CHAPTER 5. DISCUSSION

The properties of the glow discharge SiNH thin films are strongly dependent on the film composition i.e. the [N]/[Si] ratio and hydrogen content [1], which are mainly dependent on the flow ratio of the reacting gases NH₃:SiH₄ [2,3]. The mole fraction of nitrogen atoms to silicon atoms x can be approximated by [4]

\[ E_g(x) = 1.5 + 3.5 \left( \frac{3}{4}x \right)^2 \text{ (eV)} \]  \hspace{1cm} (5.1)

The above relation suggests a quadratic dependance of optical energy gap on the concentration of the incorporated nitrogen atoms. This approximation of the x value shall be adopted in this work.

Figure 5.1 presents the changes of the nitrogen to silicon ratio x with NH₃:SiH₄ gas flow ratio R. The N/Si ratio x increases smoothly from zero towards 0.88 as the gas flow ratio R increase from zero to 5. It is interesting to note the log-log plot of Figure 5.1, as presented in Figure 5.2. The plot shows a linear correlation which yields the dependance of N/Si ratio x to the gas flow ratio R, in the experimental regime, of the form

\[ x = CR^a \]  \hspace{1cm} (5.2)

Values of C=0.6 and a=0.3 are obtained in this work. The linear behaviour of \( \log_{10}X \) versus \( \log_{10}R \) plot agrees with others published work reported. Bustarret et al [5] reported a square-root dependence, i.e. C=1 and a=0.5. Whereas Noguchi [6]
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Figure 5.1: Figure illustrate the changes of [N]/[Si] ratio x as the flowrate ratio increases. x value is estimated according to a quadratic dependence with energy gap.
Figure 5.2. Log x versus log R graph displays a linear dependence. R is the ammonia to silane flowrate ratio.
reported a stronger dependance of N/Si ratio $x$ upon $\text{NH}_3$-$\text{SiH}_4$ gas flow ratio $R$, i.e. $a=1$.

5.1 Dependence on Ammonia to Silane Flowrate Ratio

5.1.1 Bonds in as-deposited films

The IR vibrational absorption has been utilized to signify the chemical composition and bonding configuration of the deposited nitride films as it provides the most direct information. The broad and dominant IR vibration extended from 700-1000 cm$^{-1}$ and centred around 860 cm$^{-1}$, reveals the incorporation of N through the Si-N matrix absorption mode [7]. Its shape reflects the broad distribution of Si-N vibration energies owing to the large variation in binding energies in the amorphous films [8]. Decomposition of the main broad feature centred around 860 cm$^{-1}$ yields 5 components identified as; Si-N (s) bondings around 860 and 960 cm$^{-1}$ [9-11], N-H (b) bonding around 1175 cm$^{-1}$, Si-H (w) bonding around 630 cm$^{-1}$ and finally Si-O (s) bonding around 1000 cm$^{-1}$. The presence of H has been readily detected in the vicinity of 2100 cm$^{-1}$ and 3300 cm$^{-1}$, ascribed to as the stretching absorption modes of the Si-H and N-H respectively. All the bonding configuration observed can be summarized as follows: the Si-N bondings with two stretching absorption modes around 860 and 960 cm$^{-1}$; the N-H groups, characterized by stretching vibration around 3330 cm$^{-1}$ and bending vibration at 1175 cm$^{-1}$; the Si-H groups, namely the stretching vibration at 2100 cm$^{-1}$ and the wagging vibration near 630 cm$^{-1}$; and finally the Si-O stretching vibration detected around 1000 cm$^{-1}$. The concentration of the respective absorption bands has been evaluated in terms of its integrated intensity, as detailed earlier, given by the expression
\[ I(\omega_0) = \int \frac{\alpha(\omega)}{\omega} d\omega \] 

(5.3)

where \( \alpha \) is the absorption coefficient at the wavenumber \( \omega \) for the mode centred at \( \omega_0 \).

