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INFRARED CHARACTERIZATION OF SiN FILMS ON Si FOR HIGH SPEED ELECTRONICS APPLICATIONS

by

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December 2004

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INFRARED CHARACTERIZATION OF SiN FILMS ON Si FOR HIGH SPEED ELECTRONICS APPLICATIONS

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ABSTRACT

In this thesis, SiN films grown on Si substrates were characterized using Fourier Transform Infrared (FTIR) spectroscopy. The stress in SiN films can be used to enhance of mobility of electrons and holes which increases the performance of metal-oxide-semiconductor (MOS) transistors. The samples used in this study were prepared by Applied Materials using chemical vapor deposition (CVD) technique with different growth parameters. The stress of the samples varied from 1.3 GPa compressive to 1 GPa tensile depending on the growth conditions employed. The FTIR measurement showed three distinct absorption peaks associated with Si-N, Si-H and N-H vibrational modes. The hydrogen was unintentionally incorporated into the SiN film during the CVD process due to its use as the carrier gas for the precursors. It was found from the FTIR data that the area under Si-H and N-H peaks (amount of bonds) varies in opposite directions when the film stress changes from compressive to tensile. In addition, the peak position of the Si-H absorption shifted to higher energy while the opposite was true for N-H as the stress changes from compressive to tensile. The strength and the position of the Si-N absorption peak were found to be relatively insensitive to the stress of the film. This indicates that the amount of Si-H and N-H bonds in the film is responsible for controlling the stress of the film. The use of quantum calculation of SiN molecules with different amount of Si-H and N-H bonds was used toward understanding the experimental absorption spectra.

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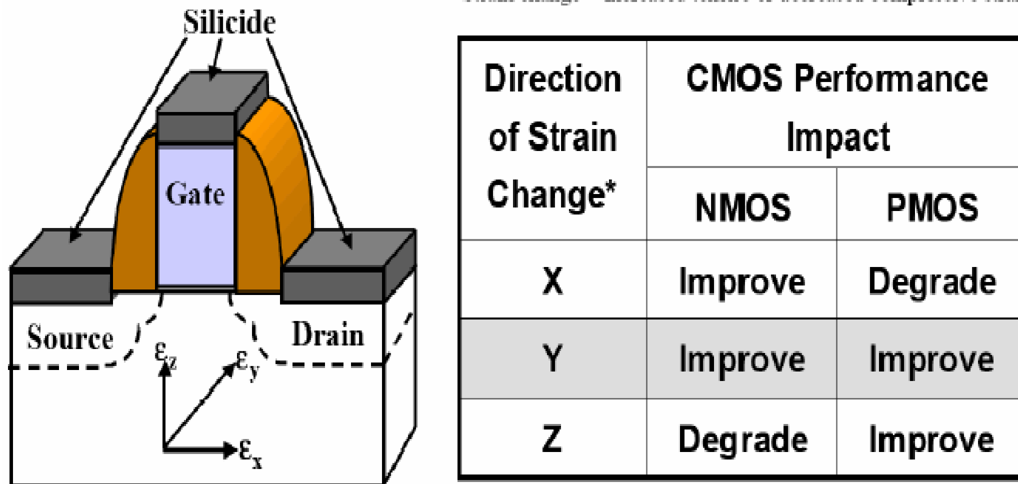
I. INTRODUCTION

The speed of metal-oxide-semiconductor (MOS) transistors used in integrated circuits is primarily determined by the channel length between the source and drain [ref. 1]. The continued scaling of the size of the transistor channel is limited by the lithography used as well as other effects associated with short channel lengths. There is a growing interest in exploring alternative approaches for further enhancing the transistor performance. One approach is to stress the channel which can influence the electron and hole mobilities which can reduce the transit time between source and channel to increase the speed of operation [ref. 1]. This process is commonly known as strain-stress engineering. The recent studies of this approach showed that the tensile stressed channel enhanced the electron mobility while the compressive stressed channel increased the hole mobility as summarized in Figure 1. [ref. 2]. The stress in the channel can be achieved in several ways, for example, using lattice mismatched materials such as SiGe grown on Si to form the channel [ref. 3] or by using stressed film on either side of the channel after fabrication of the transistor [ref. 1]. The later is the preferred approach from the fabrication stand point since the use of SiGe requires additional processing steps. One approach experimented was the use of SiN thin film on the source and drain to stress the channel. The stress of the channel depends on the type of SiN film used (compressive or tensile) and the amount of enhancement of transistor speed is found to depend on the stress of the SiN film. The purpose of this thesis is to study SiN films grown on Si substrate under various growth conditions using Fourier transform infrared (FTIR) spectroscopy to understand the effects of growth conditions on stress. In the following, a brief description of the effect of stress on the band structure of Si and electron mobility discussed.



