CHAPTER 4. EXPERIMENTAL RESULTS AND ANALYSIS

4.1 Introduction

Experimental results from the transmission spectrum of Ultraviolet-Visible (UV-Vis) and Fourier Transform Infrared (FTIR) spectroscopy are presented in this chapter together with the analytical techniques that are applied. Optical constants are deduced from the UV-Vis spectrum while analysis for chemical bondings are inferred from the FTIR spectrum.

Interference fringes appearing in the transmittance $T$ or reflectance $R$ versus wavelength traces in the optical region are widely used as a straightforward computation to determine the film optical constants as previously reported [1-3]. Apart from its ease, this method offers a directly programmable calculation as the formulae are in closed form where data solely from the transmission or reflectance are needed. The procedure is simple, fast and the precision is of the same order as the iteration method [1,2]. Nevertheless, if the interference fringes do not appear as in the case of low thickness film then such utilization of the expression involving typical quantities ($T_{\text{max}}$, $T_{\text{min}}$, $R_{\text{max}}$ and $R_{\text{min}}$) derived from the spectrum for estimating the values of optical constants becomes redundant.

Bands in the infrared (IR) spectra are assigned to a particular vibrational mode of a certain chemical bonding and the chemical bonding dependence on the deposition parameters are studied. There are extensive work on silicon - based inorganic films and as such the region of interest in the IR study is between 3500 - 400 cm$^{-1}$. Our study on silicon nitride shall be based along the same line. Silicon nitride film exhibits its main absorption region of Si-N stretching bond at around 890 cm$^{-1}$, along with
Si-H stretching at 2180 cm⁻¹ and N-H stretching at 3350 cm⁻¹ [4] showing that it consists of Si, N and H elements. A typical near-stoichiometric Si₃N₄ IR absorption spectra is as shown in Figure 4.1. The vibrational spectrum obtained for plasma-deposited a-SiNH exhibits no appreciable difference from that of Figure 4.1, except for the absorption intensities due to the N-H stretching mode and the Si-N lattice vibrational mode [5]. However, the interaction between separate molecular vibrational mode will influence the IR spectra and can result in a broadening or shifting of the bands, or even the appearance of new bands. The band assignments investigated by different workers on SiNH alloy are summarized in Table 4.1.

4.2 Film Preparation Condition

As mentioned in Section 3.3, two batches of samples were produced from the DC plasma decomposition of silane and ammonia using the home-built PGD1 system. The samples from batch 1 consist of 6 samples prepared at a substrate temperature of 250°C and a fixed silane flowrate of 10 sccm. The first sample from this batch had no ammonia introduced into the deposition chamber during the deposition. The ammonia flowrates were fixed at 10 sccm, 20 sccm, 30 sccm, 40 sccm and 50 sccm respectively. Samples from batch 2 were prepared with ammonia and silane flowrates of 30 sccm and 10 sccm respectively. These samples were prepared at different substrate temperatures 31°C (room temperature), 100°C, 150°C, 200°C, 250°C and 300°C respectively.

Throughout the preparation of these samples the discharge current was maintained at 12 mA by regulating the voltage supply via the regulating transformer RT2 (refer figure 3.7). The voltage was varied between 400 to 550 V to maintain the
Figure 4.1. A typical near-stoichiometric Si$_3$N$_4$ FTIR transmission spectrum in the range of 4000 cm$^{-1}$ to 200 cm$^{-1}$ showing the respective bands designation.
A typical near-stoichiometric Si$_3$N$_4$ FTIR transmission spectrum in the range of 4000 cm$^{-1}$ to 200 cm$^{-1}$ showing the respective bands designation.
<table>
<thead>
<tr>
<th>BAND ASSIGNMENTS</th>
<th>WAVENUMBER (1/cm)</th>
<th>REFERENCES</th>
</tr>
</thead>
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<tr>
<td>Si-N (Bending)</td>
<td>480</td>
<td>45</td>
</tr>
<tr>
<td>Si-N (Asym.-Stretching)</td>
<td>490</td>
<td>48</td>
</tr>
<tr>
<td>Si-Si (Breathing)</td>
<td>470</td>
<td>46</td>
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<tr>
<td></td>
<td>495</td>
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<tr>
<td>Si-H (Wagging)</td>
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<td>18, 31</td>
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<tr>
<td></td>
<td>640</td>
<td>24</td>
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<td></td>
<td>630-650</td>
<td>48</td>
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<tr>
<td></td>
<td>630-660</td>
<td>21</td>
</tr>
<tr>
<td>Si-N (Stretching)</td>
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<td>24, 31</td>
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<td></td>
<td>850</td>
<td>47, 48</td>
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<td></td>
<td>860</td>
<td>18</td>
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<td></td>
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</tr>
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<td></td>
<td>840,970</td>
<td>44</td>
</tr>
<tr>
<td>Si-O (Stretching)</td>
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<td>31</td>
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<tr>
<td></td>
<td>1050</td>
<td>45</td>
</tr>
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<td></td>
<td>1070</td>
<td>46</td>
</tr>
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<td>N-H (Bending)</td>
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<td>45, 46, 24, 48</td>
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<td>2150</td>
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<tr>
<td></td>
<td>2100-2200</td>
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<td>N-H (Stretching)</td>
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<td>18</td>
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<td>47</td>
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<td></td>
<td>3300-3400</td>
<td>46</td>
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Table 4.1: Comparison of IR absorption band assignments ascribed by few workers.
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>FLOWRATE (sccm)</th>
<th>SUBSTRATE TEMPERATURE °C</th>
<th>TOTAL CH. PRESSURE mbar</th>
<th>DEPOSITION TIME (HOURS)</th>
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<tbody>
<tr>
<td></td>
<td>NH₃</td>
<td>SiH₄</td>
<td></td>
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<tr>
<td>R12</td>
<td>0</td>
<td>10</td>
<td>250</td>
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<tr>
<td>R10</td>
<td>10</td>
<td>10</td>
<td>250</td>
<td>0.3</td>
</tr>
<tr>
<td>R11</td>
<td>20</td>
<td>10</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>R7</td>
<td>30</td>
<td>10</td>
<td>250</td>
<td>0.3</td>
</tr>
<tr>
<td>R8</td>
<td>40</td>
<td>10</td>
<td>250</td>
<td>0.4</td>
</tr>
<tr>
<td>R9</td>
<td>50</td>
<td>10</td>
<td>250</td>
<td>0.4</td>
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<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>BATCH 1</td>
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</tr>
<tr>
<td>BATCH 2</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>R16</td>
<td>30</td>
<td>10</td>
<td>31</td>
<td>0.3</td>
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<tr>
<td>R15</td>
<td>30</td>
<td>10</td>
<td>100</td>
<td>0.3</td>
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<tr>
<td>R14</td>
<td>30</td>
<td>10</td>
<td>150</td>
<td>0.3</td>
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<tr>
<td>R13</td>
<td>30</td>
<td>10</td>
<td>200</td>
<td>0.3</td>
</tr>
<tr>
<td>R18</td>
<td>30</td>
<td>10</td>
<td>250</td>
<td>0.3</td>
</tr>
<tr>
<td>R17</td>
<td>30</td>
<td>10</td>
<td>300</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 4.2: Table shows parameters for the preparation condition of batch 1 and batch 2 samples together with the respective designations.
Figure 4.2. Results from UV-Vis spectroscopy obtained from batch 1 samples.
Figure 4.3. Results from UV-Vis spectroscopy obtained from batch 2 samples.
4.4 Optical Constants Determination