Concerning the Si-N bondings, generally the absorptions around 860 cm\(^{-1}\) is attributed to asymmetric stretching of a Si-rich Si-N bonding. Whereas the mode around 960 cm\(^{-1}\) is regarded originated from a more N-rich Si-N bonding [9]. The nitrogen concentration in the films is deduced from the sum of the integrated intensity of both the Si-N absorption modes [11], as shown in Figure 5.3. Although there is some scatter in the plot, the curve is in increasing trend. Nitrogen content increases slowly with increasing gas flow ratio. Figures 5.4 and 5.5 illustrate the changes of the Si-N bonding concentrations with the N/Si ratio \( x \). The changes displayed suggest that as the Si-matrix becoming N-rich, the integrated intensity of the 860 cm\(^{-1}\) mode decreases while that of 960 cm\(^{-1}\) mode increases with increasing \( x \).

Della et al [9] proposed that the 860 cm\(^{-1}\) mode is due to the vibration of the trigonal Si\(_3\)N site, in agreement with the vibration modes of the crystalline silicon nitride. This vibration is present in the one-phonon density of states (DOS) of \( \alpha - \) and \( \beta - \) Si\(_3\)N\(_4\) and becomes IR-active in a-SiN due to the lattice disorder. Further, they attributed the 960 cm\(^{-1}\) mode to a 13-atom Si-(NSi\(_2\))\(_4\) "stoichiometric clusters" precursors of the crystal structure, i.e. assuming that this minimum stoichiometric clusters produces a "crystal-like" vibration extends up to the third nearest neighbour.

Watanabe et al [12] evaluated the molar ratio of nitrogen to silicon \( x \) by using the integrated intensity of the Si-N absorption. They approximated the number of Si
Figure 5.3. Plot shows the total nitrogen concentration as measured from the sum of the integrated intensity of the Si-rich and N-rich Si-N absorption mode.
Figure 5.4. Graph of integrated intensity versus N/Si ratio x for the Si-rich Si-N (s) absorption mode.
Figure 5.5. Graph of integrated intensity versus $\text{N/Si ratio } x$ for the $\text{N-rich Si-N (s)}$ absorption mode.
atom per unit volume as $5 \times 10^{22} \text{ cm}^{-3}$, adopted from the data on Si wafers implanted by nitrogen by Yadav et al [13], and they claimed this approximation is fairly adequate. Figure 5.6 compares the N/Si ratio $x$ as calculated by assuming the Si concentration of $5 \times 10^{22} \text{ cm}^{-3}$ and proportionally constant of $9.2 \times 10^{18} \text{ cm}^{-2}$ [12], and to that obtained from the relation between optical energy gap and composition $x$ (Eq. 5.1). The result indicates a fair agreement between these estimates.

The hydrogen is detected bonded to nitrogen through the stretching and bending vibration near 3330 and 1175 cm$^{-1}$ respectively. The N-H group absorptions grow stronger as the nitrogen content increases. The N-H stretching vibration is identified by the tiny emergence around 3330 cm$^{-1}$ and the signal becomes more noticeable as the nitrogen content rises. Figure 5.7 and 5.8 show the increasing trends of the integrated intensity of the N-H group vibration as a function of nitrogen content $x$. Most probably, the trend implies that with increasing nitrogen incorporation the Si-Si and Si-H bonds are partially substituted by the Si-N-H groups [14].