Direction of Strain Change*	CMOS Performance Impact	
	NMOS	PMOS
X	Improve	Degrade
Y	Improve	Improve
Z	Degrade	Improve

Figure 1. Effect of stress on NMOS and PMOS transistor performance.

A. EFFECTS OF STRESS ON BAND STRUCTURE OF SI AND MOBILITY

There were many studies of effects of stress on semiconductor band structure using external pressure or by growing a film of semiconductor on a lattice mismatched substrate such as SiGe on Si [ref. 3]. Osbourn in 1982 proposed that strained-layer structures could display new and improved electronic and optical characteristics that are not present in unstrained semiconductor structures. Osbourn suggested that the semiconductor characteristics can be changed in a desire and predictable manner.

The strain on a semiconductor structure produces changes in lattice parameter, which in turn produces changes in the electronic band structure. This can affect the energy band gap, effective mass and other electrical and optical properties [ref. 3].

The Figure 2 shows two materials with different lattice constants. The material A (substrate) has a smaller lattice constant than the material B (film). When the material A is grown on B, it will experience a compression in the plane of growth and elongation along the growth direction. Since the film is typically

much thinner than the substrate the deformation mainly occurs in the film. As a consequence of this process the film suffers in-plane compressive stress and tensile stress along the growth direction as illustrated in Figure 2.

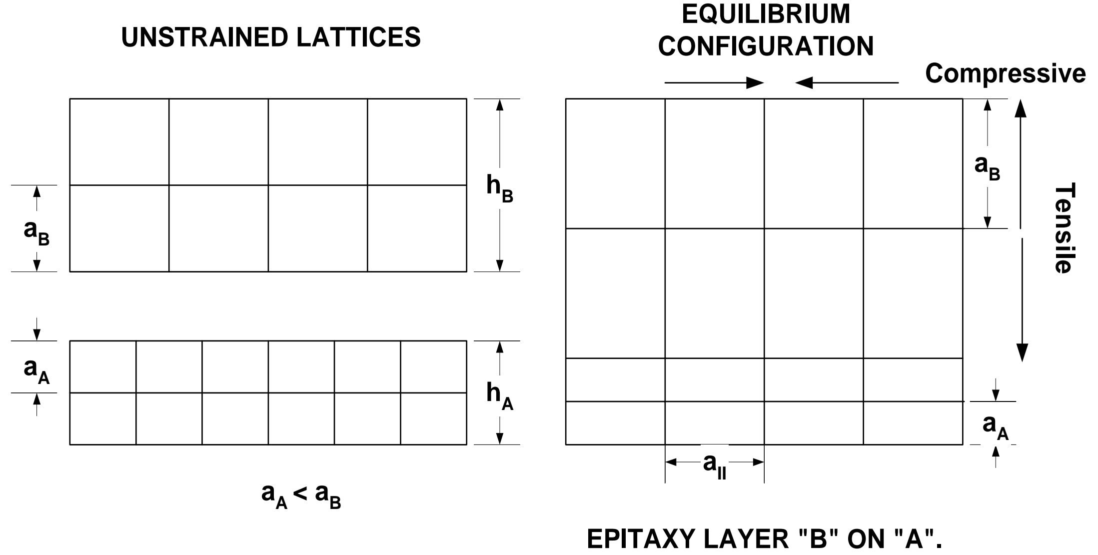


Figure 2. Schematic of unstrained and equilibrium configuration of two materials with different lattice constants [ref. 3].