The envelope method is utilized in determining the optical constants of the films. This method exploits the interference phenomena appearing in the UV-Visible spectrum. The curves enveloping the maximum points and the minimum points on the interference fringes produce the $T_{\text{max}}$ and $T_{\text{min}}$ values in equation 4.6 used to determine the refractive index of the films [1,2]. Figure 4.4 generally describes the envelope method.

For a system of thin film on a transparent thick substrate, Figure 4.5, the expressions for transmission $T$ is a complex function [1,6] represented by

$$T = T(\lambda, n_1, n, d, \alpha) \quad (4.1)$$

where

$$T = \frac{C_1 x}{C_2 - C_3 x + C_4 x^2} \quad (4.2)$$

where

$$C_1 = 16n_0n_1n^2$$
$$C_2 = (n + n_0)^2(n + n_1)^2$$
$$C_3 = \left( n^2 - n_0^2 \right) \left( n^2 - n_1^2 \right) 2\cos \phi$$
$$C_4 = (n - n_0)^2(n - n_1)^2$$
$$\phi = \frac{4\pi k}{\lambda}, x = e^{-\alpha d}$$

$n_0, n_1, n$ are the refractive indices of air, substrate and film respectively.
$\alpha, k$ are the absorption and extinction coefficient respectively.
$\lambda$ is incident wavelength.
$d$ is film thickness.

The above expression is valid only in the weak absorption region, where

$$k^2 \ll (n - n_0)^2 \quad \text{and} \quad k^2 \ll (n - n_1)^2 \quad (4.3)$$
Figure 4.4. Typical transmission spectrum with interference fringes. The curves $T_{\text{max}}$ and $T_{\text{min}}$ show how envelope method is applied to calculate the optical constants of the thin films.
Figure 4.5. Schematic structure of the thin film samples bounded by two transparent media. \( n_0 \), \( n_1 \), and \( n \) denote the refractive indices of air, substrates, and film respectively. The transparent substrate has a thickness several orders of magnitude larger than that of the film.
R. Swanepoel derived Equation 4.1 without ignoring the contribution of multiple reflections from the back of the substrate by considering a finite substrate. His expression for \( T \) varies slightly from equation 4.2 where

\[
    C_2 = (n + n_0)^3(n + n_1)^2
    C_4 = (n - n_0)^3(n - n_1)^2
\] (4.4)

Manifacier et al [1] applied the infinite substrate approximation, while R. Swanepoel [2] used the finite substrate theory, however, in both cases the expression obtained for the refractive index \( n \) is

\[
    n = \left[ N + (N^2 - s^2)^{1/2} \right]^{1/2}
\] (4.5)

where

\[
    N = 2s\left[ (T_M - T_m)/T_MT_m \right] + [(s^2 + 1)/2]
\] (4.6)

Equations 4.5 and 4.6 are used to calculate the refractive index \( n \) in this work. The values of \( n \) obtained from these equations are fitted to the Cauchy relation [2]

\[
    n = a/\lambda^2 + c
\] (4.7)

and extrapolated to longer wavelengths to obtain static refractive index, \( n_0 \)

The value of film thickness \( d \) is determined by a simple graphical method [2]. Consider \( m_1 \) as the order number (integer or half integer) of the first extreme. From the basic equation of the interference fringes

\[
    2nd = m\lambda
\] (4.8)
this equation can be rearranged such that

$$2nd = (m_1 + l/2)\lambda \quad , \quad l = 0, 1, 2, 3, ...$$

or

$$l/2 = 2d(n/\lambda) - m_1 \quad (4.9)$$

A plot of $l/2$ vs. $n/\lambda$ will result in a straight line curve with a slope of $2d$, where $d$ is the film thickness. Only values of $n$ and $\lambda$ at the extremes are considered when determining the values of $d$ and also $m_1$.