The Si-H groups are observed with two bonding configurations, i.e. the stretching vibration located around 2100 cm$^{-1}$ and the wagging vibration around 630 cm$^{-1}$. The Si-H(s) bonding concentration increases with increasing nitrogen content, $x$ and when $x=0.88$, the increase is abrupt, as depicted in Figure 5.9. The same trend is observed in the changes of the N-H (s) concentration in Figure 5.7. Observations producing similar trends are reported previously [15-17], but with different rates of variation. Whereas for the wagging mode, the concentration rises gradually for $x \leq 0.55$, drops rapidly at $x = 0.72$ and the concentration then remains nearly constant, as shown in Figure 5.10.
Figure 5.6. Comparison between the N/Si ratio obtained from the intensity of the Si-N (s) IR absorption and the value as estimated from the energy gap dependance.
Figure 5.7. Figure depicts the changes of the concentration of the N-H (s) mode with x. The concentration is deduced from its normalised peak area [39].
Figure 5.8. The integrated intensity variation with N/Si ratio x of the N-H (b) mode shows an increasing trend although there is some scatter in the plot.
Figure 5.9. The changes of the Si-H (s) bonding mode concentration with N/Si ratio x. As for the N-H (s) mode, the bonding concentration is elaborated in terms of its normalised peak absorption area.
Figure 5.10. Integrated intensity of the Si-H (w) mode as a function of N/Si ratio x.
Total hydrogen content in the film is elaborated as the sum of the Si-H (s) and N-H (s) vibrational modes, after the method proposed by Lanford and Rand [18], i.e. Eq. 4.28. From Figure 5.11, it can be noted that the hydrogen content increases markedly with the nitrogen content, especially for x > 0.8. Interestingly the total hydrogen content of the films are comparatively lower to that reported by other workers, using the same method developed by Lanford and Rand; for example Giorgis et al [15] and Makino et al [41] reported values in the magnitude of $10^{-21}$ to $10^{-22}$ cm$^3$ for nitride films prepared from SiH$_4$/NH$_3$ mixtures and at substrate temperature of 200°C and 350°C respectively. For all samples the concentration of the Si-H (s) bonds is nearly four times higher than that of N-H (s) bonds, thus the hydrogen contents is primarily due to the increase of Si-H bonds although for x > 0.8 the rise in the N-H bond concentration also causes a slight rise in the overall hydrogen concentration. As the hydrogen is mainly bonded to silicon, even at N/Si ratio x around 0.9, implies that dehydrogenated nitrogen atoms are predominantly incorporated into the silicon matrix.

It has been observed that glow discharge nitride films containing more nitrogen atoms tend to contain more hydrogen atoms at a given substrate temperature, which suggests that the nitrogen incorporation has a role in retaining the hydrogen effusion from the solid phase during plasma deposition [19]. This fact is most probably due to the the differences in bond angle between the Si-Si-Si and Si-N-Si configurations (due to the sp$^3$ hybrid orbital of the Si atom and sp$^2$ hybrid orbital of the N atom respectively) and in bond lengths between Si-Si (3.01Å) and Si-N (1.75Å) [20]. As the N/Si ratio x increases and the N atom replaces the Si atom
at random, stress is induced in the amorphous network. Releasing of this stress seems to be a reason for the increase in H bonds.

An appreciable amount oxygen incorporation is also detected in the form of Si-O stretching vibration in the vicinity of 1000 cm\(^{-1}\). The presence of oxygen in nitride films has been reported [21]. Evidence of oxygen incorporation may also be deduced from the low value of refractive index measured [22], as shall be provided preceedingly. There are a few possible sources contributed to the oxygen contamination. Moisture or oxygen released from the surfaces of the reaction chamber during preparation is thought to be more likely the source [21]. Paloura however pointed out experimentally, that glow discharge wall sputtering of the reaction chamber can lead to high oxygen contamination [23]. In this work the normal microscope glass slides are used to deposit films for UV-Vis spectrum characterization. It is strongly believed that continuous energetic ion bombardments onto these substrates, and particularly in a dc-induced field, causes the oxygen to be sputtered out from the glass substrate and consequently incorporated into the films. The oxygen content is found to lie nearly at a constant concentration around 1200 cm\(^{-1}\) as evaluated from the integrated intensity of the Si-O (s) mode absorption, as depicted in Figure 5.12. The roughly constant oxygen concentration incorporated into the films may indicate that it was originated from a common source. Another indication to the oxygen content is the Si-O (s) mode peak wavenumber [24]. An increase in oxygen content leads to a shift in the Si-O (s) mode absorption peak towards higher wavenumber. Figure 5.13 represents the changes of the absorption peak wavenumber with its concentration and definitely complies with the above mentioned trend.
Figure 5.11. Figure displaying the variation of the total hydrogen concentration as the nitrogen content increases.
Figure 5.12. The oxygen concentration detected in the prepared samples.
Figure 5.13. The variation of the absorption peak position of the Si-O (s) band.
5.12 Properties of as-deposited films