The effect of stress on the conduction band edge of a SiGe film grown on Si substrate was theoretically studied by People [ref. 4] and the results are summarized in Figure 3. Note that we have converted the Ge composition to the equivalent stress values using the Equation 1 [ref. 5]:

$$\sigma = \frac{E}{1-\nu}\varepsilon \tag{1}$$

Where the σ is the stress, ε is the strain, E the young modulus, and ν is the Poisson's ratio. The values of these parameters were obtained using the correspond values for Silicon and Germanium employing Vegard's Law.

The SiGe is an indirect band gap material and has six conduction band minima along [100] directions [ref. 4]. It can be seen in Figure 3 that as the Ge

composition of the film is increased (i.e., higher lattice mismatch or more in-plane compressive stress) the two conduction band minima along the growth direction gained energy while the other four minima in the plane decreased energy relative to that of the unstrained values [ref. 4]. This implies that the tensile stress moves the conduction band edge up in energy while compressive stress reduces the energy. The change in conduction band energy can affect the occupation of electrons in different valleys which can influence the electronic properties. The above analysis was carried out for a SiGe layer grown on Si substrate; however, the results can be extended for pure Si since the band structure of SiGe is similar to that of Si for Ge concentrations less than 85% [ref. 4]. A discussion of how the stress in Si affects electron mobility is presented.

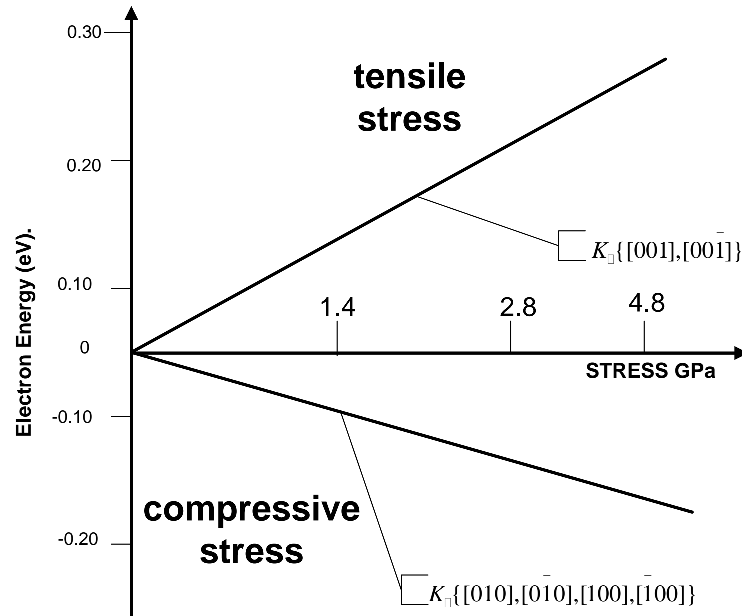


Figure 3. Dependence of conduction band edges as a function of uniaxial stress along [001] direction. [ref. 4].

B. EFFECTS OF STRESS ON MOBILITY IN SILICON

The effect of the conduction and valence bands of Si is discussed below.

Since silicon is an indirect band gap material, the conduction minima appears away from zone center (k = 0) along [100] directions. There are 6 equivalent valleys for electron to occupy with equal probability. Figure 4 shows the constant energy surfaces of the conduction band of unstrained silicon along [100] directions.

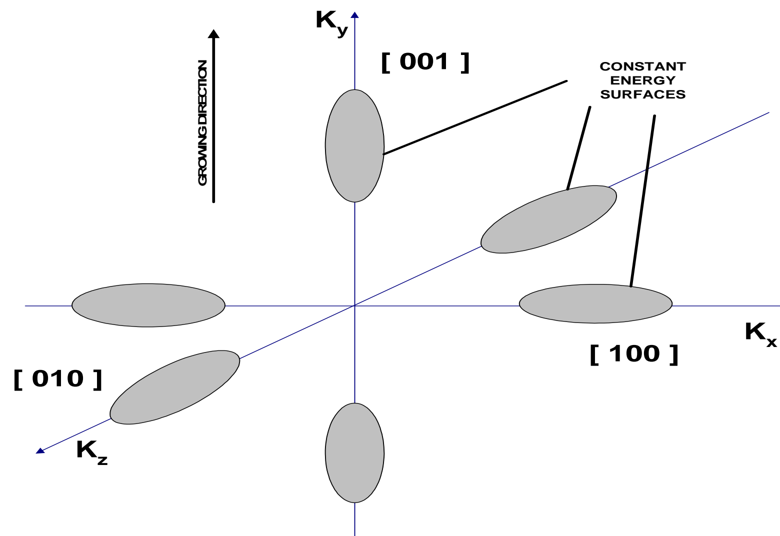


Figure 4. Constant energy surfaces of unstrained silicon.