The values of $n$ and $d$ obtained from above equations are used to calculate the absorption coefficient $\alpha$ based on the relation

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{X} \right) \quad (4.10)$$

where $d$ is the film thickness and $X$ represents the value of $e^{-ad}$. $X$ is obtained from the following simplified expression for transmission through an air/film/substrate system [7,8]

$$T = \frac{(1 - R_1)(1 - R_2)(1 - R_3)e^{-ad}}{(1 - R_2 R_3)\left[1 - \left[R_1 R_2 + R_1 R_3 (1 - R_2)^2\right]e^{-2ad}\right]} \quad (4.11)$$

where the reflectivities ($R_1, R_2$ and $R_3$) are given by by the following relationship,

$$R_1 = \left(\frac{n_f - 1}{n_f + 1}\right)^2 \quad (4.12a)$$

$$R_2 = \left(\frac{n_f - n_s}{n_f + n_s}\right)^2 \quad (4.12b)$$

$$R_3 = \left(\frac{n_s - 1}{n_s + 1}\right)^2 \quad (4.12c)$$
where

\[ R_1 \] - air/film reflectivity
\[ R_2 \] - film/substrate reflectivity
\[ R_3 \] - substrate/air reflectivity
\[ n_s \] - refractive index of substrate
\[ n_f \] - refractive index of film
\[ n_a \] - refractive index of air, taken as 1.0

Equation 4.11 expressed in a simplified form

\[
T = \frac{C_1 X}{(1 - C_2)(1 - C_3 X^2)}
\]  (4.13)

here

\[ C_1 = (1 - R_1)(1 - R_2)(1 - R_3) \]
\[ C_2 = R_1 R_3 \]
\[ C_3 = R_1 R_2 + R_1 R_3 (1 - R_2)^2 \]

Rearranging equation 4.13 into quadratic form and solving for \( X \) gives

\[
X = \frac{-C_1 \pm \sqrt{C_1^2 + 4T^2 C_3 (1 - C_2)^2}}{2TC_3(1 - C_2)}
\]  (4.14)

A measure of the optical energy gap \( E_g \) in amorphous semiconductor is commonly deduced from a Tauc's plot of \((\alpha h\nu)^{1/2}\) vs. \( h\nu \) in the strong absorption region [9-14]. The strong absorption region can be expressed as

\[
\alpha h\nu = A(h\nu - E_g)^2
\]  (4.15)
where $\alpha$ is the absorption coefficient as calculated from Equation 4.10, $hv$ is the incident photon energy and $A$ is a constant. The value $A^{1/2}$ is sometimes referred to as Tauc factor. This relation allows the determination of the optical energy gap from a linear extrapolation of the linear part of the curve to the energy axis.

4.5 Computed Values of Optical Constants

In this section the dependence of the static refractive index $n_0$, optical energy gap $E_g$ and average deposition rate on the deposition parameters are presented. The refractive indices are computed using Equations 4.5 - 4.7 and the optical energy gaps are deduced from the Tauc's plot, as discussed in Section 4.4. Film thicknesses are determined from the basic relation for interference fringes in the linear form. (i.e. Equations 4.8 - 4.9.)

4.5.1 Effect of Ammonia to Silane Flowrate Ratio

4.5.1.1 Refractive index

Figure 4.6 presents the $n$ vs. $\lambda$ plots. Samples prepared with different NH$_3$-SiH$_4$ ratio follows the Cauchy relationship of $n$ vs. $\lambda$. The Cauchy relationship in form of $n = \frac{a}{\lambda^2} + n_o$ was fitted to these curves to determine the static refractive index value $n_0$. An example of the application of the envelope method to calculate the refractive indices is presented in Appendix 1. Static refractive index $n_0$ decreases with increasing ammonia to silane flowrate ratio as shown in Figure 4.7. The refractive index $n_0$ decreases from the value of 2.24 for sample obtained from the discharge of pure silane to a value of 1.72 for samples obtained from the discharge of SiH$_4$ and NH$_3$ gas mixture with NH$_3$ to SiH$_4$ ratio of 5.
Figure 4.6. Plots of static refractive index vs. wavelength of batch 1 samples as obtained utilizing the envelope method. The solid line is a fit to the Cauchy relation to deduce the static refractive index values.
Figure 4.6. Plots of static refractive index vs. wavelength of batch 1 samples as obtained utilizing the envelope method. The solid line is a fit to the Cauchy relation to deduce the static refractive index values.
Figure 4.7. Changes of static refractive index $n(0)$ with ammonia to silane flowrate ratio
4.512 Optical energy gap

The Tauc’s plot is as shown in Figure 4.8. These plots indicate that the optical energy gap $E_g$ increases with the increase in NH$_3$ to SiH$_4$ flowrate ratio. The variation of the $E_g$ with NH$_3$ to SiH$_4$ ratio is presented in Figure 4.9. $E_g$ increases from 2.03 to 2.76 when the NH$_3$ to SiH$_4$ ratio increases from 0 to 3. However, the energy gap remains constant when the NH$_3$ to SiH$_4$ ratio increases to 4 before increases again to 3.02 eV when this ratio was increased to 5.

4.513 Average Deposition Rate

Figures 4.10 show the typical plot of $\frac{I}{2}$ vs. $\frac{N}{\lambda}$ obtained from sample R10, used to determine the film thicknesses. As the deposition time is not the same for these samples, the variation of average deposition rate (i.e. the film thickness divided by the deposition time) with NH$_3$:SiH$_4$ flowrate ratio is studied. The plot showing the variation of the average deposition rate with NH$_3$:SiH$_4$ flowrate ratio is presented in Figure 4.11. The deposition time is taken from the moment the potential is applied across the electrodes until this potential is cut off. The average deposition rate was not more than 5 nm/min. The average deposition rate initially decreases with NH$_3$:SiH$_4$. However when the flowrate ratio is increased to 4 the average deposition rate increases to approximately 4 nm/min before decreases again to approximately 3 nm/min when the flowrate ratio increases to 5.
Figure 4.8. Tau's plot of the respective samples. The straight lines denote the linear interpolation from the linear part of the curves.
Figure 4.9. The variation of optical energy gap as the ammonia to silane flowrate ratio increases.
Figure 4.10. Figure illustrating a typical graph used to determine the films thicknesses.
Figure 4.11. Figure displaying the changes of the average deposition rate with ammonia to silane flowrate ratio.
4.52 Effect of Substrate Temperature

4.521 Refractive index

The $n$ vs. $\lambda$ plots are as given in Figure 4.12. The static refractive index values are again obtained from the extrapolated Cauchy plots which are fitted to the $n$ vs. $\lambda$ plots. From Figure 4.13 it is observed that $n_0$ increases with increasing substrate temperature, from an initial value of 1.52 to 1.80. From the plot of $n_0$ vs. substrate temperature, two significant trends are observed. The increment in $n_0$ is faster for samples prepared at substrate temperature above 150°C.

