text{Si-C}}$ may be due to the formation of Si-C bonds as in case (1) as there is no hydrogen content in the film. However, for the hydrogenated samples, from the fact that $N_{\text{Si-C}}$ increases and $N_{\text{Si-H}}$ and $N_{\text{C-H}}$ decreases after annealing, it is reasonable to expect that case (2) is the more likely mechanism to account for the increase in Si-C bonds.
From Table 5.6, the Si-C absorption peak shifts to a higher wavenumber with increase in annealing temperature. Basa et al. [27] and Gomez et al. [28] also observed such a trend. Due to the breaking of the Si-H and C-H bonds with increase in annealing temperature and due to an increased tendency for Si and C to bond to each other, more number of Si-C bonds are formed which result in the increase in area under Si-C peak. The increase number of Si-C bonds with increase in annealing temperature in the amorphous network result in the increase in the bonding of more electronegative neighbouring atoms like C to Si leading to an increase in the effective force constant and shift to a higher wavenumber. Thus, it can be concluded that the chemical ordering increases as the annealing temperature increases as this is shown in the increased relative intensity of the Si-C stretch modes and in the movement of the peak center to higher frequency.

From Table 5.5, it was observed that the hydrogen related modes decrease whereas the Si-C stretching mode increases when annealing temperature is increased. As hydrogen effuses, a transformation of the structure occurs and Si-C bonds are created in substitution of Si-H and C-H bonds. The introduction of higher relative electronegativity carbon (2.5) into lower relative electronegativity of silicon (1.8) will lead to the strengthening of the interaction among atoms in films and make the film more compact leading to film contracting. This is confirmed by the increase in the refractive index [29] due to the increase in the film density or a reduction of voids in the film. [22] The increase in Si-C bond density is consistent with film compaction deduced from ellipsometry. [28] As a result, the compressive stress is weakened due to film contracting. [22]
For a-Si$_x$C$_{1-x}$:H films, hydrogen is responsible for the intrinsic compressive stress. The general trend is to associate the hydrogen present in a-Si$_x$C$_{1-x}$:H films to the compressive stress state whereas the hydrogen depletion or its outer-diffusion yields a zero or low tensile stress states. [21] The stress of the films changes from compressive to tensile stress by the addition of C, and the stress free composition is a-Si$_{0.77}$C$_{0.23}$:H. It is clearly shown that Si-H and C-H hydrogenated bond breaking is responsible for the compressive stress relaxation whereas the tensile stress is mainly due to the Si-C bond formation. The films will crack if the tensile stress exceeds a certain pressure as seen in our samples annealed at higher temperatures. Kim et al. [31] observed micro cracks on their films after annealing at 600°C and attributed it to excessive tensile stress.

The sputtered films remain amorphous even at 800 °C annealing, in agreement with the work reported by Khakani et al. [21] and Derst et al. [30]. There is no significant decrease in the width of the Si-C absorption band indicating the formation of Si-C crystallites. This suggests that the observed chemical environment variations are mainly due to the local environment rearrangements resulting in additional Si-C bond formation.

Si-C bonds are much shorter (1.88 Å) than Si-Si bonds (2.35 Å) and so bond angle distortion in the amorphous network is enhanced with the formation of Si-C bonds. An increase in annealing temperature leads to an increase in the number of Si-C bonds which results in the increase in the bond angle distortion. This increases the structural disorder in the annealed films. The increase in the bond angle distortion increases the width (FWHM) of the Si-C absorption band. [27] However, the change in the FWHM is not as significant as that mentioned in the literature. It seems that the increase in
$N_{\text{Si-C}}$ does not necessarily affect the structural ordering of the films. According to Khakani et al. [23], it could be due to the possible distribution of H atoms to form Si-H and C-H bonds under configuration which minimise Si-C bond angle distortion. Another possible reason could be due to the low hydrogen content in our films. Both Basa et al. [27] and Khakani et al. [21] observed structural disorder in samples with high hydrogen content (~30%).

Another interesting point to note is that the films become oxidised after annealing at temperatures greater than 600°C. Figures 5.2(a) to (d) shows a small shoulder at about 1040 cm$^{-1}$. Kim et al. [31] observed that beyond 500°C the film appears to become oxidized. Note that their film was annealed in an air environment. Ray et al. [25] also observed oxidation in their samples and suggested that due to the hydrogen evolution from the film at 400°C, some voids or pores may be formed and the film probably absorbs oxygen when exposed to air after annealing. However, it is also possible that oxidation occurs at the surface during annealing.
Table 5.5 Density of Si-C bonds ($N_{\text{Si-C}}$), Si-H bonds ($N_{\text{Si-H}}$) and C-H bonds ($N_{\text{C-H}}$) calculated from the IR spectra of the as-prepared and annealed rfh samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_H$</th>
<th>Annealing</th>
<th>$N_{\text{Si-C}}$</th>
<th>$N_{\text{Si-H}}$</th>
<th>$N_{\text{C-H}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Pa)</td>
<td>Furnace °C</td>
<td>(x 10^{21} cm^{-3})</td>
<td>(x 10^{21} cm^{-3})</td>
<td>(x 10^{21} cm^{-3})</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>4.68</td>
</tr>
<tr>
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<td>400</td>
<td>-</td>
<td>-</td>
<td>5.46</td>
</tr>
<tr>
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<td>600</td>
<td>-</td>
<td>-</td>
<td>6.30</td>
</tr>
<tr>
<td>rfh06A</td>
<td>0</td>
<td>-</td>
<td>600</td>
<td>-</td>
<td>7.05</td>
</tr>
<tr>
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<td>800</td>
<td>-</td>
<td>-</td>
<td>6.64</td>
</tr>
<tr>
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<td>-</td>
<td>800</td>
<td>-</td>
<td>8.98</td>
</tr>
<tr>
<td>rfh05</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>4.26</td>
</tr>
<tr>
<td>rfh54</td>
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<td>400</td>
<td>-</td>
<td>-</td>
<td>5.02</td>
</tr>
<tr>
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<td>600</td>
<td>-</td>
<td>-</td>
<td>5.29</td>
</tr>
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<td>-</td>
<td>600</td>
<td>-</td>
<td>5.16</td>
</tr>
<tr>
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<td>800</td>
<td>-</td>
<td>-</td>
<td>5.88</td>
</tr>
<tr>
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<td>-</td>
<td>800</td>
<td>-</td>
<td>5.29</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>4.05</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>4.84</td>
</tr>
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<td>600</td>
<td>-</td>
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</tr>
<tr>
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<td>600</td>
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</tr>
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<td>-</td>
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<tr>
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<td>0.30</td>
<td>-</td>
<td>800</td>
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<td>5.16</td>
</tr>
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</tr>
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<td>400</td>
<td>-</td>
<td>-</td>
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</tr>
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<td>-</td>
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<td>5.23</td>
</tr>
<tr>
<td>rfh158A</td>
<td>0.45</td>
<td>-</td>
<td>800</td>
<td>-</td>
<td>4.98</td>
</tr>
</tbody>
</table>
Table 5.6  Peak position of Si-C, Si-H and C-H absorption band of the as prepared and annealed rfh samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_h$ (Pa)</th>
<th>Annealing Temperature</th>
<th>Si-C Stretching Mode (cm$^{-1}$)</th>
<th>Si-H Stretching Mode (cm$^{-1}$)</th>
<th>C-H Stretching Mode (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
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<td>-</td>
<td>785</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>rfh04</td>
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<td>400</td>
<td>787</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>rfh06</td>
<td>0</td>
<td>600</td>
<td>791</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>rfh06A</td>
<td>0</td>
<td>600</td>
<td>788</td>
<td>-</td>
<td>-</td>
</tr>
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<td>rfh08</td>
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<td>800</td>
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<td>790</td>
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<td>-</td>
</tr>
<tr>
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<td>-</td>
<td>778</td>
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<td>-</td>
</tr>
<tr>
<td>rfh54</td>
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<td>400</td>
<td>776</td>
<td>2100</td>
<td>2868</td>
</tr>
<tr>
<td>rfh56</td>
<td>0.15</td>
<td>600</td>
<td>776</td>
<td>2100</td>
<td>2870</td>
</tr>
<tr>
<td>rfh56A</td>
<td>0.15</td>
<td>600</td>
<td>791</td>
<td>-</td>
<td>2872</td>
</tr>
<tr>
<td>rfh58</td>
<td>0.15</td>
<td>800</td>
<td>795</td>
<td>2088</td>
<td>-</td>
</tr>
<tr>
<td>rfh58A</td>
<td>0.15</td>
<td>800</td>
<td>791</td>
<td>-</td>
<td>2871</td>
</tr>
<tr>
<td>rfh10</td>
<td>0.30</td>
<td>-</td>
<td>776</td>
<td>2091</td>
<td>2868</td>
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<tr>
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<td>779</td>
<td>2094</td>
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<tr>
<td>rfh106</td>
<td>0.30</td>
<td>600</td>
<td>782</td>
<td>2089</td>
<td>2870</td>
</tr>
<tr>
<td>rfh106A</td>
<td>0.30</td>
<td>600</td>
<td>782</td>
<td>2091</td>
<td>2870</td>
</tr>
<tr>
<td>rfh108</td>
<td>0.30</td>
<td>800</td>
<td>795</td>
<td>2094</td>
<td>-</td>
</tr>
<tr>
<td>rfh108A</td>
<td>0.30</td>
<td>800</td>
<td>788</td>
<td>2091</td>
<td>-</td>
</tr>
<tr>
<td>rfh15</td>
<td>0.45</td>
<td>-</td>
<td>773</td>
<td>2093</td>
<td>2871</td>
</tr>
<tr>
<td>rfh154</td>
<td>0.45</td>
<td>400</td>
<td>777</td>
<td>2094</td>
<td>2874</td>
</tr>
<tr>
<td>rfh156</td>
<td>0.45</td>
<td>600</td>
<td>782</td>
<td>2088</td>
<td>2872</td>
</tr>
<tr>
<td>rfh156A</td>
<td>0.45</td>
<td>600</td>
<td>777</td>
<td>2090</td>
<td>2872</td>
</tr>
<tr>
<td>rfh158</td>
<td>0.45</td>
<td>800</td>
<td>792</td>
<td>2092</td>
<td>-</td>
</tr>
<tr>
<td>rfh158A</td>
<td>0.45</td>
<td>800</td>
<td>779</td>
<td>2090</td>
<td>-</td>
</tr>
</tbody>
</table>
5.2.2 Rfp Samples

The IR absorption spectra for the annealed rfp samples are shown in Figures 5.3(a)-(d). Similar to the rfh samples in section 5.2.1, it can be seen that the intensity of the Si-C absorption band increases with increasing annealing temperature for all the samples. For the rfp08, rfp15 and rfp20 series of samples, other than the Si-C absorption peak, no other absorption peak was observed. Note that the C-H absorption band cannot be observed for all samples as the hydrogen content in the sputtering gas is only 5%. For the rfp30 samples, the intensity of the Si-H absorption band decreases with annealing.

The bond densities (i.e. $N_{\text{Si-C}}$ and $N_{\text{Si-H}}$) and absorption peak position of the annealed rfp samples are listed in Table 5.7 and 5.8 respectively. An increase in the value of $N_{\text{Si-C}}$ can be observed with increasing annealing temperature, like in the case of the rfh samples. For rfp08, rfp15 and rfp20 samples, the hydrogen incorporation is low as can be deduced from the IR spectra. Therefore, the increase in $N_{\text{Si-C}}$ can be attributed to the recombination of Si and C dangling bonds in the film. For the rfp30 sample, the presence of the Si-H stretching band suggests that the increase of $N_{\text{Si-C}}$ may be partly due to the recombination of the Si dangling bonds formed from the dissociation of Si-H bonds due to annealing and the existing C dangling bonds in the film.

As can be seen from Table 5.8, the Si-C peak position increases after annealing. This shows that the chemical ordering of the film increases as the annealing temperature increases like in the case for the rfh samples. (see explanation in section 5.2.1)
Fig. 5.3a Infrared spectra of rfp08 series of samples, with annealing temperatures of 400-800 °C.
Fig. 5.3b Infrared spectra of rfp15 series of samples, with annealing temperatures of 400-800 °C.
Fig. 5.3c Infrared spectra of rfp20 series of samples, with annealing temperatures of 400-800 °C.
Fig. 5.3d Infrared spectra of rfp08 series of samples, with annealing temperatures of 400-800 °C.
Table 5.7  Density of Si-C bonds ($N_{\text{Si-C}}$) and Si-H bonds ($N_{\text{Si-H}}$) calculated from the IR spectra of the as-prepared and annealed rfp samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_S$ (Pa)</th>
<th>Annealing Temp. ($^\circ$C)</th>
<th>$N_{\text{Si-C}}$ ($x 10^{21} \text{ cm}^{-3}$)</th>
<th>$N_{\text{Si-H}}$ ($x 10^{21} \text{ cm}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>0.8</td>
<td>-</td>
<td>6.12</td>
<td>-</td>
</tr>
<tr>
<td>rfp084</td>
<td>0.8</td>
<td>400</td>
<td>6.26</td>
<td>-</td>
</tr>
<tr>
<td>rfp086</td>
<td>0.8</td>
<td>600</td>
<td>6.30</td>
<td>-</td>
</tr>
<tr>
<td>rfp088</td>
<td>0.8</td>
<td>800</td>
<td>7.04</td>
<td>-</td>
</tr>
<tr>
<td>rfp15</td>
<td>0.15</td>
<td>-</td>
<td>5.81</td>
<td>-</td>
</tr>
<tr>
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<td>400</td>
<td>6.13</td>
<td>-</td>
</tr>
<tr>
<td>rfp156</td>
<td>0.15</td>
<td>600</td>
<td>6.39</td>
<td>-</td>
</tr>
<tr>
<td>rfp158</td>
<td>0.15</td>
<td>800</td>
<td>6.97</td>
<td>-</td>
</tr>
<tr>
<td>rfp20</td>
<td>0.20</td>
<td>-</td>
<td>5.63</td>
<td>-</td>
</tr>
<tr>
<td>rfp204</td>
<td>0.20</td>
<td>400</td>
<td>5.98</td>
<td>-</td>
</tr>
<tr>
<td>rfp206</td>
<td>0.20</td>
<td>600</td>
<td>6.16</td>
<td>-</td>
</tr>
<tr>
<td>rfp208</td>
<td>0.20</td>
<td>800</td>
<td>6.90</td>
<td>-</td>
</tr>
<tr>
<td>rfp30</td>
<td>0.30</td>
<td>-</td>
<td>4.26</td>
<td>0.93</td>
</tr>
<tr>
<td>rfp304</td>
<td>0.30</td>
<td>400</td>
<td>5.02</td>
<td>0.64</td>
</tr>
<tr>
<td>rfp306</td>
<td>0.30</td>
<td>600</td>
<td>5.29</td>
<td>0.46</td>
</tr>
<tr>
<td>rfp308</td>
<td>0.30</td>
<td>800</td>
<td>5.88</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Table 5.8  Peak position of Si-C and Si-H absorption band of the as-prepared and annealed rfp samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_S$ (Pa)</th>
<th>Annealing Temp ($^\circ$C)</th>
<th>Si-C Stretching Mode (cm$^{-1}$)</th>
<th>Si-H Stretching Mode (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>0.8</td>
<td>-</td>
<td>787</td>
<td>-</td>
</tr>
<tr>
<td>rfp084</td>
<td>0.8</td>
<td>400</td>
<td>787</td>
<td>-</td>
</tr>
<tr>
<td>rfp086</td>
<td>0.8</td>
<td>600</td>
<td>789</td>
<td>-</td>
</tr>
<tr>
<td>rfp088</td>
<td>0.8</td>
<td>800</td>
<td>794</td>
<td>-</td>
</tr>
<tr>
<td>rfp15</td>
<td>0.15</td>
<td>-</td>
<td>785</td>
<td>-</td>
</tr>
<tr>
<td>rfp154</td>
<td>0.15</td>
<td>400</td>
<td>785</td>
<td>-</td>
</tr>
<tr>
<td>rfp156</td>
<td>0.15</td>
<td>600</td>
<td>786</td>
<td>-</td>
</tr>
<tr>
<td>rfp158</td>
<td>0.15</td>
<td>800</td>
<td>789</td>
<td>-</td>
</tr>
<tr>
<td>rfp20</td>
<td>0.20</td>
<td>-</td>
<td>782</td>
<td>-</td>
</tr>
<tr>
<td>rfp204</td>
<td>0.20</td>
<td>400</td>
<td>784</td>
<td>-</td>
</tr>
<tr>
<td>rfp206</td>
<td>0.20</td>
<td>600</td>
<td>787</td>
<td>-</td>
</tr>
<tr>
<td>rfp208</td>
<td>0.20</td>
<td>800</td>
<td>790</td>
<td>-</td>
</tr>
<tr>
<td>rfp30</td>
<td>0.30</td>
<td>-</td>
<td>778</td>
<td>2100</td>
</tr>
<tr>
<td>rfp304</td>
<td>0.30</td>
<td>400</td>
<td>787</td>
<td>2100</td>
</tr>
<tr>
<td>rfp306</td>
<td>0.30</td>
<td>600</td>
<td>793</td>
<td>2090</td>
</tr>
<tr>
<td>rfp308</td>
<td>0.30</td>
<td>800</td>
<td>795</td>
<td>2088</td>
</tr>
</tbody>
</table>
5.3 Conclusion