In the case of Si, the constant energy surfaces are ellipsoidal which implies that the effective mass of electron depends on the direction of travel as illustrated in Figure 5. For example, the electrons in the valley along [100] direction can be represented by two principal effective masses m_l along [100] direction (longitudinal) and m_t perpendicular to it (transverse). In the case of Si, the values of m_l and m_t are 1.08 m_o and 0.15 m_o, respectively [ref. 6], where m_o is the rest mass of electron.

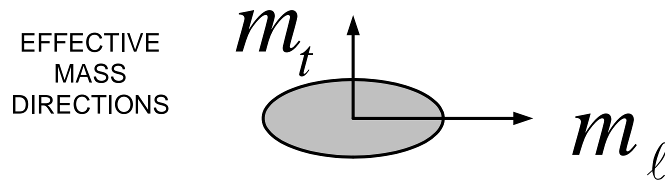


Figure 5. Directional dependence of effective mass of electrons in the conduction band of silicon.

In an n-type doped unstrained Si, the electrons occupy in the six valleys with equal concentrations. Since the effective mass (m*) of electrons is not isotropic, the mobility of electrons $\mu = e\tau/m^*$ depends on the direction of the applied electric field as well as which valley they occupy, where e is the electron charge and τ is the scattering lifetime. For example, if an electric field is applied along [100] direction of unstrained silicon, the mobility (μ_o) along this direction can be written as the average of mobilities due to all the six valleys [ref 6].

$$\mu_o = \frac{1}{6}\left(2\frac{e\tau}{m_\ell} + 4\frac{e\tau}{m_t}\right). \tag{2}$$

However, under stress the six conduction band valleys will have different energies depending on the nature of the stress (compressive or tensile) and direction. For example, if tensile stress is applied along [100] direction of silicon the two valleys along this direction will have higher energy than the four valleys perpendicular to it [ref. 4] as schematically illustrated in Figure 6

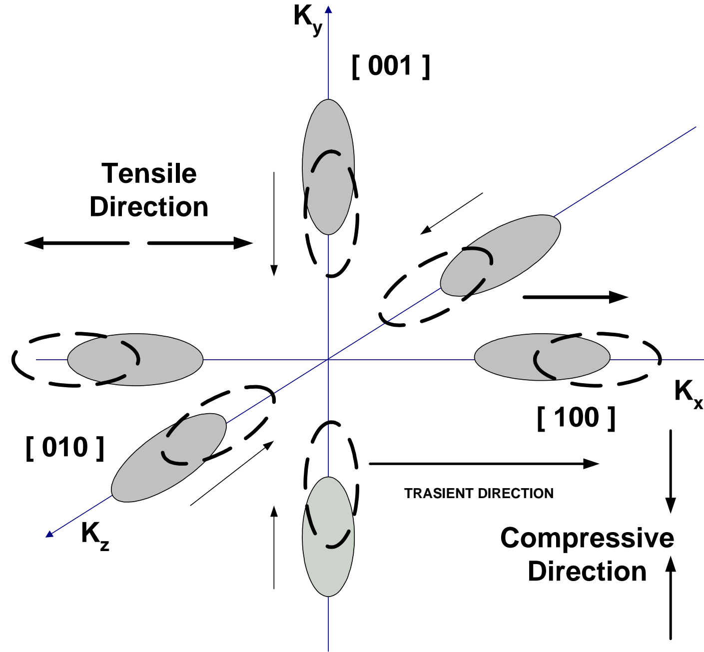


Figure 6. Conduction band structure of silicon under tensile stress along [100] direction. This will induce a compressive stress in the perpendicular plane.