4.522 Optical energy gap

The Tauc's plot for samples prepared at different deposition temperatures are presented in 4.14. The plot clearly exhibits the shift of the absorption edge towards lower energy as the substrate temperature increases. The optical energy gap $E_g$ decreases from 3.6 eV to 2.8 eV with increasing substrate temperature, as shown in Figure 4.15.

4.523 Average Deposition Rate

Figure 4.16 shows the variation of the average deposition rate with increasing substrate temperature. The film thickness ranges between 380 to 900 nm. As observed in Figure 4.16, the average deposition rate decreases with increasing substrate temperature. The deposition rate at room temperature is about 5 nm/min and reduces to 3.5 nm/min at the substrate temperature of 300°C.
Figure 4.12. Refractive index versus wavelength plots of batch 2 samples. These curves are fitted to the Cauchy relation as shown by the solid lines which is extrapolated at infinite wavelength for static refractive index values.
Figure 4.13: Figure shows the effect of substrate temperature on the static refractive index.
Figure 4.14. Tauc's plot of Batch 2 samples.
Figure 4.15. Graph of optical energy gap versus substrate temperature.
Figure 4.16. Variation of average deposition rate with deposition temperature.
4.6 Fourier Transform Infrared (FTIR) Spectroscopy

A Perkin Elmer System 2000 FTIR Spectrometer was utilized in obtaining the optical transmission spectrum for the films. Scanning was performed in the range 400 to 4000 cm\(^{-1}\) and for each run 16 scans were taken. The spectral resolution was 4 cm\(^{-1}\) while the J-stop and B-stop parameters selected were 2.300 cm\(^{-1}\) and 16.0 mm respectively.

Figures 4.17a-f present the FTIR spectra for samples obtained from batch 1 while the spectra obtained from batch 2 samples are shown in Figures 4.18a-f.

The FTIR spectra for these samples display the similar features i.e. a major broad band is observed in the range 600 - 1200 cm\(^{-1}\) and the presence of isolated bands are observed around 2100 and 3350 cm\(^{-1}\). The broad peak is suspected to be due to the overlapping of a few absorption bands, as indicated by the shape of the band and the appearance of shoulders. The isolated peaks around 2100 and 3350 cm\(^{-1}\) are H-related that are attributed to the Si-H and N-H stretching modes respectively.

A detailed study on the changes of the IR absorption with different ammonia to silane flowrate ratio is presented in the following section.

4.6.1 Effect of Ammonia to Silane Flowrate Ratio

Figure 4.19 displays the IR spectra in the range where the broad absorption peak is observed. Significant difference in the IR absorption spectra in this region are observed when ammonia is introduced in the preparation. The a-Si spectrum shows a broad non-symmetric absorption peak, with a dominant absorption peak emerging at around 1010 cm\(^{-1}\). Also, an obvious absorption peak appears at around 650 cm\(^{-1}\) and another small absorption peak emerges at around 790 cm\(^{-1}\). As ammonia is introduced
Figures 4.17 (a)-(f). FTIR spectra for samples from batch 1 preparation with different NH₃ to SiH₄ flowrate ratio.

a) Zero (a-Si sample)

b) 1:1
e) 4:1

f) 5:1
Figures 4.18 (a)-(f). FTIR spectrum from batch 2 samples displaying the IR absorptions in the range 4000 - 400 cm$^{-1}$.

a) 31°C (Room temperature)

b) 100°C
into the preparation of the film, the FTIR spectrum obtained produced a near-symmetric absorption peak centred around 860 cm\(^{-1}\). A most significant change observed as the NH\(_3\) to SiH\(_4\) flowrate ratio increases is that the maximum absorbance constantly increases and the absorbance continually is broadened towards higher frequency. The presence of shoulders are observed in the range of 1000 to 1200 cm\(^{-1}\) and around 950 cm\(^{-1}\) regions. As more ammonia is introduced during the preparation, the presence of shoulders become more significant. The broad absorption peak wavenumber seems to shift towards lower wavenumber.

The changes of the H-related bands are shown in Figure 4.20. The Si-H stretching mode peaks at around 2100 cm\(^{-1}\) and the N-H stretching mode emerges at around 3350 cm\(^{-1}\). The Si-H stretching mode are observed in all samples. The shift in the peak wavenumber of the Si-H (s) mode towards higher wavenumber as the NH\(_3\) to SiH\(_4\) flowrate ratio increased from zero towards 5 is also observed. The presence of N-H (s) mode band is indicated by the tiny emergence in the vicinity of 3500 cm\(^{-1}\). As the ammonia flowrate increases, emergence of tiny peak is observed more clearly. Note that this peak is not present in a-Si samples (R12).

4.62 Effect of Substrate Temperature

As for samples from batch 1, the main absorption band is the broad band which lies in the range of 600 to 1200 cm\(^{-1}\) and centred around 860 cm\(^{-1}\). Figure 4.21 exibits this main broad region. At room temperature (RT) the 3 components contributing to this broad band are peaks appearing in the region around 1050-1060 cm\(^{-1}\), 930-980 cm\(^{-1}\) and 850-870 cm\(^{-1}\). The component representing the peak appearing in the region around 1050-1060 cm\(^{-1}\) appears to be the most dominant,
Figure 4.19. The IR absorption spectra in the main broad absorption region for samples obtained from batch 1.
Figure 4.20. Figure depicts the isolated H-related absorption bands, N-H and Si-H stretching at around 3500 cm\(^{-1}\) and 2100 cm\(^{-1}\) respectively. These absorption bands are observed to shift as the ammonia to silane flowrate ratio increases.
followed by the peak appearing in the region around 850-870 cm\(^{-1}\) and finally the peak appearing in the region around 930-980 cm\(^{-1}\). The broad absorption band gradually decreases with increasing substrate temperature. The contribution of the absorption peaks appearing in the region around 1060 and 970 cm\(^{-1}\) become less dominant as the substrate temperature increases, and for substrate temperature above 200\(^\circ\)C, the peak appearing in the region around 860 cm\(^{-1}\) becomes most prominent.