From the IR results, the dominant peaks are the Si-C stretching mode at about 780 cm\(^{-1}\) and the Si-H and Si-H\(_n\) stretching mode at about 2100 cm\(^{-1}\). The C-H\(_n\) stretching mode at 2900 cm\(^{-1}\) is absent in most of our films except for films prepared with higher \(P_H\) values. For the rfh and rfp samples, hydrogen incorporation in the sputtered films increases as \(P_H\) and \(P_S\) increases respectively, leading to a lesser degree of chemical ordering in the films as Si-C bonds decreases. Annealing of both the unhydrogenated and hydrogenated films lead to an increase in the Si-C bonds. However, the mechanism for the increase is somewhat different for the two types of films. For the unhydrogenated samples, the increase in the Si-C bonds is mainly due to the recombination of the existing Si and C dangling bonds. For the hydrogenated samples, the increase is largely due to the recombination of the Si and C dangling bonds that resulted from the breaking of the Si-H and C-H bonds as well as the first mechanism. Annealing, in general, will lead to an increase in the Si-C bonds and a reduction in the hydrogenated bonds, thus increasing the chemical ordering in the films.
References


5. W. C. Mohr, C. C. Tsai and R. A. Street. Properties and Local Structure of Plasma-Deposited Amorphous Silicon-Carbon Alloys,


Chapter Six

X-Ray Photoelectron Spectroscopy Results

X-Ray photoelectron spectroscopy is widely used to study the chemistry of semiconductor because of its sensitivity to the local chemical environment around a given atom. In particular, it has the advantage of resolving the different bonding states of individual elemental atoms in an alloy. In this study, the r.f. sputtered a-Si_{1-x}C_x:H films will be characterised by the XPS technique. In particular, the position, stoichiometry and the bonding composition will be discussed and analysed.

6.1 XPS Results of As-Deposited Samples

Using a MgKα source (1253.6 eV) and a photoelectron take-off angle of 75° with respect to the surface, a wide scan of energy range of 0 – 1000 eV was carried out for all the XPS samples. A typical widescan spectrum is shown in Figure 6.1. The background steps occurring at each peak are attributed to inelastic photoemission (energy loss within the solid) [1]. From the figure, the dominant peaks are the silicon (Si2p), carbon (C1s) and oxygen (O1s) peaks. No Ar peak is observed to suggest the incorporation of Ar atoms into the films by sputtering. To obtain relevant information on the chemical environment of the element concentration, narrow scans of the individual peaks are performed.
Figure 6.1 Typical widescan XPS spectrum of r.f. sputtered a-Si$_{1-x}$C$_x$:H film.

Figure 6.2 shows the typical narrow scans of the Si2p and C1s peaks of the sputtered films. The Si2p peak (97 to 107 eV) was deconvoluted into the Si-Si/Si-H, Si-C, O-Si-C and Si-O$_x$ peaks, and the C1s peak (279 to 291 eV) was deconvoluted into the C-Si, C-C/C-H, C-O/C-O-H and C=O peaks. According to Hicks et al. [2], the contribution of the C-C bonds (284.4 eV) and C-H bonds (284.6 eV) could not be separated at present due to the small energy difference between the peaks. The same could be said of the Si-Si/Si-H bonds as a-Si:H exhibit only a 0.1 eV shift (possibly to a-Si) when annealed at temperatures higher than 500 °C [3]. Therefore, in our work, the Si-Si/Si-H and C-C/C-H bonds will be grouped together for the hydrogenated films.

6.1.1 Rfh Samples

The binding energy and stoichiometry of the rfh samples are listed in Table 6.1. The stoichiometry of the films lies between a-Si$_{0.47}$C$_{0.53}$:H and a-Si$_{0.45}$C$_{0.55}$:H. This is
slightly higher than the stoichiometric film a-Si_{0.5}C_{0.5}:H obtained by sputtering from the polycrystalline silicon carbide target, suggesting that the films are slightly carbon rich. This observation was supported by Tohda et al. [4]. With the incorporation of hydrogen, from 0 to 15%, it was observed that the stoichiometry does not change much. There is also no significant shift in the Si2p and C1s peaks except for the 0.1 eV shift between the unhydrogenated and hydrogenated samples. Gat et al. [5]
reported that changes in the carbon content in the film causes significant shifts in the Si2p and C1s peaks and therefore, our observations are accurate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PH (Pa)</th>
<th>Si2p Binding Energy (eV)</th>
<th>C1s Binding Energy (eV)</th>
<th>Stoichiometry Si:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>0</td>
<td>100.7</td>
<td>283.1</td>
<td>0.45 : 0.55</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.15</td>
<td>100.6</td>
<td>283.2</td>
<td>0.45 : 0.55</td>
</tr>
<tr>
<td>rfh10</td>
<td>0.30</td>
<td>100.6</td>
<td>283.2</td>
<td>0.46 : 0.54</td>
</tr>
<tr>
<td>rfh15</td>
<td>0.45</td>
<td>100.6</td>
<td>283.2</td>
<td>0.47 : 0.53</td>
</tr>
</tbody>
</table>

The film compositions of the samples are listed in Table 6.2. For the rfh0 sample, the % Si-C bond is 63.8%. Since the sample is unhydrogenated and contains no hydrogen, the %C-C and %Si-Si bonds are 15.8% and 1.3% respectively. When PH increases from 0 to 0.45 Pa, the %C-C/C-H and %Si-Si/Si-H bonds are observed to increase by 2.2% and 2.5% respectively. Correspondingly, the %Si-C bond decreases from 63.8% to 60.2% as the hydrogen content increases.

Due to the fact that %C-C/C-H and %Si-Si/Si-H cannot be differentiated, the explanation for the increase in these bonds cannot be accurately ascertained. However, from the IR results presented in Chapter Five, it is reasonable that part of the increase could be due to the increase in the C-H and Si-H bonds as PH increases. In fact, with the increase in hydrogen content in the film, the Si-C bond was observed to reduce due to the formation of Si-H and C-H bonds. It might also be true for the C-C and Si-Si bonds. Thus, it is possible that the increase in %C-C/C-H and %Si-Si/Si-H is due mainly to the increase in the hydrogenated bonds.
Table 6.2 Film composition of P_H samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>P_H (Pa)</th>
<th>Si-C (%)</th>
<th>C-C/C-H (%)</th>
<th>Si-H/Si-Si (%)</th>
<th>C-O-H &amp; C=O (%)</th>
<th>O-Si-C &amp; SiO_x (%)</th>
<th>Total (%)</th>
</tr>
</thead>
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<tr>
<td>rfh0</td>
<td>0</td>
<td>63.8</td>
<td>15.8</td>
<td>1.3</td>
<td>8.5</td>
<td>10.5</td>
<td>19.1</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.15</td>
<td>62.1</td>
<td>18.0</td>
<td>1.5</td>
<td>6.4</td>
<td>12.0</td>
<td>18.4</td>
</tr>
<tr>
<td>rfh10</td>
<td>0.30</td>
<td>62.0</td>
<td>17.0</td>
<td>3.7</td>
<td>3.3</td>
<td>14.0</td>
<td>17.3</td>
</tr>
<tr>
<td>rfh15</td>
<td>0.45</td>
<td>60.2</td>
<td>18.0</td>
<td>3.8</td>
<td>3.8</td>
<td>14.2</td>
<td>18.0</td>
</tr>
</tbody>
</table>

From the above results, the increase in P_H does not cause major structural or chemical changes as the binding energies of C1s and Si2p peaks remain fairly constant. However, from the IR results obtained earlier, the decrease in %Si-C and the corresponding increase in %C-C/C-H and %Si-Si/Si-H all points to an increase in the chemical disorder.

6.1.2 Rfp Samples

The binding energy and the stoichiometry of the P_S samples are shown in Table 6.3. It was observed that as the chamber pressure increases, the film approaches stoichiometric composition. Similar to what was observed for the P_H samples; the Si2p and C1s peaks remain fairly constant, indicating that the chemical composition is not drastically affected by the increase in P_S.

In Table 6.4, it was noted that the %Si-C decreases while the %Si-Si/Si-H and %C-C/C-H increases as P_S is increased. The decrease in the %Si-C as P_S increases is due mainly to the reduction of Si and C atoms in the sputtering chamber, as the energy and
mean free path of the Ar ions is reduced leading to less bombardment of the target. From the IR results obtained, it was stated that the chamber pressure is inversely related to the negative substrate bias. Therefore, a decrease in PS will lead to an increase in the negative bias, leading to greater substrate bombardment by the Ar ions. This causes weaker bonds to be broken. Likewise, an increase in PS will lead to a decrease in the substrate bombardment, resulting in greater incorporation of hydrogen through hydrogenated bonds as shown in Table 6.4. It was also observed that as hydrogen incorporation increases with an increase in PS, the silicon related oxide content is always greater than the carbon related oxide. This supports the fact that the incorporation of hydrogen in the films favours the formation of C-H bonds, which leaves the silicon bonds to form oxide.
The reduction in the %Si-C and the increase in the %C-C/C-H and %Si-H/Si-Si suggest an increase in chemical disordering. As mentioned above, with low P_s there exist re-sputtering of the film and this would suggest that the %C-C/C-H would comprise mainly of C-C bonds, which has a higher binding energy than C-H bonds. It also shows that films sputtered at lower pressure have higher carbon content, having more Si-C bonds with less hydrogen.

6.2 XPS Results of Annealed Samples

6.2.1 Rfh Samples

In this section, the samples were both furnace and rapid thermal annealed in nitrogen ambient. The binding energy and the stoichiometry of the annealed P_H samples are listed in Table 6.5. It was observed that stoichiometry of the annealed films remained relatively constant, not exceeding 10\% of the stoichiometric composition. The Si2p and C1s binding energies were observed to increase as annealing temperature increases. Khakani et al. [6] also reported a similar increase in the binding energies. Non-hydrogenated β-SiC film has the Si2p and C1s binding energies at 100.6 and 283.6 eV respectively [6,7]. Therefore, it would seem that annealing causes the shift of the local order towards that of the β-SiC-like local environment.
The film compositions of the annealed P_H samples are listed in Table 6.6. From the table, it can be seen that for the unhydrogenated samples (rfh0) the %Si-C bonds increases from 63.8% to 68% after annealing at 800 °C. The %Si-Si bonds however decreases from 1.3% to 0% after annealing at 400 °C. Note that the %C-C bonds remain relatively constant at 15.8% to 16.8%. The RTA samples also showed an

<table>
<thead>
<tr>
<th>Sample</th>
<th>P_H (Pa)</th>
<th>Si2p Binding Energy (eV)</th>
<th>C1s Binding Energy (eV)</th>
<th>Stoichiometry Si:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>0.0</td>
<td>100.7</td>
<td>283.1</td>
<td>0.45 : 0.55</td>
</tr>
<tr>
<td>rfh04</td>
<td>0.0</td>
<td>100.7</td>
<td>283.2</td>
<td>0.46 : 0.54</td>
</tr>
<tr>
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<td>283.5</td>
<td>0.45 : 0.55</td>
</tr>
<tr>
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<td>283.5</td>
<td>0.41 : 0.59</td>
</tr>
<tr>
<td>rfh08</td>
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<td>100.7</td>
<td>283.5</td>
<td>0.47 : 0.53</td>
</tr>
<tr>
<td>rfh08A</td>
<td>0.0</td>
<td>100.7</td>
<td>283.6</td>
<td>0.42 : 0.58</td>
</tr>
<tr>
<td>rfh5</td>
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<td>100.6</td>
<td>283.2</td>
<td>0.45 : 0.55</td>
</tr>
<tr>
<td>rfh56</td>
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<td>100.7</td>
<td>283.3</td>
<td>0.40 : 0.60</td>
</tr>
<tr>
<td>rfh56A</td>
<td>0.15</td>
<td>100.6</td>
<td>283.5</td>
<td>0.45 : 0.55</td>
</tr>
<tr>
<td>rfh58</td>
<td>0.15</td>
<td>100.7</td>
<td>283.6</td>
<td>0.47 : 0.53</td>
</tr>
<tr>
<td>rfh10</td>
<td>0.30</td>
<td>100.6</td>
<td>283.2</td>
<td>0.46 : 0.54</td>
</tr>
<tr>
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<td>0.30</td>
<td>100.6</td>
<td>283.3</td>
<td>0.44 : 0.56</td>
</tr>
<tr>
<td>rfh106A</td>
<td>0.30</td>
<td>100.6</td>
<td>283.4</td>
<td>0.46 : 0.54</td>
</tr>
<tr>
<td>rfh108</td>
<td>0.30</td>
<td>100.7</td>
<td>283.6</td>
<td>0.46 : 0.54</td>
</tr>
<tr>
<td>rfh15</td>
<td>0.45</td>
<td>100.6</td>
<td>283.2</td>
<td>0.47 : 0.53</td>
</tr>
<tr>
<td>rfh154</td>
<td>0.45</td>
<td>100.6</td>
<td>283.2</td>
<td>0.48 : 0.52</td>
</tr>
<tr>
<td>rfh156</td>
<td>0.45</td>
<td>100.6</td>
<td>283.3</td>
<td>0.40 : 0.60</td>
</tr>
<tr>
<td>rfh156A</td>
<td>0.45</td>
<td>100.6</td>
<td>283.3</td>
<td>0.44 : 0.56</td>
</tr>
<tr>
<td>rfh158</td>
<td>0.45</td>
<td>100.7</td>
<td>283.6</td>
<td>0.45 : 0.55</td>
</tr>
</tbody>
</table>
increase in the %Si-C bonds and a decrease in the %Si-Si bonds. The change is, however, less than the furnace annealed samples. A similar observation was made for the IR results.