In the [100] direction, where the tensile stress is applied, the elliptic energy surfaces shift away from the k=0 or gain their energy. On the other hand in the [010] and [001] directions where the compressive stress is induced by the applied tensile stress, the elliptic energy surfaces go closer to the k=0 value or reduce their energy. Thus, in the case of n-type strained silicon, the electrons in the conduction band will tend to occupy the lower energy four valleys along [010] and [001] directions. The energy difference for the two types of valleys depends on the stress and is usually larger than the thermal energy (0.026 eV) at 300 k. . Thus, the mobility (μ_s) of electrons along [100] direction in silicon with tensile stress also along the same direction can be written as:

$$\mu_s = \frac{1}{4}\left(4\frac{e\tau}{m_t}\right) = \frac{e\tau}{m_t} \quad (3)$$

The amount of electron mobility change under the stressed with respect to the unstressed silicon is estimated from the ratio of these two mobilities:

$$\frac{\mu_s}{\mu_o} = \frac{1}{2}e\tau\left(\frac{2}{m_t}\right)\Big/\frac{1}{3}e\tau\left(\frac{1}{m_\ell}+\frac{2}{m_t}\right)$$

$$= \frac{3}{m_t/m_\ell + 2} \approx 1.4 \quad (4)$$

Using the transverse and longitudinal effective mass for Si, it was found that the improvement of electron mobility is about 40%. Such a mobility enhancement of electrons has been exploited for the improvement of NMOS transistor performance [ref. 7]. which will be discussed later.

It is also well known that the stress alters the valence band structure [ref. 4]. Figure 7 schematically shows the valence E-k diagram of light and heavy hole bands in silicon. The energy bands near the k = 0 has a parabolic shape and the effective mass of holes can be obtained using the curvature of the band at k = 0 using [ref. 8]

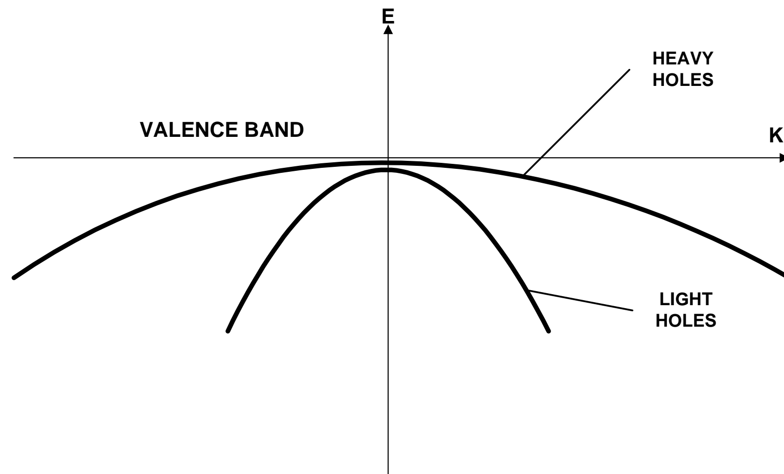


Figure 7. Schematic valence Band structure of unstressed silicon.

$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}} \tag{5}$$

It can be seen from the Eq. (5) that the higher the curvature the smaller the effective mass of holes. In a p-type Si the holes are primarily occupied in the heavy hole band and the larger mass of these holes results in a lower mobility (see Eq. (3)). It was found that under a compressive stress the band structure changes as schematically illustrated in Figure 8 [ref. 8]. The unstrained silicon heavy hole band now has a larger curvature and hence lower effective mass as indicated by the "light holes" in Figure 8. The unstrained light hole band now becomes a heavy hole. In addition, the energy of the heavy hole band moves up in energy indicating most of the holes will occupy this band enhancing the hole mobility. The enhancement of hole mobility under compressive stress has been used for the fabrication of PMOS transistors [ref. 7]. In the following sections, we will describe the use of SiN films for achieving tensile and compressive stresses in the channel of NMOS and PMOS transistors, respectively.