The Si-H and N-H stretching modes which are represented by absorption bands in the region of 2100 and 3500 cm\(^{-1}\), become less prominent as the substrate temperature increases. These observation are demonstrated in Figure 4.22. The absorption peak position moved slightly towards lower wavenumber as the substrate temperature increases.

4.7 Analytical Techniques on FTIR Spectra

In the following sections, the technique that was used to deconvolute the overlapping absorption peaks are presented. The quantitative compositional analysis is then deduced from the IR absorption spectra.

4.7.1 Decomposition of the Overlapping Bands

The components of the overlapping peaks which contribute to the broad absorption band observed in the FTIR spectra are isolated by means of a curve fitting technique discussed below.

The main region of interest is the Si-N absorption mode centred around 860 cm\(^{-1}\) but the vibrational spectra of the Si-N matrix can be rather complex. S. Hasegawa
Figure 4.21. The IR absorption spectra in the main broad absorption region (between 600 cm⁻¹ to 1200 cm⁻¹) observed for samples prepared at different substrate temperatures.
Figure 4.22. Graph illustrating the variation of the Si-H and N-H stretching absorption with deposition temperature.
et al [15] reported that the Si-N absorption can be decomposed into 5 components at around 450, 630, 750, 840 and 960 cm\(^{-1}\).

The components of the overlapping band are reproduced by the superposition of Gaussian shapes [15,16] represented by [17]

\[ y = h e^{-z^2 \ln^2} \]  \hspace{1cm} (4.16)

where \( z \) is the standard variable, \( z = \frac{p-x}{(\omega/2)} \); \( p \) is the position of the maximum intensity; \( \omega \) is the full width at half maximum (FWHM); and \( h \) is the maximum intensity of the band.

Equation 4.16 can be rearranged as [18]

\[ y = h \{ \exp[- \frac{4 \ln 2}{\omega^2} (p-x)^2] \} \]  \hspace{1cm} (4.17)

Converting equation 4.17 into linear form produces the equation

\[ \ln y = -AX + B \]  \hspace{1cm} (4.18)

where

\[ A = \frac{4 \ln 2}{\omega^2} \]
\[ X = (p-x)^2 \]
\[ B = \ln h \]

The least-squares method is performed on the plot of \( \ln y \) vs. \( X \). By selecting appropriate portion from the IR absorption band at a particular peak wavenumber \( (p) \), the values of \( A \) and \( h \) are obtained and correspondingly the simulated curve is plotted. This process is done repeatedly by adjusting the value of \( p \) and selecting other portion
from the spectrum until a good fit is achieved. The criterion for a good fit is expressed in terms of Discrepancy, DIS [19-22] defined as

\[(\Sigma \Delta^2)/n\]^{1/2} \hspace{1cm} (4.19)\]

where \( \Delta \) is the difference between the profiles at particular point and \( n \) is the number of points considered.

In infrared and Raman spectroscopy, the fit is usually considered a good fit if the DIS value does not exceed 0.01 to 0.02 [19,20], while Morrow and Cody [22] considered a good fit is obtained when the discrepancies were 0.01 or less.

The area under a Gaussian profile \( S_{\text{band}} \) is given by the following relation [23]

\[ S_{\text{band}} = \int_{-\infty}^{+\infty} h\{\exp[-A^2(p-x)^2]\} \, dx = \frac{h\sqrt{\pi}}{A} \] \hspace{1cm} (4.20)\]

Replacing the expression of \( A \) from Equation 4.17 results in

\[ S_{\text{band}} = \frac{\omega h\sqrt{\pi}}{2(\ln 2)^{1/2}} \] \hspace{1cm} (4.21)\]

Thus the area under the curve is calculated from the above Equation 4.21 and the values of \( \omega \), \( A \) and \( h \) are obtained from equation 4.18.
4.72 Determination of the Film Atomic Concentration

Quantitative composition of the film can be deduced from the IR absorption spectra. The integrated intensity $I$ is considered to be proportional to the atomic density $C$ incorporated into the film, given by the following relation [7,24-26]

$$ C = A I \quad (4.22) $$

where $A$ is the proportionality constant. Integrated intensity is calculated from

$$ I_{\text{bond (mode)}} = \int_{\omega_0} \frac{\alpha(\omega)}{\omega_0} d\omega \quad (\text{cm}^{-1}) \quad (4.23) $$

where $\alpha(\omega)$ is the absorption coefficient, $\omega$ is the wavenumber and $\omega_0$ is the peak wavenumber.

While the absorption coefficient can be defined from the relation [18]

$$ \alpha(\omega) = \frac{1}{d} \ln \left( \frac{I_0}{I} \right) \quad (4.24) $$

where $I_0$, $I$ and $d$ are the intensity of the incident photon, intensity of the transmitted photon and film thickness respectively.

Since absorbance $A_b$ is given by

$$ A_b(\omega) = \log_{10} \left( \frac{I_0}{I} \right) \quad (4.25) $$

Equation 4.24 becomes
\[ \alpha(\omega) = \frac{2.303}{d} A_b(\omega) \]  
(4.26)

where \( A_b \) is the absorbance at wavenumber \( \omega \).

The relation \( \int_{\omega_o} A_b(\omega)d\omega \) gives the area under the absorption band at a particular peak wavenumber \( \omega_o \) whereby its area under the curve is obtained from Equation 4.20 in Section 4.6.