Table 6.6 Film composition of annealed and as-prepared P_H samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>P_H</th>
<th>Si-C</th>
<th>C-C/C-H</th>
<th>Si-H/Si-Si</th>
<th>Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Pa)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>C-O-H &amp; C=O (%)</td>
<td>O-Si-C &amp; SiOx (%)</td>
</tr>
<tr>
<td>rfh0</td>
<td>0</td>
<td>63.8</td>
<td>15.8</td>
<td>1.3</td>
<td>8.5</td>
<td>10.5</td>
</tr>
<tr>
<td>rfh04</td>
<td>0</td>
<td>64.8</td>
<td>15.8</td>
<td>-</td>
<td>5.9</td>
<td>13.5</td>
</tr>
<tr>
<td>rfh06</td>
<td>0</td>
<td>65.3</td>
<td>16.0</td>
<td>-</td>
<td>5.2</td>
<td>13.5</td>
</tr>
<tr>
<td>rfh06A</td>
<td>0</td>
<td>64.6</td>
<td>19.0</td>
<td>0.3</td>
<td>7.0</td>
<td>9.2</td>
</tr>
<tr>
<td>rfh08</td>
<td>0</td>
<td>68.0</td>
<td>15.9</td>
<td>-</td>
<td>5.6</td>
<td>10.5</td>
</tr>
<tr>
<td>rfh08A</td>
<td>0</td>
<td>64.8</td>
<td>16.8</td>
<td>-</td>
<td>8.1</td>
<td>10.3</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.15</td>
<td>62.1</td>
<td>18.0</td>
<td>1.5</td>
<td>6.4</td>
<td>12.0</td>
</tr>
<tr>
<td>rfh56</td>
<td>0.15</td>
<td>64.7</td>
<td>18.9</td>
<td>0.8</td>
<td>6.1</td>
<td>9.5</td>
</tr>
<tr>
<td>rfh56A</td>
<td>0.15</td>
<td>62.5</td>
<td>18.3</td>
<td>0.4</td>
<td>8.3</td>
<td>10.4</td>
</tr>
<tr>
<td>rfh58</td>
<td>0.15</td>
<td>67.1</td>
<td>15.3</td>
<td>-</td>
<td>5.9</td>
<td>11.7</td>
</tr>
<tr>
<td>rfh10</td>
<td>0.30</td>
<td>62.0</td>
<td>17.0</td>
<td>3.7</td>
<td>3.3</td>
<td>14.0</td>
</tr>
<tr>
<td>rfh106</td>
<td>0.30</td>
<td>64.2</td>
<td>16.1</td>
<td>1.1</td>
<td>7.2</td>
<td>11.4</td>
</tr>
<tr>
<td>rfh106A</td>
<td>0.30</td>
<td>62.9</td>
<td>16.9</td>
<td>1.5</td>
<td>5.4</td>
<td>13.3</td>
</tr>
<tr>
<td>rfh108</td>
<td>0.30</td>
<td>67.2</td>
<td>15.1</td>
<td>-</td>
<td>2.9</td>
<td>14.8</td>
</tr>
<tr>
<td>rfh15</td>
<td>0.45</td>
<td>60.2</td>
<td>18.0</td>
<td>3.8</td>
<td>3.8</td>
<td>14.2</td>
</tr>
<tr>
<td>rfh154</td>
<td>0.45</td>
<td>62.0</td>
<td>17.2</td>
<td>1.9</td>
<td>2.9</td>
<td>16.0</td>
</tr>
<tr>
<td>rfh156</td>
<td>0.45</td>
<td>63.9</td>
<td>15.3</td>
<td>1.9</td>
<td>8.0</td>
<td>10.9</td>
</tr>
<tr>
<td>rfh156A</td>
<td>0.45</td>
<td>61.1</td>
<td>16.9</td>
<td>1.5</td>
<td>6.8</td>
<td>13.8</td>
</tr>
<tr>
<td>rfh158</td>
<td>0.45</td>
<td>64.9</td>
<td>14.3</td>
<td>-</td>
<td>4.3</td>
<td>16.5</td>
</tr>
</tbody>
</table>
For the hydrogenated films, the %Si-C bonds increases by 4.7 to 5.2% while the %Si-H bonds decreases by 1.5 to 3.8% when furnace annealed at 800 °C. The RTA samples also exhibit similar behaviour except that the percentage increase is less. The increase in %Si-C bonds is only 0.4 to 0.9% as compared to the 2.2 to 3.7% increase of the furnace annealed samples. Due to the incorporation of hydrogen in the film, the %C-C/C-H bonds shows a decrease of 1.9 to 3.7% when furnace annealed at 800 °C. This was not the case for the unhydrogenated samples.

The XPS results generally agree very well with the IR results presented in Chapter 5 in that the %Si-C bonds increases while the %Si-H and C-H bonds decreases as the annealing temperature increases. This suggests that more Si-C bonds are formed from the dissociation of the Si-H and C-H bonds due to annealing.

With the effusion of hydrogen from the films coupled with the increase in the %Si-C and the shift in the C1s binding energy towards 283.6 eV, it shows that annealing causes the shift of the local order of the films towards that of the unhydrogenated β-SiC-like local environment. As the annealed films remain amorphous even after annealing at 800 °C, the reorganisation of the short-range order as the hydrogenated bonds are broken occurs through the formation of additional Si-C bond [6].

Previously, it was observed from the IR results that N_C-H decreases with annealing temperature especially after 800 °C. Therefore, it can be deduced that the %C-C/C-H for the annealed samples consists predominantly C-C bonds. However, this value is less than the unhydrogenated sample. This would seem reasonable as carbon has a high affinity for hydrogen, thus reducing the formation of Si-C and C-C bonds. This in turn will lead to a lesser amount of C-C bonds present in the film after annealing as
most of the Si and C dangling bonds, from the dissociation of Si-H and C-H bonds, will combine to form additional Si-C bonds.

### 6.2.2 Rfp Samples

Similar to the observations for the P\textsubscript{H} samples, the Si2p and C1s binding energies for the P\textsubscript{S} samples listed in Table 6.7 shows that annealing causes an upward shift of the energies to that of unhydrogenated $\beta$-SiC. As in the case of the P\textsubscript{H} samples, the stoichiometry of the P\textsubscript{S} samples remains relatively constant after annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P\textsubscript{S} (Pa)</th>
<th>Si2p Binding Energy (eV)</th>
<th>C1s Binding Energy (eV)</th>
<th>Stoichiometry Si:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>0.8</td>
<td>100.5</td>
<td>283.4</td>
<td>0.43 : 0.57</td>
</tr>
<tr>
<td>rfp088</td>
<td>0.8</td>
<td>100.6</td>
<td>283.6</td>
<td>0.43 : 0.57</td>
</tr>
<tr>
<td>rfp15</td>
<td>1.5</td>
<td>100.5</td>
<td>283.4</td>
<td>0.44 : 0.56</td>
</tr>
<tr>
<td>rfp158</td>
<td>1.5</td>
<td>100.7</td>
<td>283.6</td>
<td>0.46 : 0.54</td>
</tr>
<tr>
<td>rfp20</td>
<td>2.0</td>
<td>100.5</td>
<td>283.4</td>
<td>0.44 : 0.56</td>
</tr>
<tr>
<td>rfp208</td>
<td>2.0</td>
<td>100.7</td>
<td>283.6</td>
<td>0.44 : 0.56</td>
</tr>
<tr>
<td>rfp30</td>
<td>3.0</td>
<td>100.6</td>
<td>283.2</td>
<td>0.45 : 0.55</td>
</tr>
<tr>
<td>rfp308</td>
<td>3.0</td>
<td>100.7</td>
<td>283.6</td>
<td>0.47 : 0.53</td>
</tr>
</tbody>
</table>

The film composition of the furnace annealed samples is listed in Table 6.8. After annealing at 800 °C, the %Si-C of the films increases whereas the %C-C/C-H and %Si-H/Si-Si decreases. This trend is similar to that observed for the P\textsubscript{H} samples. It was observed that the largest degree of change occurs for the rfp30 sample, which has the highest hydrogen content for P\textsubscript{S} samples.
Table 6.8 Film composition of furnace annealed and as-prepared P$_S$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P$_S$ (Pa)</th>
<th>Si-C (%)</th>
<th>C-C/C-H (%)</th>
<th>Si-H/Si-Si (%)</th>
<th>C-O-H &amp; C=O (%)</th>
<th>O-Si-C &amp; SiO$_x$ (%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>0.8</td>
<td>65.7</td>
<td>15.8</td>
<td>0.4</td>
<td>8.2</td>
<td>9.9</td>
<td>18.1</td>
</tr>
<tr>
<td>rfp088</td>
<td>0.8</td>
<td>68.9</td>
<td>15.3</td>
<td>-</td>
<td>4.9</td>
<td>10.9</td>
<td>15.8</td>
</tr>
<tr>
<td>rfp15</td>
<td>1.5</td>
<td>65.3</td>
<td>15.0</td>
<td>1.2</td>
<td>9.0</td>
<td>9.5</td>
<td>18.5</td>
</tr>
<tr>
<td>rfp158</td>
<td>1.5</td>
<td>67.4</td>
<td>14.5</td>
<td>-</td>
<td>5.2</td>
<td>9.4</td>
<td>14.6</td>
</tr>
<tr>
<td>rfp20</td>
<td>2.0</td>
<td>62.5</td>
<td>17.0</td>
<td>1.6</td>
<td>8.0</td>
<td>10.9</td>
<td>18.9</td>
</tr>
<tr>
<td>rfp208</td>
<td>2.0</td>
<td>65.3</td>
<td>16.7</td>
<td>-</td>
<td>6.1</td>
<td>11.9</td>
<td>18.0</td>
</tr>
<tr>
<td>rfp30</td>
<td>3.0</td>
<td>62.1</td>
<td>18.0</td>
<td>1.5</td>
<td>6.4</td>
<td>12.0</td>
<td>18.4</td>
</tr>
<tr>
<td>rfp308</td>
<td>3.0</td>
<td>67.1</td>
<td>15.3</td>
<td>-</td>
<td>5.9</td>
<td>11.7</td>
<td>17.6</td>
</tr>
</tbody>
</table>

From the increase in %Si-C and the decrease in %C-C/C-H and %Si-H/Si-Si, there is an indication that the chemical ordering of the films increase after annealing.

6.3 Conclusion

From the XPS results, the dominant peaks are the silicon (Si2p), carbon (C1s) and oxygen (O1s) peaks. The stoichiometry of the as-deposited films shows that they are slightly carbon-rich and it remained fairly constant as $P_H$ and $P_S$ increases. For both the rfh and rfp samples, the %Si-C decreases while the %C-C/C-H and %Si-H/Si-Si increases which leads to a decrease in chemical ordering. The annealing results of the rfh and rfp samples generally agree very well with the IR results presented in Chapter 5 in that the %Si-C increases while the %Si-H and %C-H decreases as the annealing temperature increases. It was observed that stoichiometry of the annealed films remained relatively constant, not exceeding 10% of the stoichiometric composition. The Si2p and C1s binding energies were observed to increase as annealing temperature
increases. All this leads to an increase in the chemical ordering of the films. Another point to note is that the percentage change in the bonds is always higher for the furnace annealed samples than the RTA samples.
References


Chapter Seven

Electrical Characterisation Results

Characterisation of the r.f. sputtered $a$-SiC:H-Si system would not be complete without a detailed evaluation of its electrical properties. As work done on the electrical properties of the $a$-SiC:H-Si system are relatively few, references to the $a$-Si:H system will be made to aid in the explanation of the results obtained. In this chapter, the electrical characterisation results, namely the steady state current-voltage ($I$-$V$), capacitance ($C$-$V/f$) and conductance ($G$-$V/f$) obtained as a function of voltage and frequency will be investigated. The current conduction mechanisms, dielectric constant ($\varepsilon$) and interface trap density ($D_{it}$) extracted from these measurements will be discussed in this chapter. The current-voltage measurements will be presented first. This will be followed by the capacitance-voltage and the interface trap density measurements. Like in the previous chapter, the results of the as-deposited films will be dealt first, followed by the results of the furnace and rapid thermal annealed films.

7.1 Current-Voltage Characteristics of As Deposited Films

The I – V characteristics of the Al/$a$-SiC:H/Si structure of the rfh and rfp series of samples are shown in Figures 7.1 (a) - (b) respectively. It was observed that, in general, for a fixed bias the current magnitude decreases as $P_H$ and $P_S$ increases. In hydrogenated amorphous semiconductor, the role of hydrogen is to passivate
Figure 7.1(a) Current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different hydrogen partial pressures.
Figure 7.1(b) Current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different sputtering pressures.
the existing unterminated dangling bonds in the film. Therefore, as hydrogen is incorporated into the film, the density of the dangling bonds decreases. Electrical conduction in amorphous semiconductor may be by charge carrier hopping through the dangling bonds to a certain extent. Thus, as the number of dangling bonds decreases, less current will flow through the film. Referring to the results in Tables 5.5 and 5.7 in Chapter five, as $P_H$ increases $N_{Si-H}$ increases and this reduces the number of dangling bonds. Likewise as $P_S$ increases, more hydrogen is incorporated into the film and this results in the increase in $N_{Si-H}$ i.e. a reduction in the density of dangling bonds. Thus, as there are less dangling bonds available for electrical conduction, the current magnitude will be less.

Another possible explanation could be obtained from the optical bandgap, $E_g$, of the a-SiC:H films. Choi et. al. [1] observed that as the $P_H$ increases, the bandgap of the sputtered a-SiC:H film increases. With the increase in the bandgap, it would be more difficult for electrons to overcome the forbidden gap to the conduction band and thus the electrical conduction would reduce. Dutta et. al. [2] also observed an increase in the bandgap as the $P_H$ increases from 0.0 to 0.66 Pa. and this corresponds to a reduction in the current level in their sputtered films. Banerjee et. al. [3] also found that with the increase hydrogen incorporation, the optical bandgap increases and the electrical conductivity decreases due to the decrease in the number of states in the bandgap. Likewise, for the rfp samples, Choi et. al. [1] observed that the optical bandgap increases as $P_S$ increases due to the increase in hydrogen incorporation in the film and as mentioned above, the electrical conductivity decreases.
7.1.1 Rfh Samples

Much more information can be gathered from the current-voltage characteristics. A plot of log I against V for the rfh samples is shown in Figure 7.2. It can be seen that there are at least 2 distinct regions in the I-V characteristics. This can be classified into the low and high fields region. It is interesting to note that for samples rfh5 and rfh10, there is an extra shoulder in the I-V curve in the low field region, though it is more prominent in the rfh5 sample. This shows that there are two different transport mechanisms at work in the low field region and this would be explained in detail later in the chapter. Figure 7.3 shows the forward and reverse bias current of the rfh samples. From the figure, the d.c. conductivity (σ), saturation current (I_s), the ideality factor (n) and the rectifying ratio can be obtained as mentioned in Chapter 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D.C. Conductivity</th>
<th>Saturation Current (A)</th>
<th>Ideality Factor</th>
<th>Rectifying Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>(2.76 \times 10^{-6})</td>
<td>(5.85 \times 10^{-8})</td>
<td>1.11</td>
<td>2270</td>
</tr>
<tr>
<td>rfh5</td>
<td>(5.05 \times 10^{-7})</td>
<td>(2.52 \times 10^{-9})</td>
<td>1.44</td>
<td>1056</td>
</tr>
<tr>
<td>rfh10</td>
<td>(3.86 \times 10^{-8})</td>
<td>(1.65 \times 10^{-8})</td>
<td>3.33</td>
<td>31</td>
</tr>
</tbody>
</table>

The room temperature d.c. conductivity (σ) of the samples were obtained from the low field region using the relation \(σ = \frac{l I}{AV}\), where \(l\) and \(A\) are the thickness of the film and the area of the metal contact. The results are listed in Table 7.1. It was observed that \(σ\) lies between \(2.76 \times 10^{-6}\) to \(3.86 \times 10^{-8}\) \(\Omega^{-1}\text{cm}^{-1}\) and is very dependent on the sample preparation conditions. It was observed that as \(P_H\) increases the conductivity
Figure 7.2. Log scale current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different hydrogen partial pressures.
Figure 7.3. Log scale current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different hydrogen partial pressures for forward and reverse bias.
decreases. This is expected as the magnitude of the current decreases as shown in Figures 7.2 and 7.3. Dutta et al. [2] also reported a decrease in $\sigma$ from $8 \times 10^{-7}$ to $6 \times 10^{-9}$ as $P_H$ was increased from 0.04 to 0.66 Pa. It was suggested that $\sigma$ is related to the hydrogen content in the films. From the results in Table 5.2, it can be seen that $\sigma$ decreases as the number of Si-H bonds ($N_{Si-H}$) increases. A higher value in $N_{Si-H}$ invariably results in a lower conductivity. This is reasonable as higher $N_{Si-H}$ means a lower amount of silicon dangling bonds and this will result in lowering the conductivity.