The plot of optical energy gap $E_\text{g}$ with N/Si ratio $x$ is shown in Figure 5.14. $E_\text{g}$ increases gradually for $x \leq 0.55$ and $E_\text{g}$ widening occurs after $x > 0.55$, i.e. around 0.72. Previous studies on the SiNH alloys optical gap are in agreement with this trend [1,4,25-27], that it increases slowly and roughly linearly at lower value of $x$ and later increases sharply as stoichiometry is approached. The opening the the optical gap around $x=0.72$ is in close agreement as reported by Lin and Lee [25]. They found an abrupt changes occurs around $x=0.8$. However other workers published a higher value of $x=1.1$ [1,4,26].

The presence of 2 different $x$ regions implies that the factors producing the absorption edge, i.e. the Si-Si bonding network [28], are changing at the concentration where the discontinuity occurs. At lower N content region, $E_\text{g}$ is due to the extended path of Si-Si bonding. $E_\text{g}$ increases with increasing $x$ as its optical absorption is similar to a-SiH, modified by the presence of N [2]. In a-Si:H, the valence and conduction band are due the bonding and antibonding orbital of Si $(3s,3p^3)$ hybridization. When a N atom is a neighbour to Si-Si bond, the Si-Si bond energy is considered to increase. Since the N atom is more electronegative than the Si atom, the Si atom forming the Si-N bond becomes positively polarized. Due to this polarization, the Si-Si bonding energy is expected to increase. Consequently, the energy level of the antibonding state shifts upward and the bandgap energy increases as observed in the optical absorption.

As the N content is increased, more Si-Si bonds are replaced by the Si-N bonds. Finally when the concentration of the Si-Si bonds fall below the concentration where the Si-Si bonds fail to form a continuous percolation path across the network
Figure 5.14. Figure displays the variation in optical energy gap as the nitrogen content increases.
(the Si-Si bonds only form a series of disconnected clusters), the optical gap opens up leading to a more insulating material [28]. Martinez and Yndurain [29] proposed that this phenomena occurs when the Si-Si bond concentration falls below 25%.

Experimental and theoretical calculation supported that hydrogen incorporation into a plasma nitride plays an important role in modifying its properties [2]. Hydrogenation has a contribution in widening the optical gap particularly on the Si-rich side [2,3,30]. Hydrogenation has a strong tendency to replace Si-Si bonds with Si-H and N-H bonds in the Si-rich region and to replace Si-N bonds with Si-H and N-H bonds in the N-rich region. Theoretical calculation utilizing Tight-Binding Model revealed that replacement of Si-Si bonds with two Si-H bonds lowers the valence band $E_v$ and has little effect on the conduction band $E_c$ as in a-Si-H, hence increases $E_g$ in the Si-rich region [3]. However in the N-rich region, replacing Si-N bonds with Si-H and N-H bonds has little effect on the optical gap as Si-N bonds do not determine the band edges whilst Si-Si bonds are still present. Therefore hydrogen incorporation into a nitride films deposited by glow discharge is expected to raise $E_g$ only in Si-rich region but not in N-rich region. This has been reported experimentally by Davis et al [30]. They reported that the hydrogenation influenced the variation of the band gap in the SiN films up to $x \leq 1.0$ and thereafter the band gap of the films are independent of whether or not contain hydrogen. Figure 5.15 displays the plot of $E_g$ against the hydrogen concentration. The hydrogen concentration is estimated from the IR stretching absorption of the Si-H and N-H bands. The results are in agreement with the above mentioned arguments. The influence of hydrogenation towards widening the optical gap appears to be less dominant as the N/Si ratio $x$ increases,
Figure 5.15. Graph displays the relation between the energy gap and the hydrogen content.
and finally for \( x > 0.8 \) increment in hydrogen concentration does not result in opening the optical gap further.