Proportionality constant is determined from the calibration curve of integrated intensity \( I \) versus the atomic ratio content \( x \). The value for \( x \) can be measured from Elastic Recoil Detection Analysis (ERDA) [24,27], Electron Probe Microanalysis (EPMA) [25,28-30], Auger Electron Spectroscopy (AES) [30,31], X-ray Photoelectron Spectroscopy (XPS) [12,24,29,30,32] and Rutherford Backscattering (RBS) [30,33,34]. Atomic ratio \( x \) is also related to the atomic density (concentration) through

\[ C = x C_{Si} = A I \]  
(4.27)

where \( C_{Si} \) is the silicon atomic concentration while \( x = C / C_{Si} \) is the atomic ratio content.

For this work, values for the proportionality constant \( A \) that have been obtained by several workers shall be adopted, as the laboratory is not equip with the facilities required to calibrate the value of \( A \).

In the case of atomic concentration for hydrogen, the concentration \( C_H \) is determined from Si-H and N-H stretching mode respectively [30,33,34], following
the quantitative method developed by Lanford and Rand [35]. They showed that the total density of the hydrogen bonds can be calculated by the equation

\[ C_H = \frac{\text{Area}_{N-H}}{\sigma_{N-H}} + \frac{\text{Area}_{Si-H}}{\sigma_{Si-H}} \]  \hspace{1cm} (4.28a)

where \( \text{Area}_{N-H} \), \( \text{Area}_{Si-H} \) are the areas of the N-H and Si-H stretching-mode absorption peaks and \( \sigma_{N-H} \), \( \sigma_{Si-H} \) are the absorption cross-sections, respectively. Adopting the values obtained by Lanford and Rand from a calibration with nuclear reaction analysis,

\[ \sigma_{N-H} = 7.4 \times 10^{-18} \text{ cm}^2, \sigma_{Si-H} = 5.3 \times 10^{-18} \text{ cm}^2 \]

yields the following equation

\[ C_H (\text{cm}^3) = \frac{1.36 \times 10^{17} \times \{ \text{Total Band Area} \}}{\text{Area}_{Si-H} + 1.4 \text{Area}_{N-H}} \]  \hspace{1cm} (4.28b)

The factor 1.4 is due to the fact that Si-H bond in SiN films was found to have 1.4 times the absorptivity (absorption per bond) of the N-H band. The area under the absorption band is measured as normalised area which is calculated using the relation

\[ \text{Area}, A = A_b \Delta \nu \]  \hspace{1cm} (4.29)

where \( A_b \) is the absorbance and \( \Delta \nu \) is the bandwidth at half-absorbance.

The nitrogen density \( C_N \) is regarded proportional to the Si-N stretching mode at around 860 cm\(^{-1}\) and is estimated as [24,25,28,31,36-38]
\[ C_N = A(Si-N)_s \cdot I(Si-N)_s \] (4.30)

where \( A(Si-N)_s \) is the proportionality constant of the Si-N stretching mode and \( I(Si-N)_s \) is the integrated intensity of the Si-N stretching mode.

4.8 IR Vibrational Mode Quantitative Composition

This section presents the quantitative composition of the film as deduced from the analysis of the IR absorption spectra described earlier in the previous section. The atomic density incorporated into the film is estimated from the integrated intensity of the respective IR vibrational mode.

4.81 Si-H and N-H Stretching Bands

The isolated H-related peaks at 2100 and 3500 cm\(^{-1}\) are discussed separately from the main broad band that occurs around 860 cm\(^{-1}\). Its respective concentration is deduced from the normalised absorption peak area since it has been considered to be proportionately related [35].

4.8.11 Effect of Ammonia to Silane Flowrate Ratio

Figure 4.23 shows the variation in the Si-H (s) mode normalised peak area with ammonia to silane flow rate ratio. The peak area increases with flowrate ratio, from 2 cm\(^{-1}\) at zero flowrate ratio to 7 cm\(^{-1}\) when the flowrate ratio is 5. The peak wavenumber of the Si-H (s) mode shifts towards higher wavenumber as the ammonia flowrate increased from 0 to 50.0 sccm as clearly displayed in Figure 4.24. The
increment shows a linear trend from 2100 to 2207 cm\(^{-1}\) when the flowrate ratio is increased from zero to 5.

The N-H (s) mode only appears when the NH\(_3\) to SiH\(_4\) flowrate ratio is 2, as a tiny emergence in the vicinity of 3500 cm\(^{-1}\). However the presence of the peak becomes more noticeable as the ammonia flowrate increases. The normalised peak area increases gradually from 0.4 to 0.7 cm\(^{-1}\) as the flowrate ratio increases from 1 to 4, and rapidly increases to 1.4 cm\(^{-1}\) at flowrate ratio of 5. The peak position for this mode shifted slightly from 3320 towards 3330 cm\(^{-1}\). Both these trends are displayed in Figures 4.25 and 4.26 respectively.

4.8.12 Effect of Deposition Temperature

Figure 4.27 shows that the density of the Si-H (s) mode, as inferred from its normalised absorption peak area, continuously decreases from 21 cm\(^{-1}\) to 4 cm\(^{-1}\) as the deposition temperature is increased. The variation of the peak wavenumber is displayed Figure 4.28. The peak position shifts slightly from 2204 cm\(^{-1}\) to 2187 cm\(^{-1}\) as the deposition temperature increased from 31 to 200\(^{\circ}\)C. Then it remains around 2187 cm\(^{-1}\), position when the deposition temperature is increased to 250\(^{\circ}\)C. However, when the deposition temperature is increased to 300\(^{\circ}\)C, the peak position shifted to 2213 cm\(^{-1}\).