The saturation current, obtained by extrapolating the linear region to zero bias, in general, decreases as the hydrogen partial pressure increases. In the low current region, the current varies as $\exp\left(\frac{qV}{nkT}\right)$. The ideality factor $n$ was obtained by plotting $\ln I$ against $V$ and measuring the gradient. Its value increases from 1.11 to 3.33 as the hydrogen content in the film increases from 0 to 10%. For the ideal case, the ideality factor is 1. The low value of $n$ for the rfh0 and rfh5 samples indicates that the diode quality is good. The low value also shows that the current is dominated by the injection of carriers over the barrier rather than the recombination of carriers at the SiC/Si interface [4]. In the high-current region, the I-V plot deviates from linearity due to the voltage drop across the series resistance of the structure. From Figure 7.3, it shows that the structure is rectifying. The rectifying ratios were best for rfh0 sample (2270:1 at $\pm 1.0$ V) and as the hydrogen partial pressure increases, the rectifying ratios become worse (1056:1 and 31:1 at $\pm 1.0$ V for rfh5 and rfh10 respectively).

From the above results, it could be observed that film sputtered with no hydrogen (rfh0) shows the lowest ideality factor and the best rectifying ratio. As hydrogen
incorporation increases, the ideality factor increases and the rectifying ratio became worse. This shows that films prepared without hydrogen has better electrical properties and is more suitable to be used as material in Si heterojunction devices. As hydrogen is added, the film becomes less conductive and tends towards becoming an insulator and as such, has poorer electrical properties. This is expected as film without hydrogen contains many dangling bonds and this will enhance the electrical conductivity.

7.1.1.1 Temperature Dependence of Conductivity

Prior to evaluating the temperature dependence of conductivity, the behaviour of the current as a function of temperature will be looked into first. Figures 7.4(a) to (c) shows that as the ambient temperature increases, the current magnitude increases for samples rfh0, rfh5 and rfh10. Several researchers have observed similar trends [5-7] and this is expected as the increase in temperature provides increasing energy to the electrons thereby leading to an increase in current. To investigate the temperature dependence of conductivity, the current was measured at different ambient temperatures ranging from 250 K to 440 K. The conductivity was then obtained and plotted against (1000/T).

Figure 7.5 shows the log conductivity against (1000/T) plots of samples rfh0, rfh5 and rfh10. It was seen that the increase in hydrogen concentration lowers the conductivity
Figure 7.4(a) Current versus voltage characteristics of rfh0 sample as a function of ambient temperature.
Figure 7.4(b) Current versus voltage characteristics of rfh5 sample as a function of ambient temperature.
Figure 7.4(c) Current versus voltage characteristics of rfh10 sample as a function of ambient temperature.
by a few orders of magnitude. At high temperatures, the activated conduction can be described by an equation that obeys the Arrhenius relationship $\sigma = \sigma_0 \exp [-E_a / kT]$, where $E_a$ is the activation energy derived from the high temperature slope and $\sigma_0$, obtained by extrapolating this slope, is a constant which depends on the conduction mechanism. It was observed in Figure 7.5 that as the temperature decreased the log $\sigma$ against $(1000/T)$ plot gives a shallower slope with a lower $\sigma_0$ and $E_a$ consistent with hopping conduction in a level of localised states situated in the mobility gap [5,8]. The activation energy was found to increase from 0.145 to 0.254 eV with the increasing hydrogen concentration, as shown in Table 7.2. Dutta et al. [2] also reported a similar increase in $E_a$ from 0.45 to 0.55 eV when $P_H$ was increased from 0 to 0.4 Pa. Therefore, the incorporation of hydrogen into the film satisfies the dangling bonds and makes the random network more complete thereby lowering conductivity and increasing activation energy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N_{Si-H} (x10^{21} cm^{-3})</th>
<th>$\sigma$ ($\Omega^{-1} cm^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>-</td>
<td>2.76 x 10^{-6}</td>
<td>0.145</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.93</td>
<td>5.05 x 10^{-7}</td>
<td>0.218</td>
</tr>
<tr>
<td>rfh10</td>
<td>1.10</td>
<td>3.86 x 10^{-8}</td>
<td>0.254</td>
</tr>
</tbody>
</table>
Figure 7.5  Log conductivity versus (1000/T) plot of samples rfh0, rfh5 and rfh10.
7.1.1.2 Conduction Mechanism

There exist very few reports on the conduction mechanism in amorphous silicon carbide. Most of the reports are on their crystalline counterparts. To determine the conduction mechanism, the current-voltage characteristics of the film need to be analyzed first. Figure 7.7(a) to (c) shows the log scale current against voltage as a function of ambient temperature for samples rfh0, rfh5 and rfh10 respectively. It can be seen that there are clear differences between rfh0 sample and rfh5 and rfh10 samples for the low voltage region at $250 \, K < T < 300 \, K$. At low forward bias, the current-voltage characteristics for sample rfh5 and rfh10 exhibits a shoulder, which is not apparent in sample rfh0. This is because the current is in excess of the ideal diode current. The origin of this excess current shall be investigated shortly. Looking at Figures 7.7(b) and (c), it was observed that as the ambient temperature increases above room temperature, the shoulder gradually disappears and the current-voltage characteristics behaves like a typical diode like that of sample rfh0. This implies that there are two different mechanisms at play here for samples rfh5 and rfh10. One that manifests itself at lower bias and at temperatures lower than room temperature [6] and the other at higher bias regardless of temperature.

From Figures 7.7(a) to (c), the linear segment of the forward current (region I) may be described as

$$I = I_S \exp \left(\frac{qV}{\eta kT}\right) \quad (7.1)$$

where $I_S$ is the saturation current determined by extrapolating the linear region to zero bias, $\eta$ is the ideality factor, and $k$ is the Boltzmann constant.
$I_S$ can be expressed as $I_S \sim \exp (-\Delta E_{AS} / kT)$. The activation energy $\Delta E_{AS}$, as obtained from the Arrhenius plot of Figure 7.8 are presented in Table 7.3.

Table 7.3: Density of Si-H bonds and the activation energy $\Delta E_{AS}$ and $\Delta E_{AF}$ and barrier height $\Phi_B$ of as-prepared rfh films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{Si-H}$ (x10$^{21}$ cm$^{-3}$)</th>
<th>$\Delta E_{AS}$ (eV)</th>
<th>$\Phi_B$ (eV)</th>
<th>$\Delta E_{AF}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>-</td>
<td>0.542</td>
<td>0.494</td>
<td>-</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.93</td>
<td>0.683</td>
<td>0.634</td>
<td>0.303</td>
</tr>
<tr>
<td>rfh10</td>
<td>1.10</td>
<td>0.424</td>
<td>0.376</td>
<td>0.325</td>
</tr>
</tbody>
</table>

Figure 7.9 shows the plot of log $I_S / T^2$ against 1000/T for the rfh sample. By calculating the gradient of the graph, the barrier height of the SiC:H-Si heterojunction is determined. As can be seen, the activation energy $\Delta E_{AS}$ is slightly higher than the barrier height $\Phi_B$. Therefore, the activation energy $\Delta E_{AS}$ might be due to the barrier height of the heterojunction. This indicates that the linear region (region I) of the forward current is dominated by the thermionic emission of carriers over the barrier height $\Phi_B$.

At lower current (region II) and temperature (below 300 K), the heterojunction current can be expressed as $I_O \exp (BV)$, where $I_O \sim \exp (-\Delta E_{AF} / kT)$ and $B = 16$ V$^{-1}$ is a constant independent of temperature. Figure 7.10 shows a plot of log $I_O$ against 1000/T. $I_O$ is determined by extrapolating the low current region to zero bias. The value of the activation energy $\Delta E_{AF}$ as determined from the figure is presented in Table 7.3. The exponential dependence of $I_O$ on $-1/T$ indicates that the current may be described by the multitunneling capture–emission (MTCE) model [11] as presented in Figure 7.6 below.
In the MTCE model, under forward bias, a hole in the valence band of the crystalline p type c-Si flows from one localized state to another in the band gap of a-SiC:H located at $E_T = E_V + 0.303$ eV or $E_T = E_V + 0.325$ eV, followed by the subsequent emission of these holes from $E_T$ to the valence band of a-SiC:H. This multitunneling process continues until the rate of hole release into the valence band or of recombination with an electron in the conduction band becomes greater than the tunneling rate.

At higher forward bias, the current-voltage characteristics of all the rfh samples deviate from linearity. This is due to the series resistance associated with the contacts [6,11]. Other investigations were done to determine whether other mechanisms were at play at higher fields like poole-frenkel or schottky. However, the results were not conclusive and did not yield any positive answers.
Figure 7.7(a) Log current versus voltage characteristics of rfh0 sample as a function of ambient temperature.
Figure 7.7(b) Log current versus voltage characteristics of rfh5 sample as a function of ambient temperature.
Figure 7.7(c) Log current versus voltage characteristics of rfh10 sample as a function of ambient temperature.
Figure 7.8 Log $I_s$ against (1000/T) plot for rfh samples.
Figure 7.9 Log $I_s / T^2$ against $(1000/T)$ plot for rfh samples.
Figure 7.10  Log $I_0$ against $(1000/T)$ plot for rfh samples.
7.1.2 Rfp Samples

A plot of log I against V for the rfp samples is shown in Figure 7.11. It can be seen that for the samples prepared at lower pressures, the 2 region characteristics of the I-V curve can be observed with rfp15 sample having the more prominent feature. As mentioned earlier for the rfh samples, this shows that there are two distinct transport mechanisms in the low field region. Table 7.4 lists the d.c. conductivity (\(\sigma\)), saturation current (\(I_S\)) and the ideality factor (\(n\)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>D.C. Conductivity ((\Omega^{-1} \text{ cm}^{-1}))</th>
<th>Saturation Current ((\text{A}))</th>
<th>Ideality Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>6.18 x 10^{-7}</td>
<td>1.38 x 10^{-9}</td>
<td>1.32</td>
</tr>
<tr>
<td>rfp15</td>
<td>3.39 x 10^{-7}</td>
<td>2.95 x 10^{-9}</td>
<td>1.58</td>
</tr>
<tr>
<td>rfp25</td>
<td>1.61 x 10^{-7}</td>
<td>3.34 x 10^{-9}</td>
<td>1.18</td>
</tr>
</tbody>
</table>

The room temperature d.c. conductivity (\(\sigma\)) of the samples were obtained from the low field region using the relation \(\sigma = l I/AV\), where \(l\) and \(A\) are the thickness of the film and the area of the metal contact. The results showed that as chamber pressure increases, the conductivity decreases from 6.18 x 10^{-7} to 1.61 x 10^{-7} \(\Omega^{-1} \text{ cm}^{-1}\). This is expected as the magnitude of the current decreases as shown in Figure 7.11. The reduction in conductivity is not as drastic compared to that of the rfh samples. This could be due to the fact that increasing the chamber pressure (\(P_S\)) is not as effective in introducing hydrogen into the film as compared to increasing the hydrogen partial pressure (\(P_H\)). Another point to note is that the change in pressure is quite small and it may require a much larger change in \(P_S\) to have the same effect as changing \(P_H\). As
suggested earlier, $\sigma$ is related to the amount of hydrogen present in the film. From the IR results of Chapter 5, it was observed that as chamber pressure ($P_S$) increases, more hydrogen is incorporated into the film. Therefore, $\sigma$ decreases as $N_{Si-H}$ increases, an observation similar to the rfh samples.

The saturation current does not change much due to the fact that the current magnitude only reduces by a small amount when $P_S$ is increased. The ideality factor $\eta$ too does not change much. An interesting point to note is that as the shoulder in the I-V curve becomes more distinct, the ideality factor would increase. In general, the value is low and quite close to unity and from the analysis of the rfh samples, this is an indication that the current is dominated by the injection of carriers over the barrier rather than the recombination of carriers at the SiC/Si interface [4]. This will be proven later in the chapter.
Figure 7.11. Log scale current versus voltage characteristics of r.f. sputtered a-SiC:H films prepared under different chamber pressures.
7.1.2.1 Temperature Dependence of Conductivity

The behaviour of the current as a function of temperature for the rfp samples is similar to that of the rfh samples in that as the ambient temperature increases, the current magnitude increases for samples rfp08, rfp15 and rfp25. This is verified by Figures 7.12(a) to (c). An interesting point to note is that at very high ambient temperature of about 440K, the I-V characteristics begin to change. This happens to all the rfp samples. This phenomena, however, was not observed for the rfh samples from Figures 7.4(a) to (c). To investigate the temperature dependence of conductivity, the current was measured at different ambient temperatures ranging from 250 K to 440 K. The conductivity was then obtained and plotted against \((1000/T)\).