The behaviour of low energy refractive index or static refractive index \( n_0 \) with N/Si ratio \( x \) is displayed in Figure 5.16. For \( x \leq 0.55 \), \( n_0 \) remains around 2.3. An abrupt drop occurs for \( x > 0.55 \). \( n_0 \) decreases almost linearly from 2.3 towards 1.7. The tendency of decreasing \( n_0 \) with the N/Si ratio \( x \) is also reported by earlier workers [5,16,28,30]. This decrease may be viewed in terms of the increasing amorphous network density as more Si-Si bondings are replace by the Si-N bondings [20]. The longer 3.01 Å Si-Si bond length definitely will produce a less denser network compared to the 1.75 Å Si-N bond length. With increasing number of Si-N replacing the Si-Si bonds, the network becomes denser and hence \( n_0 \) lowers. However the refractive index values obtained in this work are slightly lower compared to the reported values. Davis et al [30] for instance reported \( n_0 \) decreases from 3.7 towards 2.2 as \( x \) increases from zero to 0.9. Whereas Classen et al [31] reported for \( x \) values ranges between 0.6 and 1.4, \( n_0 \) decreases linearly from 2.68 towards 1.90 with increasing \( x \). A semiempirical relation between the N/Si ratio \( x \) and the refractive index has been proposed by Makino [32]. The refractive index of the a-Si\( _x \)N\( _4 \)-H alloy is proposed to be a representation of a bonding-density-weighted linear combination of refractive indices of a-Si:H and a-Si\( _x \)N\( _4 \), according to

\[
n(x) = \frac{n_{Si} + \frac{3}{4}x\left(2n_{Si3N_4} - n_{Si}\right)}{1 + \frac{3}{4}x} \quad (5.4)
\]

Choosing the values \( n_{Si} = 3.3 \) and \( n_{Si3N_4} = 1.9 \), Bustarret [5] supported that the correlation between between N/Si ratio \( x \) and refractive index as proposed by Makino
Figure 5.16. Figure shows the changes of static refractive index with N/Si ratio x.
provides a reliable dependencies. They compared N/Si ratios deduced from X-ray Photoelectron Spectroscopy (XPS), Elastic Recoil Detection Analysis (ERDA) and refractive index-atomic density relation. The agreement between these data is remarkable. Figure 5.17 depicts the comparison between the refractive index values calculated from the optical method and with that deduced from the N/Si ratio according to Eq. 5.3. Discrepancies between these two curves seems wide apart. However the discrepancies are most probably caused by the oxygen incorporation found in the deposited SiNH alloys. Oxygen impurities known has an effect in reducing the refractive index [22]. The oxygen concentration incorporated into the films is given in Figure 5.12. Comparing the oxygen concentration of the films and the variation the the two curves in Figure 5.17 proofs the expected explanation. The highest oxygen concentration registered at R = 0, yields the largest discrepancies between the two curves at x = 0; and on the other hand the smallest oxygen concentration detected for R = 1 sample, resulted in the closest values between the two curves. Whereas as the oxygen concentrations are almost the same for R ≥ 2 samples, the portion x ≥ 0.72 in Figure 5.17 are nearly parallel.

The average deposition rate of the films are relatively lower compared to that produced by alternating-current excitation glow discharge. In the present work the values measured are not more than 5 nm/min, as compared to the frequently cited values around 12 nm/min [33]. In the preparation of a non-conducting material in a dc-induced field, the resulting film will rapidly coat one or both electrodes, reducing the conduction path and hence reducing the film growth rate significantly. Variation of the average deposition rate as a function of flowrate ratio R, reillustrated in Figure 5.18, exhibits two separate changes. A decreasing film growth rate as the flowrate
ratio R increases (from zero towards 3) at a given deposition temperature has been reported in literatures [2,34]. The film growth rate is said to be limited by the supply rate of silane reacting species to the substrate surface region or the plasma sheath zone [34]. As the ammonia flowrate increases while that of silane fixed, the density of the silane reacting species in the gas phase are low compared to the density of the Si in the solid phase. Since the film deposition proceeds by network formation of Si-N bonds, the growth rate reduces.