The N-H (s) mode shows a similar trend as the normalised peak area reduces significantly from 6 cm\(^{-1}\) decreases to 0.4 cm\(^{-1}\). Whereas the peak position however shifts towards lower wavenumber from 3368 to 3343 cm\(^{-1}\) with increasing substrate temperature. These changes are illustrated in Figures 4.29 and 4.30.
Figure 4.23. The variation of the Si-H (s) normalised absorption peak area with ammonia to silane flowrate ratio.
Figure 4.24. The variation of the Si-H (s) absorption peak position with Ammonia to Silane flowrate ratio.
Figure 4.25. The variation of the N-H (s) normalised absorption peak area with Ammonia to Silane flowrate ratio.
Figure 4.26. The variation of the N-H (s) absorption peak position with Ammonia to Silane flowrate ratio.
The plot shows a monotonic decrement of the Si-H (s) normalised absorption peak area with increasing deposition temperature.
Figure 4.28. The shift in the Si-H (s) peak wavenumber with substrate temperature.
Figure 4.29. Figure depicting the normalised peak area of the N-H(s) mode reduces with increasing substrate temperature.
Figure 4.30. The changes of the N-H (s) peak wavenumber with substrate temperature.
4.82 Components of the Overlapping Profiles

Regardless of whether the samples were prepared with or without NH₃, the IR spectrum produced a major broad band in the region 600-1200 cm⁻¹. The components underlying the broad band were reproduced by superposition of Gaussian profiles using least - squares method as described in Section 4.71.

For the spectrum of samples from batch 1 consisting of samples R7 - R11 (that were prepared with NH₃), this broad band could be deconvoluted into 5 components at around 650 cm⁻¹, 840 cm⁻¹, 950 cm⁻¹, 1040 cm⁻¹ and 1170 cm⁻¹. These bands were assigned as the Si-H wagging mode (w), the Si-N stretching mode (s), the Si-N stretching mode, the Si-O stretching mode and the N-H bending mode (b) respectively. For sample R12 however the spectrum could only be deconvoluted into 4 components. The absorption band at around 650 cm⁻¹ is attributed to Si-H wagging mode, whereas the absorption bands at 790 cm⁻¹ and 877 cm⁻¹ most likely originated from H bond-bending sites with more than one H atom, and the 1010 cm⁻¹ band could be related to the Si-O stretching mode.

As from samples of batch 2, the same components were obtained, however, at lower substrate temperatures of 31 and 100°C another component emerges around 745 cm⁻¹, that is assigned to polyhydride (Si-H)ₙ mode.

Figures 4.31a-f show the experimental and the simulated IR absorption curves obtained for samples from batch 1. The respective curves for samples obtained from batch 2 are presented in Figures 4.32a-f. DIS values (goodness of fit criterion) for all the fitted curves are less than 0.02 which support that the simulated curves fit the experimental curve satisfactorily.
The following section detailed the changes of the components of the overlapping bands with deposition parameters.

4.821 Effect of NH$_3$ to SiH$_4$ Flowrate Ratio

The integrated intensity of silicon-rich Si-N (s) mode at around 860 cm$^{-1}$ decreased and that of nitrogen-rich Si-N (s) mode at around 960 cm$^{-1}$ increased as the ammonia flowrate increased. These indicated that more nitrogen were incorporated into the film as the ammonia flowrate was increased. Figure 4.33 shows the variation of the integrated intensity of the Si-rich Si-N mode and Figures 4.34 presents the variation of the N-rich Si-N mode as the NH$_3$ flowrate was increased. The Si-rich Si-N bond concentration varied from 2900 to 5800 cm$^{-1}$ while that of N-rich Si-N bond concentration varied from 560 to 1060 cm$^{-1}$. The peak position for silicon-rich Si-N (s) mode shifted slightly towards higher wavenumber while that of nitrogen-rich Si-N (s) mode varied between 952 cm$^{-1}$ to 958 cm$^{-1}$, as the flowrate ratio was increased. Figures 4.35 and 4.36 demonstrates these trends.

For the N-H (b) mode, the integrated intensity and the peak wavenumber increased with increasing ammonia flowrate. Figures 4.37 and 4.38 depicted these changes. The integrated intensity increased from 150 to 210 cm$^{-1}$ while the peak wavenumber shifted from 1167 towards 1192 cm$^{-1}$.

Another H-related components of the overlapping band is the Si-H wagging mode. The integrated intensity decreased with increasing flowrate ratio, from 1080 to 300 cm$^{-1}$. The peak wavenumbers were centred at around 647 cm$^{-1}$, except when the flowrate ratio was 1 where the peak position shifted to a lower value of 615 cm$^{-1}$. Figures 4.39 and 4.40 show the trends.
Figures 4.31 (a)-(f). Figures illustrate the fitted curves of the IR spectrum for samples prepared with different Ammonia to Silane flowrate ratios (batch 1 samples), in the broad absorption region along with the deconvoluted absorption component peaks.

a) Zero (a-Si Sample)

b) 1:1
c) 2:1

d) 3:1
e) 4:1

f) 5:1
Figures 4.32 (a)-(f). Figures illustrate the fitted curves of the IR spectrum for samples prepared at different substrate temperatures (batch 2 samples), in the broad absorption region along with the deconvoluted absorption component peaks.

a) 31°C

b) 100°C
c) 150°C

d) 200°C
e) 250°C

f) 300°C
The last component of the overlapping band is Si-O (s) mode. Apparently the integrated intensity remained constant at around 1240 cm\(^{-1}\) and the peak position remained at about 1050 cm\(^{-1}\) as the flowrate ratio was varied. The lowest concentration was registered when flowrate ratio was 1 and the highest was recorded when no NH\(_3\) was present during deposition. Conversely the highest peak wavenumber of 1173 cm\(^{-1}\) was observed when flowrate ratio was 1 and lowest peak wavenumber of 1016 cm\(^{-1}\) was recorded when no NH\(_3\) was present during deposition. Figures 4.41 and 4.42 show these variation.