Figure 7.13 shows the log conductivity against \((1000/T)\) plots of samples rfp08, rfp15 and rfp25. By increasing the chamber pressure \(P_S\), more hydrogen is introduced into the film as mentioned in Chapter 5. This will lead to a lower conductivity value. Similar to what was observed for the rfh samples in Figure 7.5, as the temperature decreased the log \(\sigma\) against \((1000/T)\) plot gives a shallower slope with a lower \(\sigma_0\) and \(E_a\) consistent with hopping conduction in a level of localised states situated in the mobility gap [5,8]. As described earlier, the activation energy \(E_a\) is derived from the high temperature slope of the plot. The activation energy was found to increase from 0.202 to 0.280 eV with increasing hydrogen concentration, as shown in Table 7.5. This is consistent with the results of the rfh samples. Therefore, in general, it can be concluded that with the incorporation of hydrogen into the film, the dangling bonds are passivated leading to a more complete network thereby lowering conductivity and increasing activation energy.
Figure 7.12(a) Current versus voltage characteristics of rfp08 sample as a function of ambient temperature.
Figure 7.12(b) Current versus voltage characteristics of rfp15 sample as a function of ambient temperature.
Figure 7.12(c) Current versus voltage characteristics of rfp15 sample as a function of ambient temperature.
Figure 7.13 Log conductivity versus (1000/T) plot of samples rfp08, rfp15 and rfp25.
Table 7.5  D.C. conductivity and activation energy of as-prepared rfp films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ ($\Omega^{-1} \text{cm}^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>$6.18 \times 10^{-7}$</td>
<td>0.202</td>
</tr>
<tr>
<td>rfp15</td>
<td>$3.39 \times 10^{-7}$</td>
<td>0.249</td>
</tr>
<tr>
<td>rfp25</td>
<td>$1.61 \times 10^{-7}$</td>
<td>0.280</td>
</tr>
</tbody>
</table>

7.1.2.2  Conduction Mechanism

From Figures 7.14(a) to (c), the log scale current against voltage plots resembles that of the rfh samples. Samples rfp08 and rfp15 exhibits the two regions that were mentioned in Section 7.1.1.2. The observations were very similar and the behaviour of the I-V characteristics were identical as the ambient temperature increases, i.e. the shoulder gradually disappears as the temperature increases. The analysis of the I-V characteristics has been presented in section 7.1.1.2, therefore only the results will be presented here.

Table 7.6  Density of Si-H bonds and the activation energy $\Delta E_{AS}$ and $\Delta E_{AF}$ and barrier height $\Phi_B$ of as-prepared rfp films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_{AS}$ (eV)</th>
<th>$\Phi_B$ (eV)</th>
<th>$\Delta E_{AF}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>0.625</td>
<td>0.575</td>
<td>0.566</td>
</tr>
<tr>
<td>rfp15</td>
<td>0.567</td>
<td>0.517</td>
<td>0.343</td>
</tr>
<tr>
<td>rfp25</td>
<td>0.473</td>
<td>0.424</td>
<td>-</td>
</tr>
</tbody>
</table>

The transport mechanism for samples rfp08 and rfp15 follow that of sample rfh05 and rfh10. At region I, the forward current is dominated by the thermionic emission of carriers over the barrier height $\Phi_B$. And at region II, the current is described by the
multitunneling capture-emission (MTCE) model [11] depicted in Figure 7.6. For the rfp samples, in the MTCE model, a hole in the valence band of the crystalline p type silicon flows from one localised state to another in the band gap of a-SiC:H located at \( E_T = E_V + 0.566 \text{ eV} \) or \( E_T = E_V + 0.543 \text{ eV} \), followed by the subsequent emission of these holes from \( E_T \) to the valence band. At higher voltages, the current-voltage curves of all rfp samples deviate from linearity, like those of the rfh samples.

One point to note is that for rfp25 sample, there exist only 1 region in the low field I-V curve. From the observation, it would seem that as \( P_S \) increases (rfp08 and rfp15), the 2 region characteristics becomes more prominent. However, this is not the case for rfp25.
Figure 7.14(a) Log current versus voltage characteristics of rfp08 sample as a function of ambient temperature.
Figure 7.14(b) Log current versus voltage characteristics of rfp15 sample as a function of ambient temperature.
Figure 7.14(c) Log current versus voltage characteristics of rfp25 sample as a function of ambient temperature.
Figure 7.15  Log $I_s$ against (1000/T) plot for rfp samples.
Figure 7.16 Log $I_s / T^2$ against $(1000/T)$ plot for rfp samples.
Figure 7.17 Log $I_0$ against (1000/T) plot for rfp samples.
7.2 Capacitance-Voltage Characteristics of As-Deposited Films

In this section, the results of the $C-V$ experiments will be presented. The $C-V$ measurements were carried out with the voltage swept from 0 to -5 V and then back from -5 to 5 V in steps of 0.2 V. The $C-V$ characteristics of the rfh5 and rfp15 samples are shown in Figure 7.18 and 7.19 respectively and these are representative results for all our samples (See Appendix). The $C-V$ curve can be described in terms of the accumulation, depletion and deep depletion regions. The existence of the deep depletion region is due to our relatively leaky film, which prevents the formation of an inversion layer. As a result, a further increase in the gate charge can only be balanced by an increase in the depletion layer width, causing the capacitance to decrease below its minimum value in depletion. Note that no hysterisis was observed in the $C-V$ measurements.

7.2.1 Rfh Samples

The dielectric constant ($\varepsilon$) of the films was calculated from the accumulation capacitance using the equation $C = \varepsilon \varepsilon_0 A/d$ where $\varepsilon_0$ is the permittivity of free space, $A$ is the area of the metal contact and $d$ is the thickness of the film deposited. The results are listed in Table 7.7. $\varepsilon$ of the as-deposited films decreases from 13.5 to 11.4 to 11.1 as $P_H$ increases from 0 to 0.3 Pa. The incorporation of hydrogen is seen to reduce the dielectric constant of the film. As the hydrogen content of the film increases, Choi et al. [9] observed that both the refractive index and the density of the film decreases. This relationship between density (and thus refractive index) and hydrogen content was also observed by Guivarc’h et al. [10] for their reactive sputtered films. This may be due to the terminating property of hydrogen, which reduces the compactness of the
films, thus resulting in a lower density. The relationship between the refractive index $n$ and the dielectric constant $\varepsilon$ is given by the following equation $n = \sqrt{\varepsilon}$. Therefore, with the reduction of the refractive index as $P_H$ increases, the dielectric constant of the film will decrease as seen from the above results.

### 7.2.2 Rfp Samples

The dielectric constant ($\varepsilon$) of the rfp samples are listed in Table 7.8. It was observed that as $P_S$ increases, $\varepsilon$ decreases from 14.5 to 10.8. This observation is similar to that of the rfh samples and is due to the properties of hydrogen when incorporated into the film. The same explanation applies to the rfp samples (section 7.2.1).
Figure 7.18  The capacitance-voltage characteristic of rfh5 sample.
Figure 7.19  The capacitance-voltage characteristic of rfp15 sample.
7.3 Interface Trap Density of As-Deposited Films

In this section, the interface trap density of the Al-a-SiC:H-Si structure will be investigated. Prior to obtaining the interface trap density, the capacitance (conductance) – frequency, \(C(G) - f\), measurements need to be carried out. The frequency of the \(C(G) - f\) experiments was swept from 100 Hz to 10 MHz with bias varied from depletion to weak inversion region.

From the conductance method [12], the relationship between the parallel conductance \((G_p)\) and the interface trapped density \((D_{it})\) of the Al-a-SiC:H-Si structure can be expressed as

\[
\frac{G_p}{\omega} = \frac{qAD_{it}}{2\omega\tau} \ln(1 + \omega^2 \tau^2)
\]  

(7.2)

where \(\omega = 2\pi f\) \((f = \text{measurement frequency})\) and \(\tau\) is the interface trap time constant.

The \(D_{it}\) value can then be determined from the peak value of a \(G_p/\omega\) vs \(\omega\) plot as

\[
D_{it} = \left(\frac{G_p}{\omega}\right)_{\text{max}} \frac{2.5}{Aq}
\]

(7.3)

Note that the influence of the series resistance of the silicon substrate has been taken into account in our calculation of \(G_p/\omega\). The \(G_p/\omega\) was obtained as a function of frequency from 100 Hz to 10 MHz. The applied voltage was varied to bias the MIS capacitor into region of depletion and weak inversion. This enables us to determine the interface trap density at different energy levels in the silicon band gap. A typical \(G_p/\omega\) against \(\omega\) plot is shown in Figure 7.20 for the sample rfh5 (See Appendix for the rest of the samples). It can be seen that the peaks shift along the \(\omega\) axis as a function of
applied bias. The interface trap density ($D_{it}$) was obtained from the conductance peak using equation (7.3).

### 7.3.1 Rfh Samples

The interface trap density as a function of energy level in the band gap for the rfh samples are shown in Figure 7.21. It was observed that increasing $P_H$ from 0 (rfh0) to 0.15 Pa (rfh15) reduces $D_{it}$ from $4.5 \times 10^{12}$ to $4.5 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$. The $D_{it}$ values are taken at midgap throughout this work. Harjono et al. [13] reported a $D_{it}$ value of $10^{11}$ - $10^{12}$ cm$^{-2}$ eV$^{-1}$ for their Al/undoped a-SiC/Si structures. The a-SiC in this case was deposited by the plasma enhanced chemical vapour deposition (CVD) method.

Note that in Table 7.7, $N_{Si-H}$ increases as $P_H$ (rfh series) increases. This means that the number of silicon dangling bonds decreases as a result of an increase $P_H$ due to the fact that the hydrogen atoms have passivated the silicon dangling bonds. Although the results obtained from the IR spectroscopy is for the bulk, the overall reduction of the silicon dangling bonds should also include that at the interface, and this should lead to a decrease in $D_{it}$. This agrees well with the $D_{it}$ results obtained for the rfh samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{Si-H}$ (x10$^{21}$ cm$^{-3}$)</th>
<th>$\varepsilon$</th>
<th>$D_{it}$ (x10$^{11}$ eV$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>-</td>
<td>13.5</td>
<td>45.0</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.93</td>
<td>11.4</td>
<td>5.0</td>
</tr>
<tr>
<td>rfh10</td>
<td>1.10</td>
<td>11.1</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Figure 7.20  The $\frac{G_p}{\omega}$ as a function of frequency at different applied biases for rfh5 sample.
Figure 7.21 Interface trap density as a function of energy level in the silicon band gap for samples prepared under different hydrogen partial pressures.
7.3.2 Rfp Samples

Figure 7.22 shows that increasing $P_S$ from 0.8 to 2 Pa generally reduces $D_{it}$. For rfp08 and rfp15, $D_{it}$ decreases monotonously from about 9 to $5 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$. For rfp20, $D_{it}$ remains fairly constant at $5 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$.

Note that in Table 7.7, $N_{Si-H}$ increases as $P_H$ (rfh series) increases, likewise for the rfp series as mentioned in Chapter Five. This means that the number of silicon dangling bonds decreases as a result of an increase in $P_S$ or $P_H$, and this should lead to a decrease in $D_{it}$. This agrees well with the $D_{it}$ results for the rfp and rfh samples. It is interesting to note that as more hydrogen in introduced into the film during deposition, the overall reduction in $D_{it}$ decreases.

Table 7.8 Dielectric constant and interface trap density of as-prepared rfp films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon$</th>
<th>$D_{it}$ (x10$^{11}$ eV$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>14.5</td>
<td>8.8</td>
</tr>
<tr>
<td>rfp15</td>
<td>11.6</td>
<td>7.2</td>
</tr>
<tr>
<td>rfp20</td>
<td>11.4</td>
<td>5.3</td>
</tr>
<tr>
<td>rfp25</td>
<td>10.8</td>
<td>5.1</td>
</tr>
</tbody>
</table>
Figure 7.22  The $G_p/\omega$ as a function of frequency at different applied biases for rfp20 sample.
Figure 7.23  Interface trap density as a function of energy level in the silicon band gap for samples prepared under different chamber pressures.
7.4 Current-Voltage Characteristics of Annealed Films

The current-voltage characteristics of the Al/a-SiC:H/Si structure of the rfh and rfp series of samples after annealing are shown in Figures 7.24 (a) - (c) and Figures 7.30 (a) – (c) respectively. It was observed that, in general, the current magnitude decreases as annealing temperature increases. In section 7.1, it was said that the current is related to the number of dangling bonds in the films and this has a close relationship with the Si-H bonds. From the IR spectroscopy results of the annealed films, it was observed that the density of the Si-H bonds decreases as the annealing temperature increases for the hydrogenated samples. At the same time, there is an increase in the density of Si-C bonds for all samples. The dissociation of the Si-H bonds leads to the formation of more Si-C bonds and this in turn will result in the decrease in the number dangling bonds in the film. Thus, as the number of dangling bond decreases, less current will flow through the film. Referring to the results in Table 5.5 and 5.7 in Chapter five, as annealing temperature increases $N_{\text{Si-H}}$ decreases while $N_{\text{Si-C}}$ increases by a greater amount and this will reduce the number of dangling bonds. Although the number of Si-H bonds is too small to be detected for the rfp samples, the Si-C bonds increases as a result of annealing. Thus, as there is less dangling bonds available for electrical conduction, the current magnitude will be less after annealing.

7.4.1 Rfh Samples

The graph of log I against V is shown in Figure 7.25. As with the as deposited samples, there are at least 2 distinct regions in the I-V characteristics. This can be classified into the low and high field regions. It is interesting to note that for sample
Figure 7.24(a) Current versus voltage characteristics of rfh0 sample annealed at temperatures 400, 600 and 800°C.
Figure 7.24(b) Current versus voltage characteristics of rfh5 sample annealed at temperatures 400 and 600°C.
Figure 7.24(c) Current versus voltage characteristics of rfh10 sample annealed at temperatures 400 and 600°C.
rfh04, there is an extra shoulder in the I-V curve in the low field region after annealing at 400 °C.

This is similar to what was observed in the rfh5 and rfh10 samples in Section 7.1.1. This shows that there is a change in the transport mechanism after annealing in the low field region, from thermionic emission over a potential barrier to a combination of both multi-tunneling capture emission (MTCE) and conduction over a potential barrier. However, after annealing at 600 and 800 °C, the shoulder disappears. The same behaviour also manifests itself for the RTA samples except that the annealing temperature is higher with rfh06A sample showing a similar profile to that of rfh04 after annealing. For the rfh5 and rfh10 samples, it was also observed that annealing causes some changes in the transport mechanism in that the extra shoulder in the low field region disappears after annealing. Similar observation was made for the rfh56A sample. However, for the rfh106A sample, there seems to be drastic change in the I-V characteristic in that the shoulder is more prominent and the curve appears to be stretched out along the voltage-axis as the extra shoulder appears at a higher voltage.

From the figure, the d.c. conductivity ($\sigma$), saturation current ($I_S$) and the ideality factor ($n$) can be obtained as mentioned in Chapter 3 and are listed in Table 7.9. Annealing causes $\sigma$ to reduce in all the RTA and furnace annealed films, and the reduction in $\sigma$ is larger for films prepared at higher $P_H$ values. It is interesting to note that the reduction in $\sigma$ is generally less in the RTA samples compared to the furnace annealed samples. The bigger reduction in $\sigma$ for the furnace annealed films may be due to the longer annealing time used in such annealing process. The saturation current and the ideality factor were observed to decrease after annealing except for rfh106 sample where the
values increase after annealing at 600 °C. Similar to the furnace annealed sample, rfh106A sample also showed major changes after annealing. Both saturation current and ideality factor increases and are both higher than the as-deposited rfh10 sample. Also note that for the unhydrogenated sample rfh04 and rfh06A, the ideality factor increases. This change coincides with the change in the I-V characteristics as observed in figure 7.25(a) and 7.26(a).