At higher flowrate ratio R>3, the film average deposition rate rises slightly. As the silane concentration is maintained at 10 sccm for this particular batch of samples, it indicates that at high flowrate ratios the dissociation of silane is enhanced. This could be viewed by the increase in the fast electron concentration with an increase in ammonia gas supply, which in turn enhances the ionization efficiency. Sasaki et al [19] results may support this observation. They deposited SiNₓ:H alloys from SiH₄/N₂/H₂ mixtures and recorded an almost constant films growth rate of 2-3 Å/s as the nitrogen flowrate increases from 0 to 80 sccm, while maintaining a fixed silane flowrate of 10 or 20 sccm. When the nitrogen flowrate was raised further to 100 sccm the film growth rate rose abruptly towards 10 Å/s, and they explained the phenomenon in term of enhanced silane dissociation caused by the exceeding nitrogen flow.

5.2 Dependance on Substrate Temperature

The variation of SiNₓ:H films properties with substrate temperatures are also related to the changes in the structure and composition of the films. High temperatures stimulates the rearrangement of atoms and ions on the substrate surface
Figure 5.17. Plot illustrates the comparison of the refractive index values as measured from two different techniques.
Figure 5.18. Average deposition rate as a function of ammonia to silane flowrate ratio $R$. 
hence resulting films with fewer defects [35]. Therefore it has been noted that films deposited at higher temperatures have an almost perfect structure, i.e. the closest to stoichiometric composition, the higher density and the lower hydrogen content [36].

5.2.1 Bonds in as-deposited films.

The IR absorption of the films detected are typically similar to that described previously, a pronounced broad vibration band lies between 700 to 1100 cm\(^{-1}\), contributed mainly by the Si-N matrix absorption. However the changes of the IR absorption with regards the deposition temperature are particularly interesting, not much information can be acquired from literatures regarding this behaviour. Blaauw [37] for instance studied the preparation and characterization of plasma silicon nitride as a function of several parameters, including systematically varying the deposition temperatures 20-500°C, however no coverage was made on the effect of deposition temperature on the IR spectrum.

The broad band IR absorption in the region 700-1100 cm\(^{-1}\) continuously 'shrink' as the substrate temperature rises, the changes is displayed again in Figure 5.19. At lower substrate temperature of 31°C (room temperature) and 100°C, the contribution of at least three components are clearly observed through the distinctive sharp features of the broad spectrum. Decomposition of the broad spectrum resulted in 5 components, as previously reported, namely the Si-N vibrations around 840 cm\(^{-1}\) and 960 cm\(^{-1}\), N-H bending vibration at 1175 cm\(^{-1}\), Si-H wagging vibration around 630 cm\(^{-1}\) and finally the Si-O stretching vibration in the region 1000 cm\(^{-1}\). However at low substrate temperatures, i.e. 31°C and 100°C, another component is discovered around 750 cm\(^{-1}\) and most probably attributed to the SiH\(_2\) scissoring mode.
Figure 5.19. The significant variation of the main broad absorption region with deposition temperature.
This component may have resulted from an incomplete bond-breaking process during low deposition temperature [38]. The Si-H and N-H stretching vibrations are also observed.

The overall concentration of the Si-N bonds initially increases with increasing substrate temperature, from RT to 150°C, however towards 300°C the bond concentration decreases markedly, as shown in Figure 5.20. It is known that higher deposition temperature promotes the plasma reaction probability and most likely this fact contributed to the increment of N-incorporation as the temperature rises from RT to 150°C. Nevertheless higher deposition temperature also has the effect of reducing the sticking coefficient of the plasma active species [39]. It has been suggested that the sticking coefficient of the nitrogen species decrease faster than the sticking coefficient of the depositing silicon species [39]. Hence it seems that the subsequent decrease in the nitrogen content of the films beyond the depositing temperature of 150°C, may be due to this factor.