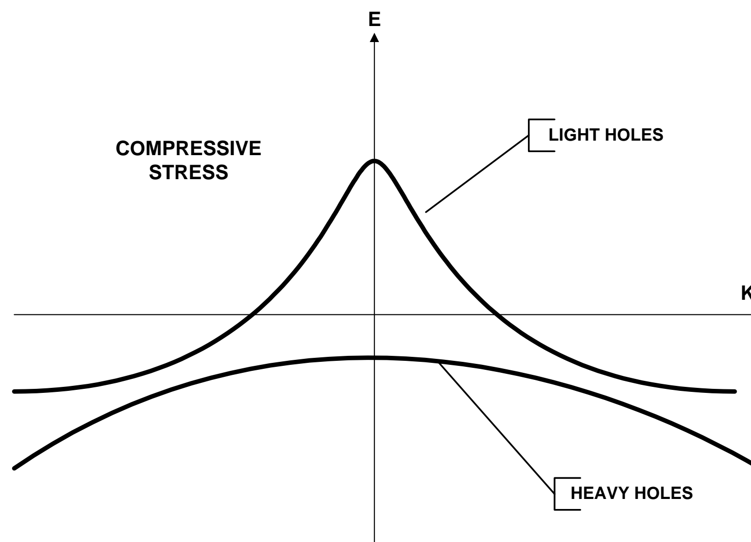


Figure 8. Schematic valence band structure of compressively stressed silicon.

C. USE OF SIN FOR STRESSING THE CHANNEL OF CMOS TRANSISTORS

As discussed earlier the tensile stress in silicon increases the mobility of electrons and vise versa for holes. There are several way to achieve stress in the channel of the transistor, for example, growth of Si on a relaxed SiGe buffer layer which stretches the Si due to larger lattice constant of SiGe [ref. 6] or use of mechanical stress using strain-engineered thin films such as SiN on the transistor structure [ref. 7]. The use of strain-engineered thin films provides a convenient way to achieve both tensile and compressive stress in the channel with out complicating the fabrication using standard integrated circuit (IC) technology.

Figures 9 schematically illustrate the use of SiN film to achieve tensile stress in the channel of a NMOS transistor.

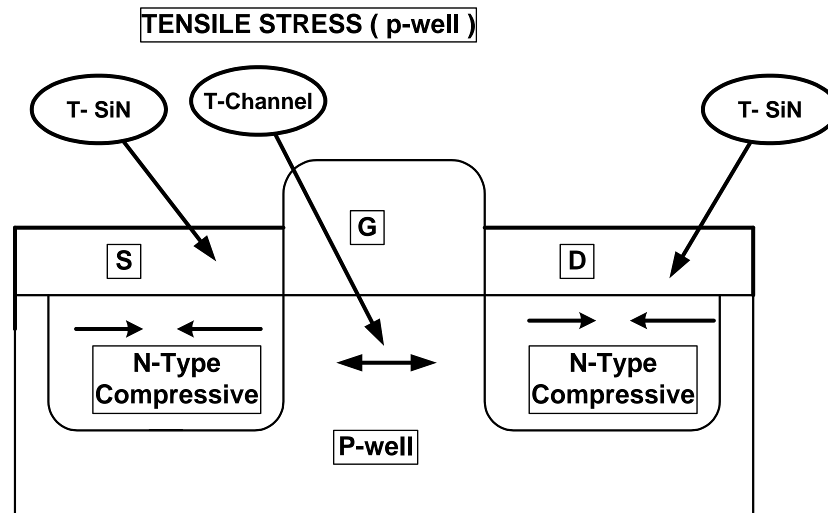


Figure 9. Tensile stress on an n-channel MOSFET.

It can be seen from Figure 9 that the use of a tensile SiN film on the source (S) and drain (D) of the transistor compresses the silicon underneath as shown by the arrows. This will in turn pull the channel apart generating a tensile stress in the channel. If the channel is aligned along the [100] direction, the two conduction band valleys along this direction will have higher energy and the electrons will occupy the other four valleys. This will enhance the electron

mobility as described in Eq. (3). It is necessary to have large enough stress (usually of the order of GPa) to increase the energies of the two [100] valleys beyond the thermal energy (kT) to achieve efficient electron transfer to the other four valleys along [010] and [001] directions. .

In the case of PMOS transistor, as described previously the channel needs to be compressively stressed to achieve the high mobility via the reduction of effective mass of holes. This can be achieved by using a compressively stressed SiN film on the source and drain of the transistor as schematically illustrated in Figure 10.