There are several interesting observations from the above results. First of all, it can be concluded that furnace annealing causes a greater reduction in current as compared to RTA, possibly due to the longer furnace annealing time. Furnace annealing and RTA both causes similar changes in the I-V characteristics although for rfh10 sample, the changes were different after furnace anneal and RTA at 600 °C. One hypothesis that can be made is that as the hydrogen content increases in the films, the quick ramp up and ramp down process of the RTA causes different changes to the structure of the film to that of the relatively slower heat treatment of furnace anneal. This change may be at the interface and/or to the bulk of the film.
Table 7.9  D.C. Conductivity, saturation current ($I_s$), and ideality factor of as-prepared and annealed rfh films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D.C. Conductivity ($\Omega^{-1}cm^{-1}$)</th>
<th>Saturation Current (A)</th>
<th>Ideality Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>$2.76 \times 10^{-6}$</td>
<td>$5.85 \times 10^{-8}$</td>
<td>1.11</td>
</tr>
<tr>
<td>rfh04</td>
<td>$5.64 \times 10^{-7}$</td>
<td>$8.03 \times 10^{-9}$</td>
<td>3.37</td>
</tr>
<tr>
<td>rfh06</td>
<td>$1.07 \times 10^{-7}$</td>
<td>$1.99 \times 10^{-9}$</td>
<td>1.04</td>
</tr>
<tr>
<td>rfh06A</td>
<td>$1.41 \times 10^{-7}$</td>
<td>$1.63 \times 10^{-8}$</td>
<td>3.74</td>
</tr>
<tr>
<td>rfh08</td>
<td>$1.73 \times 10^{-8}$</td>
<td>$4.53 \times 10^{-10}$</td>
<td>1.01</td>
</tr>
<tr>
<td>rfh08A</td>
<td>$1.24 \times 10^{-7}$</td>
<td>$1.32 \times 10^{-8}$</td>
<td>0.87</td>
</tr>
<tr>
<td>rfh5</td>
<td>$5.05 \times 10^{-7}$</td>
<td>$2.52 \times 10^{-9}$</td>
<td>1.44</td>
</tr>
<tr>
<td>rfh54</td>
<td>$2.55 \times 10^{-8}$</td>
<td>$5.57 \times 10^{-10}$</td>
<td>1.22</td>
</tr>
<tr>
<td>rfh56</td>
<td>$7.94 \times 10^{-9}$</td>
<td>$4.15 \times 10^{-10}$</td>
<td>1.07</td>
</tr>
<tr>
<td>rfh56A</td>
<td>$1.42 \times 10^{-8}$</td>
<td>$1.04 \times 10^{-9}$</td>
<td>1.16</td>
</tr>
<tr>
<td>rfh10</td>
<td>$3.86 \times 10^{-8}$</td>
<td>$1.65 \times 10^{-8}$</td>
<td>3.33</td>
</tr>
<tr>
<td>rfh104</td>
<td>$4.14 \times 10^{-9}$</td>
<td>$8.24 \times 10^{-10}$</td>
<td>1.82</td>
</tr>
<tr>
<td>rfh106</td>
<td>$3.13 \times 10^{-9}$</td>
<td>$1.45 \times 10^{-9}$</td>
<td>2.01</td>
</tr>
<tr>
<td>rfh106A</td>
<td>$2.99 \times 10^{-8}$</td>
<td>$3.06 \times 10^{-8}$</td>
<td>11.18</td>
</tr>
</tbody>
</table>
Figure 7.25(a) Log current versus voltage characteristics of rfh0 sample annealed at temperatures 400, 600 and 800°C.
Figure 7.25(b) Log current versus voltage characteristics of rfh5 sample annealed at temperatures 400 and 600°C.
Figure 7.25(c) Log current versus voltage characteristics of rfh10 sample annealed at temperatures 400 and 600°C.
Figure 7.26(a) Log current versus voltage characteristics of rfh0 sample RTA at temperatures 600 and 800°C.
Figure 7.26(b) Log current versus voltage characteristics of rfh5 sample RTA at temperature 600°C.
Figure 7.26(c) Log current versus voltage characteristics of rfh10 sample RTA at temperature 600°C.
7.4.1.1 Temperature Dependence of Conductivity

Figure 7.28 shows a typical current against voltage characteristic for the samples as a function of ambient temperature. Similar to what was observed with the as-deposited samples, the current increases with ambient temperature. Figures 7.28(a) to (c) shows the log conductivity against (1000/T) plot of samples rfh0, rfh5 and rfh10 after furnace annealing at different temperatures. Plots for the samples after RTA are shown in figures 7.29(a) to (c). The activation energies obtained from the plots are listed in Table 7.10. The activation energy was found to increase after annealing at 400 °C for the hydrogenated samples. However, after annealing at 600 °C, the activation energy was found to remain relatively constant (rfh56) or decrease (rfh106). For the unhydrogenated sample, the activation energy actually decreases from 0.145 to 0.135 eV after 400 °C annealing. This may be due to the change in the I-V characteristics as shown in Figure 7.25(a). The value then increases to 0.171 eV before reaching a value of 0.099 eV after 800 °C annealing. This value is even lower than the as-deposited sample rfh0. It was observed that for rfh08 sample, the increase in the ambient temperature produces less of an increase in the current as compared to the rest of the samples. It would seem that annealing the unhydrogenated film at a temperature as high as 800 °C causes the film to be less sensitive to changes in temperature.

For the samples that have undergone through the RTA process, the most interesting result must be that of the rfh06A and rfh08A samples. Looking at Figure 7.29(a), it can be seen that the conductivity against (1000/T) plot is different from that of the furnace annealed sample. There are more than 2 regions and this is only limited to the unhydrogenated samples. The rfh106A also showed different results in that the activation energy decreases after annealing to a value lower than that of the as-deposited rfh10 sample. This may be due to the change in the I-V characteristics after
RTA as shown in Figure 7.26(c). This result may lead to the conclusion that RTA of unhydrogenated and hydrogenated films causes different effects altogether and that hydrogen plays an important role in the properties of the films during annealing.

Table 7.10 Density of Si-H bonds, d.c. conductivity and activation energy of as-prepared and annealed rfh films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{\text{Si-H}}$ (x10$^{21}$ cm$^{-3}$)</th>
<th>$\sigma$ ($\Omega^{-1}$cm$^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>-</td>
<td>2.76 x 10$^{-6}$</td>
<td>0.145</td>
</tr>
<tr>
<td>rfh04</td>
<td>-</td>
<td>5.64 x 10$^{-7}$</td>
<td>0.135</td>
</tr>
<tr>
<td>rfh06</td>
<td>-</td>
<td>1.07 x 10$^{-7}$</td>
<td>0.171</td>
</tr>
<tr>
<td>rfh06A</td>
<td>-</td>
<td>1.41 x 10$^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>rfh08</td>
<td>-</td>
<td>1.73 x 10$^{-8}$</td>
<td>0.099</td>
</tr>
<tr>
<td>rfh08A</td>
<td>-</td>
<td>1.24 x 10$^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.93</td>
<td>5.05 x 10$^{-7}$</td>
<td>0.218</td>
</tr>
<tr>
<td>rfh54</td>
<td>0.64</td>
<td>2.55 x 10$^{-8}$</td>
<td>0.235</td>
</tr>
<tr>
<td>rfh56</td>
<td>0.46</td>
<td>7.94 x 10$^{-9}$</td>
<td>0.233</td>
</tr>
<tr>
<td>rfh56A</td>
<td>-</td>
<td>1.42 x 10$^{-8}$</td>
<td>0.238</td>
</tr>
<tr>
<td>rfh10</td>
<td>1.10</td>
<td>3.86 x 10$^{-8}$</td>
<td>0.254</td>
</tr>
<tr>
<td>rfh104</td>
<td>0.68</td>
<td>4.14 x 10$^{-9}$</td>
<td>0.264</td>
</tr>
<tr>
<td>rfh106</td>
<td>0.55</td>
<td>3.13 x 10$^{-9}$</td>
<td>0.257</td>
</tr>
<tr>
<td>rfh106A</td>
<td>0.63</td>
<td>2.99 x 10$^{-8}$</td>
<td>0.207</td>
</tr>
</tbody>
</table>
Figure 7.27.  Current versus voltage characteristics of rfh04 sample as a function of ambient temperature.
Figure 7.28(a) Log conductivity versus (1000/T) plot of sample rfh0 annealed at temperatures 400, 600 and 800 °C.
Figure 7.28(b) Log conductivity versus (1000/T) plot of sample rfh5 annealed at temperatures 400 and 600 °C.
Figure 7.28(c) Log conductivity versus (1000/T) plot of sample rfh10 annealed at temperatures 400 and 600 °C.
Figure 7.29(a) Log conductivity versus (1000/T) plot of sample rfh0 RTA at temperatures 600 and 800 °C.
Figure 7.29(b) Log conductivity versus \((1000/T)\) plot of sample rfh5 RTA at temperature 600 °C.
Figure 7.29(c) Log conductivity versus (1000/T) plot of sample rfh10 RTA at temperature 600 °C.
7.4.2 Rfp Samples

The graph of log I against V is depicted in Figures 7.31(a) – (c). There are basically at least 2 distinct regions in the I-V characteristics, the low and the high field regions. For the rfp08 sample, the extra shoulder in the low field region becomes more distinct after annealing at 400 and 600 °C. However, after annealing at 800 °C, the extra shoulder disappears. Similar behaviour was also observed for the rfp15 sample although the extra shoulder still remains after 800 °C annealing. For the rfp25 sample, the I-V curve appears to be stretched out along the voltage-axis with no visible extra shoulder in the low field region. There is a change in the transport mechanism in the low field region from the combination of multi-tunneling capture emission model (MTCE) and emission of electron over a potential barrier to that of only a single mechanism after high temperature annealing for rfp08 sample.

The d.c. conductivity (σ), saturation current (I_S) and the ideality factor (n) can be obtained from Figures 7.31(a) to (c) as mentioned in Chapter 3 and are listed in Table 7.11. Annealing causes σ to reduce in all the annealed films, and the reduction in σ is larger for films prepared at higher P_S values, that is to say, there is more hydrogen incorporated into the films. The saturation current and the ideality factor were observed to increase when the extra shoulder in the low field region gets more prominent and decreases if the shoulder disappears. This was observed for rfp08 and rfp15 samples. After annealing at 800 °C, the ideality factor and the saturation current decreases for rfp08 sample. This occurs as the extra shoulder disappears. Similar trend was observed for rfp15 sample. This change coincides with the change in the I-V characteristics, which leads to a change in the conduction mechanism. However, for
the rfp25 samples with no visible extra shoulder, the saturation current decreases after annealing while the ideality factor increases slightly.

In Section 7.4.1, it was observed that the ideality factor of the rfh5 sample changes only slightly after annealing. For the rfh10 sample, the changes were more significant. From the rfp series of samples, the ideality factor of the rfp25 sample changes the least as can be seen in Table 7.11. There seem to be a certain level of hydrogen concentration (5%) in the sputtered film that the I-V characteristics is relatively stable to heat treatment.
Figure 7.30(a) Current versus voltage characteristics of rfp08 sample annealed at temperatures 400, 600 and 800 °C.
Figure 7.30(b) Current versus voltage characteristics of rfp15 sample annealed at temperatures 400, 600 and 800 °C.
Figure 7.30(c) Current versus voltage characteristics of rfp25 sample annealed at temperatures 400 and 600 °C.
Table 7.11  D.C. Conductivity, saturation current ($I_s$), and ideality factor of as-prepared and annealed rfp films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D.C. Conductivity ($\Omega^{-1}$cm$^{-1}$)</th>
<th>Saturation Current (A)</th>
<th>Ideality Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>$6.18 \times 10^{-7}$</td>
<td>$1.38 \times 10^{-9}$</td>
<td>1.32</td>
</tr>
<tr>
<td>rfp084</td>
<td>$1.33 \times 10^{-8}$</td>
<td>$5.58 \times 10^{-9}$</td>
<td>2.01</td>
</tr>
<tr>
<td>rfp086</td>
<td>$1.01 \times 10^{-8}$</td>
<td>$1.14 \times 10^{-8}$</td>
<td>3.10</td>
</tr>
<tr>
<td>rfp088</td>
<td>$5.10 \times 10^{-10}$</td>
<td>$1.01 \times 10^{-9}$</td>
<td>2.73</td>
</tr>
<tr>
<td>rfp15</td>
<td>$3.39 \times 10^{-7}$</td>
<td>$2.95 \times 10^{-9}$</td>
<td>1.58</td>
</tr>
<tr>
<td>rfp154</td>
<td>$2.96 \times 10^{-9}$</td>
<td>$3.64 \times 10^{-8}$</td>
<td>6.51</td>
</tr>
<tr>
<td>rfp156</td>
<td>$9.83 \times 10^{-10}$</td>
<td>$2.37 \times 10^{-9}$</td>
<td>2.68</td>
</tr>
<tr>
<td>rfp158</td>
<td>$2.45 \times 10^{-10}$</td>
<td>$6.73 \times 10^{-9}$</td>
<td>8.54</td>
</tr>
<tr>
<td>rfp25</td>
<td>$1.61 \times 10^{-7}$</td>
<td>$3.34 \times 10^{-9}$</td>
<td>1.18</td>
</tr>
<tr>
<td>rfp254</td>
<td>$1.49 \times 10^{-9}$</td>
<td>$5.99 \times 10^{-10}$</td>
<td>1.86</td>
</tr>
<tr>
<td>rfp256</td>
<td>$4.09 \times 10^{-10}$</td>
<td>$1.94 \times 10^{-10}$</td>
<td>2.01</td>
</tr>
</tbody>
</table>
Figure 7.31(a) Log current versus voltage characteristics of rfp08 sample annealed at temperatures 400, 600 and 800 °C.
Figure 7.31(b) Log current versus voltage characteristics of rfp15 sample annealed at temperatures 400, 600 and 800 °C.
Figure 7.31(c) Log current versus voltage characteristics of rfp25 sample annealed at temperatures 400 and 600 °C.
7.4.2.1 Temperature Dependence of Conductivity

Figure 7.32 shows a typical current against voltage characteristic for the samples as a function of ambient temperature. Similar to what was observed with the as-deposited samples, the current increases with ambient temperature. Figures 7.33(a) to (c) shows the log conductivity against \((1000/T)\) plot of samples rfp08, rfp15 and rfp25 after furnace annealing at different temperatures. The activation energies obtained from the plots are listed in Table 7.12. The activation energy was found to increase after annealing at 400 °C for both rfp08 and rfp15 samples. However, for the rfp25 sample, it was observed that the activation energy actually decreased after annealing at 400 °C. This may be due to the change in the I-V characteristics as shown in Figure 7.31(c). After annealing at 600 °C, the activation energy was found to decrease for rfp08 and rfp15 samples or remain relatively constant for rfp25 sample. It was observed that the activation energy is even lower than the as-deposited sample after annealing at 800 °C for samples rfp08 and rfp15. Thus, the increase in the ambient temperature produces less of an increase in the current and it would seem that annealing the film at a temperature as high as 800 °C causes the film to be less sensitive to changes in temperature.

The increase in annealing temperature causes a change in the structure of the rfp films. These samples contain much less hydrogen than that of the hydrogenated samples such that it could not be detected by IR spectroscopy. It was noted that for the rfp samples, annealing at 600 °C or more causes the activation energy to decrease. This shows that the film has become less sensitive to temperature changes. This behaviour was similar to the rfh0 sample as can be seen in section 7.4.1.1., and was not observed in the rfh5 and rfh10 samples which contains more hydrogen. Thus it would seem that annealing films that contain a higher hydrogen content exhibit different properties to films that
contain little or no hydrogen content. Another interesting point of observation is that
de E\textsubscript{a} of samples with about 5% hydrogen concentration tend to remain relatively
constant after heat treatment. See also Section 7.4.1. This point was also mentioned in
the previous section.