The concentration of the N-rich Si-N component around 960 cm⁻¹, referred to as a minimum stoichiometric clusters site, rises almost linearly and only drops at a higher temperature of 250°C as compared to the Si-rich Si-N trigonal site (vibrates around 840 cm⁻¹) that decreases beyond 150°C, as reillustrated in Figures 5.21 and 5.22. This may indicate that higher deposition temperature stimulates the growth of a more ordered Si-N network. However at higher temperature 300°C the more dominant effect of reduced sticking coefficient of the active species, and especially in a DC-induced field where the substrate is continuously exposed to prolonged energetic ion bombardments, the network diminished.
Figure 5.20. The variation of the total nitrogen concentration of the films when the deposition temperature increases.
Figure 5.21. The changes of the integrated intensity of the Si-rich Si-N (s) absorption mode with substrate temperature.
Figure 5.22. Graph presents the variation of the concentration of the N-rich Si-N (s) absorption mode with substrate temperature.
Hydrogen content decreases with increasing substrate temperature based on the vibrational spectra result. Absorption due to Si-H and N-H stretching bonds, whose concentrations are customary regarded as a measure of the hydrogen content in IR analysis, decreases rapidly as substrate temperature increases. Figure 5.23 shows the total hydrogen content as a function of deposition temperature. The decrease is most probably due to the re-evaporation of weakly bonded hydrogen from the films and increasing decomposition rate of H-containing species with increasing temperature [35]. The almost exponential behaviour of the reduction of the hydrogen concentration with increasing deposition temperature is also reported by Gupta et al [33].

Oxygen incorporation into the films is detected as Si-O stretching vibration. Its concentration measured through the integrated intensity is found to decrease prominently as the deposition temperature increases. This changes is consistent with the shift in peak wavenumber towards lower frequency as the peak wavenumber is regarded a reliable approximation to its concentration, refer to Figure 5.24. Films with higher oxygen content registers a higher peak absorption frequency. The decreasing trend of the oxygen content with increasing substrate temperature seems to indicate that the oxygen contamination is contributed by the moisture trapped in the surfaces of the deposition chamber. At higher temperature the moisture is more likely to be desorbed from the surfaces and pumped out prior to deposition. Therefore with increasing temperature less oxygen content is detected in the films. Zhang et al [22] reported a compositional transition from that of silicon dioxide through silicon oxynitride to silicon nitride as the deposition temperature rises, of films deposited from SiH₄/NH₃/N₂ mixtures by a soft vacuum electron beam assisted
Figure 5.23. Figure illustrates the total hydrogen content of the films as the substrate temperature increases.

Total Hydrogen Concentration (1/cm³)
Figure 5.24. Figure displaying the variation of the concentration of the Si-O (s) absorption mode and the shifts of the peak wavenumber.
chemical vapour deposition (EBCVD). At 50°C, the major film composition detected was that of SiO₂, although they reported the substrate had been prebaked at temperature higher than 350°C for several hours. As the temperature increases, IR absorption revealed the spectrum of silicon oxynitride and finally at 350°C the spectrum was that of silicon nitride. They ascribed the large amount of oxygen originated from the limited background vacuum (~10⁻³ Torr) and moisture released from the feedstock gases, substrate and the inner wall of deposition chamber. Further they attributed the incorporation of oxygen into the films at low substrate temperature are due to a temperature sensitive preference of the radical adsorption (sticking coefficient), in which chemical reaction on the substrate surface favours the oxygen precursors than that for nitrogen species hence resulted the formation of SiO₂ film. In the present work the film deposited at room temperature as low as 31°C showed the IR absorption of a silicon oxynitride with a dominant contribution of Si-O vibration. The decreasing oxygen incorporation as a function of substrate temperature is in agreement to that reported by Zhang et al. Their high oxygen content film prepared at 50°C however may due to the low background vacuum which resulted a higher background residual oxygen. The observed formation of SiO₂ is interesting since they employed a very much higher ammonia to silane flowrate ratio of 60 compared to a ratio of 3 used in this work and moreover with a lower deposition temperature. Their explanation of a preferential adsorption of oxygen species at lower temperature seems supportive. However the quantitative comparison of other IR absorption components are not provided in detail.
5.22 Properties of as-deposited films.