4.822 Effect of Substrate Temperature

Figure 4.43 shows the variation in the integrated intensity of the silicon-rich Si-N (s) band with increasing substrate temperature. The integrated intensity started to increase when the substrate temperature was 100°C and continued to increase when the substrate temperature was 150°C. Consequently it decreased when the substrate temperature was increased further. The integrated intensity increased from 2800 to 3900 cm\(^{-1}\) when the substrate temperature was changed from 100 to 150°C, and from 150 to 300°C the integrated intensity reduced from 3900 to 2100 cm\(^{-1}\). Figure 4.44 shows the variation of the peak position with substrate temperature. The peak wavenumber continually shifted towards lower wavenumber from 867 to 850 cm\(^{-1}\) as the substrate temperature increased.

As for the nitrogen-rich Si-N (s) band, the integrated intensity increased from 480 to 820 cm\(^{-1}\) as the substrate temperature increased from 31 to 250°C before decreasing to 580 cm\(^{-1}\) when the substrate temperature was increased further to 300°C as shown in Figure 4.45. The peak wavenumber shifted from 958 cm\(^{-1}\) to 973
Figure 4.33. The variation of the integrated intensity of the Si-rich Si-N (s) mode at 860 cm\(^{-1}\) with Ammonia to Silane flowrate ratio.
Figure 4.34. Plot of the integrated intensity of the N-rich Si-N (s) mode at 960 cm⁻¹ versus Ammonia to Silane flowrate ratio.
Figure 4.35. Figure depicts the shift of the Si-rich Si-N (s) peak position as the Ammonia to Silane flowrate ratio increases.
Figure 4.36. Figure displays the absorption peak position of the N-rich Si-N (s) mode as the Ammonia to Silane flowrate ratio increases.
Figure 4.37. The variation of the integrated intensity of the N-H (b) mode with Ammonia to Silane flowrate ratio.
Figure 4.37. The variation of the integrated intensity of the N-H (b) mode with Ammonia to Silane flowrate ratio.
Figure 4.38. The graph shows the shift in the peak absorption position of the N-H (b) mode as Ammonia to Silane flowrate ratio increases.
Figure 4.40. The figure shows the shift in the peak absorption position of the Si-H (w) mode as the Ammonia to Silane flowrate ratio increases.
Figure 4.41. The variation of oxygen content in the film with Ammonia to Silane flowrate ratio as deduced from the integrated intensity of the Si-O (s) mode.
Figure 4.42. The peak position of the observed Si-O (s) bands as the Ammonia to Silane flowrate ratio increases.
cm\(^{-1}\) as the substrate temperature varied from 31 to 150\(^{\circ}\)C, and when the substrate temperature was increased to 300\(^{\circ}\)C the peak wavenumber shifted to a lower position of 968 cm\(^{-1}\), as shown in Figure 4.46.

The variation of the integrated intensity of the N-H (b) mode with substrate temperature is shown in Figure 4.47. The figure displays that generally the integrated intensity decreased with increasing substrate temperature. The integrated intensity initially increases slightly from 600 towards 800 cm\(^{-1}\) for substrate temperature of 31 to 100\(^{\circ}\)C, and when the substrate temperature was increased further from 100 to 200\(^{\circ}\)C the integrated intensity dropped abruptly to 100 cm\(^{-1}\) and remained at this value when the substrate temperature was increased to 300\(^{\circ}\)C. A similar variation in the peak wavenumber is observed in Figure 4.48 where the peak position shifted to higher wavenumber from 1190 to 1208 cm\(^{-1}\) as the temperature changed from 31 to 100\(^{\circ}\)C and when the substrate temperature was increased further the peak wavenumber shifted towards lower wavenumber from 1208 to 1188 cm\(^{-1}\).

The variation of integrated intensity of the Si-H (w) mode with substrate temperature is presented in Figure 4.49. The integrated intensity increased from 820 to 1500 cm\(^{-1}\) when the substrate temperature was increased from 31\(^{\circ}\)C to 100\(^{\circ}\)C, and decreased from 1500 to 310 cm\(^{-1}\) when the substrate temperature was increased further from 100 to 300\(^{\circ}\)C. The peak wavenumber shifted towards lower wavenumber as the substrate temperature increased, from 656 towards 652 cm\(^{-1}\) as shown in Figure 4.50.

At low substrate temperature of 31\(^{\circ}\)C (RT) and 100\(^{\circ}\)C, another H-related component i.e the polyhydride (Si-H)_n (s) mode, emerged at around 745 cm\(^{-1}\). This
band was reduced when the substrate temperature was increased to 100°C and disappeared when the substrate temperature was 150°C.

The variation of the Si-O (s) mode integrated intensity with substrate temperature is presented in Figure 4.51. The integrated intensity continually decreased with increasing substrate temperature, from 3900 to 1330 cm⁻¹. The peak wavenumber shifted towards lower wavenumber from 1066 to 1051 cm⁻¹ as the substrate temperature increased, as shown in Figure 4.52.
Figure 4.43. The changes of the integrated intensity of the Si-rich Si-N(s) absorption mode with substrate temperature.
Figure 4.44. The shift in the peak position of the Si-rich Si-N (s) mode as the substrate temperature increases.
Figure 4.45. Figure presents the variation of the integrated intensity of the N-rich Si-N (s) mode with the substrate temperature.
Figure 4.46. The absorption peak position of the N-rich Si-N (s) mode as the substrate temperature increases.
Figure 4.47. Figure shows the variation of the integrated intensity of the N-H (b) mode with substrate temperature.
Figure 4.48. The shift in the peak absorption position of the N-H (b) mode as the substrate temperature increases.
Figure 4.49. The changes of integrated intensity of the Si-H (ω) absorption mode with deposition temperature.
Figure 4.50. The shifts in the peak absorption position of the Si-H (v) mode as the substrate temperature increases.
Figure 4.51. The variation of oxygen content in the film with deposition temperature as deduced from the integrated intensity of the Si-O (s) mode.
Figure 4.52. The peak position of the observed Si-O (s) bands as the deposition temperature increases.
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