Table 7.12  D.C. conductivity and activation energy of as-prepared and annealed rfp
films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\sigma (,\Omega^{-1},\text{cm}^{-1}))</th>
<th>(E\textsubscript{a} (\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>(6.18 \times 10^{-7})</td>
<td>0.203</td>
</tr>
<tr>
<td>rfp084</td>
<td>(1.33 \times 10^{-8})</td>
<td>0.293</td>
</tr>
<tr>
<td>rfp086</td>
<td>(1.01 \times 10^{-8})</td>
<td>0.244</td>
</tr>
<tr>
<td>rfp088</td>
<td>(5.10 \times 10^{-10})</td>
<td>0.121</td>
</tr>
<tr>
<td>rfp15</td>
<td>(3.39 \times 10^{-7})</td>
<td>0.250</td>
</tr>
<tr>
<td>rfp154</td>
<td>(2.96 \times 10^{-9})</td>
<td>0.307</td>
</tr>
<tr>
<td>rfp156</td>
<td>(9.83 \times 10^{-10})</td>
<td>0.245</td>
</tr>
<tr>
<td>rfh158</td>
<td>(2.45 \times 10^{-10})</td>
<td>0.147</td>
</tr>
<tr>
<td>rfp25</td>
<td>(1.61 \times 10^{-7})</td>
<td>0.297</td>
</tr>
<tr>
<td>rfp254</td>
<td>(1.49 \times 10^{-9})</td>
<td>0.242</td>
</tr>
<tr>
<td>rfp256</td>
<td>(4.09 \times 10^{-10})</td>
<td>0.237</td>
</tr>
</tbody>
</table>
Figure 7.32. Current versus voltage characteristics of rfp154 sample as a function of ambient temperature.
Figure 7.33(a) Log conductivity versus (1000/T) plot of sample rfp08 annealed at temperatures 400, 600 and 800 °C.
Figure 7.33(b) Log conductivity versus $(1000/T)$ plot of sample rfp15 annealed at temperatures 400, 600 and 800 °C.
Figure 7.33(c) Log conductivity versus (1000/T) plot of sample rfp25 annealed at temperatures 400 and 600 °C.
7.5 Capacitance-Voltage Characteristics of Annealed Films

In this section, the results of the C-V experiments on the annealed films will be presented. Like in the as-deposited samples, the C-V curve can be described in terms of the accumulation, depletion and deep depletion regions. Figures 7.34 and 7.35 show the C-V characteristics of rfh5 and rfp15 samples after the annealing process. (See Appendix for the rest of the samples)

7.5.1 Rfh Samples

The results of the dielectric constant ε are shown in Table 7.14. From the table, it was observed that the dielectric constant ε of the films decreases after annealing. For the unhydrogenated sample (rfh0), annealing reduces ε from 13.5 to 10.6 (rfh06) and for the hydrogenated samples (rfh5 and rfh10), ε reduces from 11.4 to 8.8 (rfh56) and from 11.1 to 8.4 (rfh106). Similar reduction in ε can also be seen in the RTA samples. Note that the ε values of the annealed films are within the range quoted by Dutta et al. [2] and Davis et al. [12].

With reference to the as-deposited samples, it was noted that the decrease in ε was due to the fact that as hydrogen gets incorporated into the films, the density decreases due to the reduction in compactness of the film. However, for the annealed samples, with the evolution of hydrogen during annealing, the compactness of the films increases thereby increasing the density of the film. This should therefore lead to an increase in ε, likewise the refractive index. While the increase in the refractive index with annealing at
Figure 7.34  The capacitance-voltage characteristics of rfh5 sample after annealing.
Figure 7.35  The capacitance-voltage characteristics of rfp20 sample after annealing.
temperatures higher than 600°C have been observed by several authors [13-16], there
are mixed reports of the behaviour of the refractive index for temperatures below
600°C. This difference in the temperature at which the increase in the refractive index
occurs has been proposed to be a function of Si content [13]. Choi et al. [9] and
Trapeznikova et al. [17] have both reported a decrease in the refractive indices of their
stoichiometric samples annealed at 400 – 600°C and 350 – 450°C respectively. This
would mean a decrease in \( \varepsilon \) and is in agreement with the results of our films. For the
rfh5 sample, \( \varepsilon \) decreases with increasing annealing temperature while for the rfh10
sample, it was observed that \( \varepsilon \) increases after annealing at 600°C. For the
unhydrogenated sample (rfh0), it was seen that \( \varepsilon \) decreases with annealing.

From the above results, it would seem that the decrease in \( \varepsilon \) might be the result of both
enhanced breakage of bonds and the inefficiency of structural reorientation at 400°C
although there is an increase in the Si-C bonds. Another reason may be due to the
amount of hydrogen in the films, with films containing more hydrogen being more
likely to experience an increase in \( \varepsilon \) after annealing. For the unhydrogenated sample,
one reason for the reduction in \( \varepsilon \) might be due to the elimination of water vapour
present in the film after annealing. This could be possible because of the fact that
unhydrogenated samples contain more voids, which would allow water vapour to be
trapped when exposed to the atmosphere. The presence of water vapour would cause
an increase in the \( \varepsilon \).

7.5.2 Rfp Samples

From Table 7.15, it was observed that, similar to the rfh samples, the \( \varepsilon \) generally
decreases as the annealing temperature increases. Annealing generally reduces \( \varepsilon \)
except for the rfp08 samples where it increases from 14.47 to 17.25 after annealing at 400°C before reducing. It was also observed that for sample rfp08, ε increases slightly after annealing at 800°C. From the results, with the exception of the rfp08 sample, all the samples experience a decrease in ε after annealing. Borrowing the argument for the rfh samples, it was noted that the hydrogen content for the rfp samples is low and is lower than that of the rfh5 sample. And therefore, the behaviour of ε should follow that of rfh0 and rfh5 i.e. decreasing as the annealing temperature increases.

### 7.6 Interface Trap Density of Annealed Films

This section investigates the annealing effects on the a-Si1-xCxB:H/c-Si interface. The interface trap density values will be used to provide information on the interface properties after subjecting the samples to the annealing and RTA process.

#### 7.6.1 Rfh Samples

It can be seen from Table 7.14 that annealing reduces the $D_{it}$ values of the unhydrogenated films (rfh0) quite significantly. For example, $D_{it}$ reduces from $4.5 \times 10^{12}$ (rfh0) to $6 \times 10^{11}$ (rfh06) and $1.5 \times 10^{12}$ (rfh06A) eV$^{-1}$cm$^{-2}$ when furnace annealed and RTA at 600 °C. As can be seen in Section 5.2, annealing will cause the Si and C dangling bonds in the unhydrogenated films to reduce and form Si-C bonds. This may account for the reduction in the Si dangling bonds at the Si-SiC interface. It is, however, worth noting that $D_{it}$ was found to increase in rapid thermal annealed silicon-silicon oxide system due to the rapid ramp-up and ramp-down processes used in RTA [14,15]. This effect may also increase the $D_{it}$ value in rfh06A and it will compete with the annealing effect mentioned earlier. The net effect will then show that RTA is not as effective as furnace annealing in reducing $D_{it}$. This is indeed the case for the rfh0
and rfh5 series of films. For the rfh0 samples, RTA and furnace annealing at 600 °C reduces \( D_{it} \) by an amount of \( 3.0 \times 10^{12} \) and \( 3.9 \times 10^{12} \) eV\(^{-1}\) cm\(^{-2}\) respectively. For the rfh5 samples, \( D_{it} \) reduces by an amount of \( 5 \times 10^{10} \) and \( 9 \times 10^{10} \) eV\(^{-1}\) cm\(^{-2}\) after RTA and furnace annealing at 600 °C respectively. It is, however, interesting to note that for the rfh10 samples, \( D_{it} \) increases by an amount of \( 1 \times 10^{11} \) and \( 3 \times 10^{10} \) eV\(^{-1}\) cm\(^{-2}\) when RTA and furnace annealed at 600 °C. It is therefore obvious that the effect of annealing on \( D_{it} \) is much more complicated in the hydrogenated samples as compared to the unhydrogenated samples.

The above results may be explained by considering the thermal properties of the film and its adherence to the silicon substrate during annealing. Adherence of film is mainly influenced by the degree of match in the thermal properties of the substrate and the film, although the adhesion energy and chemical affinities are also important. By changing the amount of hydrogen in the films, the thermal properties of the a-Si\(_{1-x}\)C\(_x\):H film will most likely change. This might lead to a change in the mismatch of the substrate and the film when subjected to heat treatment. One observation to support this point is that unhydrogenated films do not crack after annealing unlike the hydrogenated films. Table 7.13 lists the values of some important thermal properties for the SiC film and the silicon substrate [16]. In most cases an average of different literature data is provided. The thermal endurance coefficient \( F \) is a measure of the thermal shock resistance.
Table 7.13   Thermal properties relevant to the adherence of SiC films to Si

<table>
<thead>
<tr>
<th>Property</th>
<th>SiC</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat (Jg⁻¹K⁻¹)</td>
<td>1.045</td>
<td>0.731</td>
</tr>
<tr>
<td>Thermal conductivity (W cm⁻¹K⁻¹)</td>
<td>1.87</td>
<td>1.31</td>
</tr>
<tr>
<td>Linear expansion (K⁻¹) x 10⁶</td>
<td>5.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Tensile strength (kgf cm⁻²) x 10⁻⁴</td>
<td>21.0</td>
<td>7.7</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>3.22</td>
<td>2.33</td>
</tr>
<tr>
<td>Young’s modulus (kgf cm⁻²) x 10⁻⁶</td>
<td>4.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Thermal endurance coefficient $F$ (cm K min⁻¹/²) x 10⁻⁴</td>
<td>1.3</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Thus, from the results of the interface trap density, it was deduced that as more hydrogen is incorporated into the film, the mismatch of the film and the silicon substrate is greater when subjected to heat treatment. This mismatch was enhanced by the quick ramp up and down of the RTA process.
Table 7.14  Density of Si-H bonds, dielectric constant and interface trap density of as-prepared and annealed rfh films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{Si-H}$ (x10$^{21}$ cm$^{-3}$)</th>
<th>$\varepsilon$</th>
<th>$D_n$ (x10$^{11}$ eV$^{-1}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfh0</td>
<td>-</td>
<td>13.5</td>
<td>45.0</td>
</tr>
<tr>
<td>rfh06</td>
<td>-</td>
<td>12.3</td>
<td>24.0</td>
</tr>
<tr>
<td>rfh06A</td>
<td>-</td>
<td>10.6</td>
<td>6.0</td>
</tr>
<tr>
<td>rfh5</td>
<td>0.93</td>
<td>11.4</td>
<td>5.0</td>
</tr>
<tr>
<td>rfh54</td>
<td>0.64</td>
<td>9.1</td>
<td>4.3</td>
</tr>
<tr>
<td>rfh56</td>
<td>0.46</td>
<td>8.8</td>
<td>4.1</td>
</tr>
<tr>
<td>rfh56A</td>
<td>-</td>
<td>8.4</td>
<td>4.5</td>
</tr>
<tr>
<td>rfh10</td>
<td>1.10</td>
<td>11.1</td>
<td>4.5</td>
</tr>
<tr>
<td>rfh104</td>
<td>0.68</td>
<td>8.2</td>
<td>3.7</td>
</tr>
<tr>
<td>rfh106</td>
<td>0.55</td>
<td>8.4</td>
<td>4.8</td>
</tr>
<tr>
<td>rfh106A</td>
<td>0.55</td>
<td>8.4</td>
<td>5.5</td>
</tr>
</tbody>
</table>

7.6.2 Rfp Samples

It can be seen from Table 7.15 that annealing reduces the $D_n$ values of all the sample except the rfp25 sample. For example, $D_n$ reduces from $8.7 \times 10^{11}$ (rfp08) to $5 \times 10^{11}$ (rfp086) and $7.2 \times 10^{11}$ (rfp15) to $4.6 \times 10^{11}$ (rfp156) eV$^{-1}$cm$^{-2}$ when furnace annealed at 600 °C. As can be seen in Section 5.2, annealing will cause the Si and C dangling bonds in the films to reduce and form Si-C bonds. This may account for the reduction in the Si dangling bonds at the Si-SiC interface. However, it was observed that for the
rfp25 sample, the $D_{it}$ actually increases after annealing at 400 °C before it decreases as the annealing temperature increases up to 600 °C. An interesting observation is that the $D_{it}$ values remain rather constant after annealing at temperatures greater than 400 °C. This shows that the interface does not improve much after further annealing at temperatures greater than 400 °C. In section 7.6.1, it was also observed that the $D_{it}$ remains rather constant for rfh5 sample after annealing at temperature greater than 400 °C.

With the introduction of hydrogen into the film, the $D_{it}$ reduces and the Si-SiC interface improves. However, as the hydrogen content increases further, it was observed that the $D_{it}$ increases after annealing at higher temperatures (rfh10). For samples with less hydrogen (rfh5 and rfp series), the $D_{it}$ remains relatively constant after annealing at higher temperatures. This shows that for films with higher concentration of hydrogen, the effect of annealing is more complicated and the interaction of bonds at the interface is more involved. This could also be due to the thermal mismatch of the film and the substrate when subjected to heat treatment at high temperatures.
Table 7.15  Dielectric constant and interface trap density of as-prepared and annealed rfp films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon$</th>
<th>$D_{it}$ (x$10^{11}$ eV$^{-1}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rfp08</td>
<td>14.47</td>
<td>8.7</td>
</tr>
<tr>
<td>rfp084</td>
<td>17.25</td>
<td>5.0</td>
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<tr>
<td>rfp086</td>
<td>12.12</td>
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<td>rfp088</td>
<td>12.79</td>
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<td>rfp15</td>
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<td>4.3</td>
</tr>
<tr>
<td>rfp156</td>
<td>8.85</td>
<td>4.6</td>
</tr>
<tr>
<td>rfp158</td>
<td>7.93</td>
<td>4.8</td>
</tr>
<tr>
<td>rfp25</td>
<td>10.75</td>
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<td>10.00</td>
<td>8.5</td>
</tr>
<tr>
<td>rfh256</td>
<td>8.74</td>
<td>4.9</td>
</tr>
<tr>
<td>rfp258</td>
<td>8.54</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Figure 7.36 Interface trap density as a function of energy level in the silicon band gap for rfh0 sample after annealing.
Figure 7.37  Interface trap density as a function of energy level in the silicon band gap for rfh5 sample after annealing
Figure 7.38 Interface trap density as a function of energy level in the silicon band gap for rfh10 sample after annealing.
Figure 7.39  Interface trap density as a function of energy level in the silicon band gap for rfp08 sample after annealing.
Figure 7.40  Interface trap density as a function of energy level in the silicon band gap for rfp15 sample after annealing.
Figure 7.41  Interface trap density as a function of energy level in the silicon band gap for rfp25 sample after annealing.
7.7 Conclusion

The d.c. conductivity was observed to decrease as $P_H$ and $P_S$ increases. With the passivation of the silicon dangling bonds by the hydrogen atoms, less of these bonds would be available for electrical conduction. $\sigma$ reduces from $2.76 \times 10^{-6}$ to $3.86 \times 10^{-8} \ \Omega^{-1}cm^{-1}$ as $P_H$ increases from 0 to 0.30 Pa and $6.18 \times 10^{-7}$ to $1.61 \times 10^{-7} \ \Omega^{-1}cm^{-1}$ as $P_S$ increases from 0.8 to 2.5 Pa. Annealing has, in general, the same effect as increasing the hydrogen concentration of the sputtered films in that the conductivity decreases after annealing. The activation energy $E_a$ was observed to increase from 0.145 to 0.254 eV as $P_H$ increases from 0 to 0.30 Pa. Similarly, for the rfp samples, $E_a$ increases from 0.202 to 0.280 eV as $P_S$ increases from 0.8 to 2.5 Pa. Annealing at lower temperature causes $E_a$ to increase slightly for the rfh5 and rfh10 samples and further increase in annealing temperature does not change $E_a$ very much. However, for the unhydrogenated sample rfh0, $E_a$ decreases then increases as the annealing temperature increases. For the rfp samples, $E_a$ increases at 400 °C annealing but decreases subsequently after further annealing.