As the substrate temperature increases, a gradual shifts to lower energy gap is observed, from 3.66 eV towards 2.71 eV. A similar trend is found by others [33,40,41]. For temperatures above 150°C the decrease in $E_g$ seems to be concurrent with the drop in total nitrogen concentration in the films but in the temperature region of 31°C to 150°C, an increase in the total nitrogen content still results in the decrease in $E_g$ from 3.66 to 3.32 eV, as illustrated in Figure 5.25. The result implies that there is other factor contributing to the decrease in $E_g$, i.e. apparently attributed to the great influence of growth temperature to the hydrogen incorporation into the layers. This fact is supported by the results published by Schalch et al [8]. They reported a strong shift in $E_g$ as more hydrogen in added (0-44%) during the sputtering of silicon target in a pure nitrogen environment. The shift in $E_g$ is assumed to be due to the compensation of weakly bound localized states present in the band gap of the amorphous nitride. They however did not measure the amount of hydrogen incorporated into the films. Another evidence is that a decreased in hydrogen content after an annealing treatment above the deposition temperature is followed by a reduced bandgap [33,42]. Figure 5.26 illustrates the variation of $E_g$ as a function of total hydrogen concentration.

The graph depicts that the reduction in the total hydrogen concentration as the substrate temperature increases, is accompanied by a shift in the energy gap towards lower energy. From the plot it seems hydrogen has a role in widening the energy gap, concurrent to that reported by Schalch. The higher rate of hydrogen loss in the temperature range of 31 to 150°C contributes to the decrease in $E_g$, despite of the fact that N/Si ratio increases in this region. Beyond 150°C, both the hydrogen content
Figure 5.25. The variation of the total nitrogen concentration of the films and its energy gap as the deposition temperature rises.
Figure 5.26. Plot displays the relation between energy gap and total hydrogen concentration.
and the N/Si ratio decrease with the shifts in $E_g$ towards lower value. Therefore it is difficult to separate which factor plays a more dominant role in determining the $E_g$. Figure 5.27 plots the changes of N/Si ratio with temperature, comparing the values obtained from the IR absorption and through the quadratic dependance of $E_g$ on N/Si ratio, i.e. Eq. 5.1. The two estimates fit considerably well for the substrate temperature above 150°C and deviate significantly at lower temperature. This discrepancy supports the observation for deposition temperature below 150°C that hydrogen content plays a more dominant role than N/Si content in determining the $E_g$, hence Eq. 5.1 predicts a higher N/Si ratio from the respective $E_g$ values. Another possible remark can be extracted from Figure 5.27 is that as the two curves fit closely beyond 150°C, thus it appears that the more dominant factor contributing to the $E_g$ shifts in this region is the N/Si ratio.

The increase in refractive index with deposition temperature are also observed by other investigators, and are mostly related to the increase in the density of the films [31,33,37,43]. As the deposition temperature increases, the contribution of the N/Si content becomes less significant. An increase in the film density with increasing growth temperature is reported to be regardless of the change in the N/Si content [36]. Hence the refractive index continue to rise as a result of the more dominant density effect overshadows the N/Si content effect [44]. Figure 5.28 evidently displays the refractive index increases with deposition temperature and irrespective of the variation of the N/Si content. The refractive index values obtained in this work is found to be slightly lower compared to that obtained by Blaauw [37]. He reported a change from about 1.6 to 1.9 as the temperature increases towards 300°C, however the respective N/Si ratio and hydrogen concentration are not provided. Most likely
Figure 5.27. Comparison between the N/Si ratio values estimated through a quadratic dependence on \( E_g \) (i.e. Eq. 5.1) to that obtained from the Si-N IR absorption intensity.
Figure 5.28. Figure illustrates the variation of refractive index and N/Si ratio against substrate temperature.
the low refractive index observed is due to the presence of non-negligible oxygen incorporation.

The higher deposition temperature results in an increase in the rate of diffusion of reactive species on the substrate surface and therefore a decrease in film growth rate with increasing temperature [33]. Figure 5.29 depicts the decrease in the average film deposition rate as the substrate temperature increases. The decrease in the deposition rate is also reported to be influenced by the reaction probability of the reacting source gases and the sticking coefficient of the depositing species [39]. At higher temperature the reaction probability increases, but the sticking coefficient decreases. Knolle and Osenbach [39] suggested that the sticking coefficient of the nitrogen species decrease at a faster rate than that of the silicon species, and this decrease leads to an overall decrease in the deposition rate.
Figure 5.29. The dependance of average deposition rate of the film on substrate temperature.
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