There are two distinct regions observed for the I-V characteristics: the low and high field region. The current conduction mechanism observed for the low field region of the I-V characteristics consist of two mechanisms namely the MTCE model and conduction over a potential barrier for most of the hydrogenated samples except rfp25 sample. For the unhydrogenated sample, there is only one mechanism at work and that is the emission over a potential barrier. The high field region deviates from linearity due to the voltage drop across the series resistance of the structure. Annealing of the samples causes a change in the transport mechanism. For the unhydrogenated sample, annealing causes the extra shoulder to appear at the low field region, thus causing a
change in the transport mechanism. For the hydrogenated samples, annealing at higher
temperatures causes the extra shoulder at the low field to disappear.

The capacitance-voltage curve can be described in terms of the accumulation,
depletion and deep depletion regions. The dielectric constant, \( \varepsilon \), obtained decreases as
\( P_H \) or \( P_S \) increases. Likewise, the dielectric constant was observed to decrease after
annealing. The interface trap density obtained for the as-deposited samples were in the
range \( 4.5 \times 10^{12} \) to \( 4.5 \times 10^{11} \) eV\(^{-1}\) cm\(^{-2}\). As \( P_H \) or \( P_S \) increases, \( D_{it} \) decreases. It was
observed that as more and more hydrogen is incorporated into the film, the reduction in
\( D_{it} \) becomes less. In most cases, annealing causes \( D_{it} \) to decrease. However, for rfh10
sample, \( D_{it} \) was observed to increase after 600 °C annealing. It was suggested that for
films containing higher content of hydrogen, the effect of annealing on \( D_{it} \) is more
involve and might be due to the thermal mismatch of the substrate and the film. It was
found that RTA is not as effective as furnace annealing in reducing \( D_{it} \).
References


Chapter Eight

Preliminary Noise Measurements

This chapter investigates the noise measurements of the hydrogenated (a-Si_{1-x}C_{x}:H) and unhydrogenated (a-Si_{1-x}C_{x}) samples. Preliminary studies were performed for the rfh samples to determine the noise characteristics of the film and the effects annealing has on the noise characteristics. Experiments showed that it was not possible to carry out noise measurements at low applied biases as the noise measured was similar to the background noise. Note that all the noise results presented were obtained with high bias (i.e. with the silicon surface in accumulation).

Figure 8.1 shows the noise spectra of sample rfh0 at different biases. It can be seen from Figure 8.1 that at bias of 2 V, there is an appreciable increase in the noise intensity measured with the 1/f noise dominating at $f = 1$-10 Hz. At $f = 20$-100 Hz, a plateau in the noise can clearly be seen. The noise spectrum between 20 and 10000 Hz can be decomposed into two Lorenztian components with transition frequencies, $f_{t1}$ and $f_{t2}$, located at approximately 90 Hz and 1 kHz, respectively. Further increase in the applied bias to 2.25 and 2.5 V increases the noise level throughout the whole frequency range measured. However, $f_{t1}$ and $f_{t2}$ remain fairly constant at 90 Hz and 1 kHz respectively.
Figure 8.1  Room temperature noise current spectral density $S_i(f)$ against frequency for rfh0 sample at $V = 0, 2, 2.25$ and $2.5$ V.
Figures 8.2(a) and (b) show the noise results of the rfh5 and rfh10 samples. It is interesting to note that the noise spectra are very similar to those of rfh0 sample shown in Figure 8.1 in that the $1/f$ noise is again dominant in the frequency range of 1-10 Hz. The higher frequency part of the spectra can also be fitted with two Lorenztian components with $f_{11}$ and $f_{12}$ remaining approximately the same at 90 Hz and 1 kHz respectively.

D’Amico et al. [1] reported the noise results of r.f. sputtered a-Si and a-Si:H films. For a-Si films, $1/f$ noise was observed. For a-Si:H films, a Lorentzian characteristic was obtained and this was attributed to the trapping and detrapping of carriers by discrete traps in the films. Teuschler et al. [2] and Choi et al. [3] had also suggested that discrete dominant traps were responsible for the Lorenztian noise spectra observed in their double barrier structures and $p^+$-doped a-Si:H films respectively. Therefore, it may be reasonable to suggest that in our as-deposited a-Si$_{1-x}$C$_x$ and a-Si$_{1-x}$C$_x$:H samples, there are two dominant discrete traps that give rise to the Lorenztian spectra shown in figures 8.1 and 8.2.

Dyalsingh et al. [4] had observed the $1/f$ characteristic in their glow discharge deposited a-SiC:H films. The noise spectra of Figures 8.1 and 8.2 are, obviously, very different from that of Dyalsingh et al. Therefore, it shows that the noise characteristics of a-SiC films are very dependent on the preparation technique. As the spectra of the a-Si$_{1-x}$C$_x$:H (rfh5 and rfh10) and a-Si$_{1-x}$C$_x$ (rfh0) films are very similar to each other, it was suggested that two distinct traps in the films are introduced by the r.f. sputtering technique.
Figure 8.2(a) Room temperature noise current spectral density $S_i(f)$ against frequency for rfh5 sample at $V = 0, 2$ and $2.5$ V.
Figure 8.2(b) Room temperature noise current spectral density $S_i(f)$ against frequency for rfh10 sample at $V = 0$, 2 and 2.5 V.
In Chapter seven, it was reported that the incorporation of hydrogen into the film reduces the interface trapped density \((D_{it})\) of the Al-a-Si\(_{1-x}C_x\):H-Si structure. It should be noted that \(D_{it}\) is related to traps at the SiC-Si interface. Therefore, it is believed that the two dominant traps manifested in the noise measurement are due to bulk traps. Thus, the results of Chapter six cannot be used to explain the noise characteristics here. As a matter of fact, a knowledge of the electronic defect distribution of the sputtered films is essential for the explanation of the noise results. It is, however, unfortunate that we are unable to obtain such information in the literature.

In Chapter five, it was reported that the increase in the Si-C bonds in the annealed films can be due to the formation of Si-C bonds from the existing Si and C dangling bonds for both the a-Si\(_{1-x}C_x\) and a-Si\(_{1-x}C_x\):H films. Alternatively, it could be from the breaking of the Si-H and C-H bonds for the a-Si\(_{1-x}C_x\):H films. It was also reported that with the present method of introducing hydrogen atoms to the sputtered films, the increase in Si-H bonds was comparatively modest \((0.93-1.1\times10^{21} \text{ cm}^3)\) as compared to that of the glow discharge films \((10^{22} \text{ cm}^3)\) [5]. Therefore, it may be reasonable to expect the noise characteristics of rfh5 and rfh10 sample to be similar to that of rfh0 sample as the degree of hydrogenation is not pronounced in the sputtered films. As both the as-deposited a-Si\(_{1-x}C_x\) and a-Si\(_{1-x}C_x\):H films contain dangling silicon and carbon bonds, it is possible that the dominant trap levels are related to these dangling bonds.

Figure 8.3 shows the noise spectra of the annealed films. It can be seen that the two Lorenztian components of the as-deposited films have disappeared and only the \(1/f^n\) \((1.2 < n < 1.25)\) characteristics can be observed at the frequency range of 1-10\(^3\) Hz. The
conversion of the Lorenztian spectra of the as-deposited films to $1/f^n$ spectra of the annealed films may be due to the reduction of the dangling Si and C bonds and also to the increase of Si-C bonds.
Figure 8.3  Room temperature noise current spectral density $S_i(f)$ against frequency for annealed rfh0 and rfh5 samples.
References


Chapter Nine
Conclusions And Recommendations

9.1 Conclusions

The r.f. sputtering process was investigated as an alternative to the glow discharge and chemical vapour deposition method of producing a-Si\textsubscript{1-x}C\textsubscript{x}:H films. To prepare hydrogenated films by r.f. sputtering has its advantages and disadvantages. Most importantly, r.f. sputtering does not make use of toxic gases like silane, unlike the glow discharge and chemical vapour deposition method and is therefore environmentally safe. The films were deposited at a low temperature of 250 °C with an input power of 200 W by varying the chamber pressure (P\textsubscript{S}) and the hydrogen partial pressure (P\textsubscript{H}).

The structural properties of the films were characterised by the infrared (IR) spectroscopy and x-ray photoelectron spectroscopy (XPS). The electrical properties were determined from the current (I-V), capacitance (C-V) and conductance (G-V) versus voltage measurements.

The infrared results showed modes of vibration that characterises a-Si\textsubscript{1-x}C\textsubscript{x}:H films, i.e., the Si-H stretching mode at about 2100 cm\textsuperscript{-1} and the Si-C stretching mode at about 780 cm\textsuperscript{-1}. The C-H stretching mode at ~ 2900 cm\textsuperscript{-1} could only be detected for films with higher hydrogen concentration (rfh10 and rfh15). Increasing $P_{H}$ will result in a decrease in Si-C bonds and an increase in Si-H and C-H bonds. Similarly, increasing
$P_S$ will cause a reduction in Si-C bond and an increase in Si-H bonds. Due to the low concentration of hydrogen (5%) in the sputtered gas, the C-H bonds cannot be determined. Annealing causes both the Si-H and C-H bonds to decrease and the Si-C bonds to increase. The Si-H bonds were observed to decrease at lower annealing temperatures than the C-H bonds due to the difference in the binding energy. It is noted that the hydrogenated films cracked at the surface when annealed at 800 °C. This shows that films with higher hydrogen content are not suitable for high temperature processes.

X-ray photoelectron spectroscopy detected three elements, namely, silicon (Si2p), carbon (C1s) and oxygen (O1s). The stoichiometry of our a-Si$_{1-x}$C$_x$:H films was 0.53<x<0.57, and it is more dependent on the target composition than the variation in annealing and preparation conditions. Therefore, r.f. sputtering is not effective when trying to vary the Si / C ratio as it uses only a single target. The changes observed for the %Si-C, %C-C/C-H and %Si-Si/Si-H of the annealed films were in agreement with the IR results in that Si-C bonds are formed to replace the Si-H and C-H bonds with annealing. With the formation of additional Si-C bonds, the chemical ordering of the films were observed to increase and approach the local ordering of the β-SiC films. Due to the rapid and random evacuation of hydrogen atoms, the newly formed Si-C bonds were likely to be angular distorted, and this would enhance the structural disorder and the tensile stress of the films. The degree of change was proportional to the hydrogen content in the films. Hence, films with low hydrogen content may be suggested to be more stable at higher temperatures.
The d.c. conductivity was observed to decrease as $P_H$ and $P_S$ increases. With the passivation of the silicon dangling bonds by the hydrogen atoms, less of these bonds would be available for electrical conduction. Annealing has, in general, the same effect as increasing the hydrogen concentration of the sputtered films in that the conductivity decreases after annealing. The activation energy $E_a$ was observed to increase from 0.145 to 0.254 eV as $P_H$ increases from 0 to 0.30 Pa. Similarly, for the rfp samples, $E_a$ increases from 0.202 to 0.280 eV as $P_S$ increases from 0.8 to 2.5 Pa. Annealing at lower temperature causes $E_a$ to increase slightly for the rfh5 and rfh10 samples and further increase in annealing temperature does not change $E_a$ very much. However, for the unhydrogenated sample rfh0, $E_a$ decreases then increases as the annealing temperature increases. For the rfp samples, $E_a$ increases at 400 °C annealing but decreases subsequently after further annealing.

The interface trap density obtained for the as-deposited samples were in the range $4.5 \times 10^{12}$ to $4.5 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$. As $P_H$ or $P_S$ increases, $D_{it}$ decreases. It was observed that as more and more hydrogen is incorporated into the film, the reduction in $D_{it}$ becomes less. In most cases, annealing causes $D_{it}$ to decrease. However, for rfh10 sample, $D_{it}$ was observed to increase after 600 °C annealing. It was suggested that for films containing higher content of hydrogen, the effect of annealing on $D_{it}$ is more involve and might be due to the thermal mismatch of the substrate and the film. It was found that RTA is not as effective as furnace annealing in reducing $D_{it}$.

The interface property is an important consideration in electronic applications. However, due to the high $D_{it}$ of the r.f. sputtered films, it is not suitable to be used as gate material. Even after annealing, the value of $D_{it}$ is still considerably high. The r.f.
sputtered a-Si_{1-x}C_x:H films can however, be used as a passivation layer to protect devices. The film can be subjected to high temperature stress although films with higher hydrogen content develop cracks when subjected to high temperature annealing.

Preliminary noise measurements were performed and two Lorenztian components were found in the noise spectra. This is attributed to the discrete traps created by the sputtering process. It was proposed that annealing has reduced the discrete trap substantially so that only 1/f noise was observed in the annealed samples.

9.2 Recommendations

In this study, annealing of the hydrogenated films lead to the development of surface cracks, as a result of the increased in tensile stress of the films. This would severely limit the applications of the hydrogenated films in high temperature devices. Therefore, further research should be dedicated to study ways to reduce the stress developed during high temperature annealing such as varying the thermal ramp rate of the annealing process.

Another area of research is on the development of a dispersion model for the a-Si_{1-x}C_x:H film. Due to the fact that the extinction coefficient, k, of the film has a non-zero value, the true refractive index of the film cannot be determined accurately unless k is known. One way is to use the spectroscopic ellipsometry whereby both the refractive index and extinction coefficient can be determined simultaneously. This study would provide an insight as to whether annealing or hydrogenation has any effect on the dispersion model.
Appendix

Figure A.1 Normalised capacitance versus voltage of as-deposited and annealed rfh0 sample.
Figure A.2 Normalised capacitance versus voltage of as-deposited and annealed rfh10 sample.
Figure A.3  Normalised capacitance versus voltage of as-deposited and annealed rfp08 sample.
Figure A.4 Normalised capacitance versus voltage of as-deposited and annealed rfp15 sample.
Figure A.5 Normalised capacitance versus voltage of as-deposited and annealed rfp25 sample.
Figure A.7  The $G_p/\omega$ as a function of frequency at different applied biases for rfp08 sample.
Figure A.8  The $G_p/\omega$ as a function of frequency at different applied biases for rfp084 sample.
Figure A.9  The $G_p/\omega$ as a function of frequency at different applied biases for rfp086 sample.
Figure A.10  The $G_p/\omega$ as a function of frequency at different applied biases for rfp088 sample.
Figure A.11  The $G_\rho/\omega$ as a function of frequency at different applied biases for rfp15 sample.
Figure A.12  The $G_p/\omega$ as a function of frequency at different applied biases for rfp154 sample.
Figure A.13  The $G_p/\omega$ as a function of frequency at different applied biases for rfp156 sample.
Figure A.14  The $G_p/\omega$ as a function of frequency at different applied biases for rfp158 sample.
Figure A.15 The $G_p/\omega$ as a function of frequency at different applied biases for rfp25 sample.
Figure A.16 The $G_p/\omega$ as a function of frequency at different applied biases for rfp254 sample.
Figure A.17  The $G_p/\omega$ as a function of frequency at different applied biases for rfp256 sample.