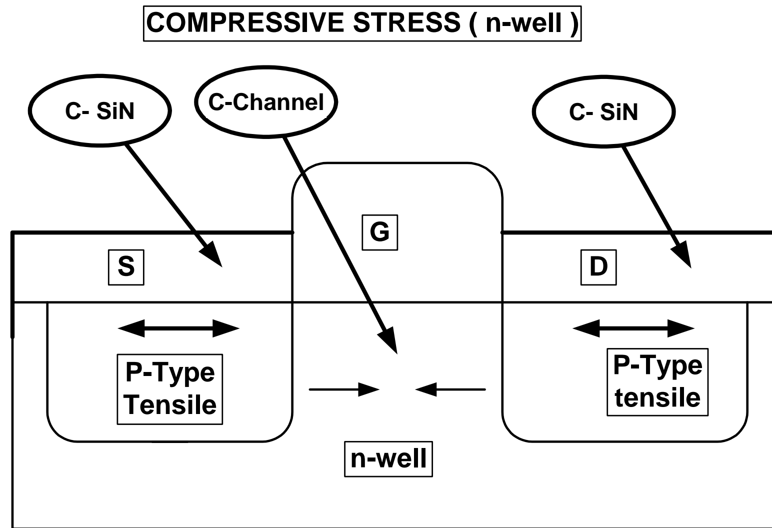


Figure 10.   Compressive stress on a p-channel MOSFET.

It is clear from the above discussion that the type and amount of stress that can be excreted in the channel determines the enhancement of the transistor performance. The detailed mechanisms for affecting and controlling the amount of stress are relatively unknown. It is the purpose of this thesis to study the SiN films grown under different growth conditions using FTIR spectroscopy.

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II. EXPERIMENTAL AND DATA ANALYSIS

A. SAMPLES AND EQUIPMENT USED

1. Samples

The SiN films grown on Si substrates (either 6 or 8 inch in diameter) were prepared by Applied Materials Corporation using chemical vapor deposition (CVD) technique. The growth conditions were altered to achieve stresses from 1.3 GPa compressive to 1 GPa tensile. The stress data for all the samples measured and provided by Applied Materials. Out of the 12 wafers provided, eight were selected with the same SiN layer thickness and growth temperature. The samples are shown in Figure 13.

Figure 11. The samples used in the FTIR measurement.

Table 1 summarizes the specifications and stress in each sample. In this thesis, the measurements based on these samples are presented.

Table1. Area positions of the three peaks as a function of stress.

STRESS	N-H LINE		Si-H LINE		Si-N LINE		THICKNESS IN ANGS.
GPa	AREA	FREQ	AREA	FREQ	AREA	FREQ	-
0.0320	1.43	3340	1.79	2189	47.17	836	3000
-0.2610	1.97	3338	1.57	2197	60.84	840	3000
-0.6040	1.85	3333	0.95	2206	56.57	849	3000
-1.311	3.59	3328	0.61	2220	58.9	856	3000
0.468	1.44	3347	2.90	2175	67.26	835	3000
0.727	1.31	3353	2.26	2169	57.11	838	3000
0.737	1.25	3358	3.12	2167	48.59	839	3000
1	1.3	3345	0.54	2188	61.00	836	3000

The FTIR spectrometer used in the measurement was a Nicolet 870 as depicted in Figure 14. Since the wafer diameter was larger than the sample compartment a flexi glass tube with a narrow opening (see Figure 15) was used to connect the optical path. This allows the purging of the spectrometer with nitrogen to remove water vapor and CO_2 which can mask the absorption peaks of SiN.

Figure 12. FTIR Spectrometer.

The sample was inserted into the narrow opening as illustrated in Figure 15. All the measurements were carried out in two steps. First the interferogram of a bare silicon wafer was taken as the reference and then the sample interferogram was taken. In order to extract the absorption spectrum of SiN film the absorption due to bare silicon sample was subtracted. The resultant infrared spectra for three samples are shown in Figure 16. It can be seen from the Figure 16 that there are three distinct absorption peaks coming from Si-N, Si-H and N-H bond in the film [ref. 7]. In addition, the Si-H and N-H peak strength (area under the peak) depend on the stress of the SiN film, as shown. For example, higher the tensile stress stronger the Si-H absorption and vise versa for the N-H bond. Furthermore, the peak positions (wave numbers) were also affected by the amount of stress in the film.

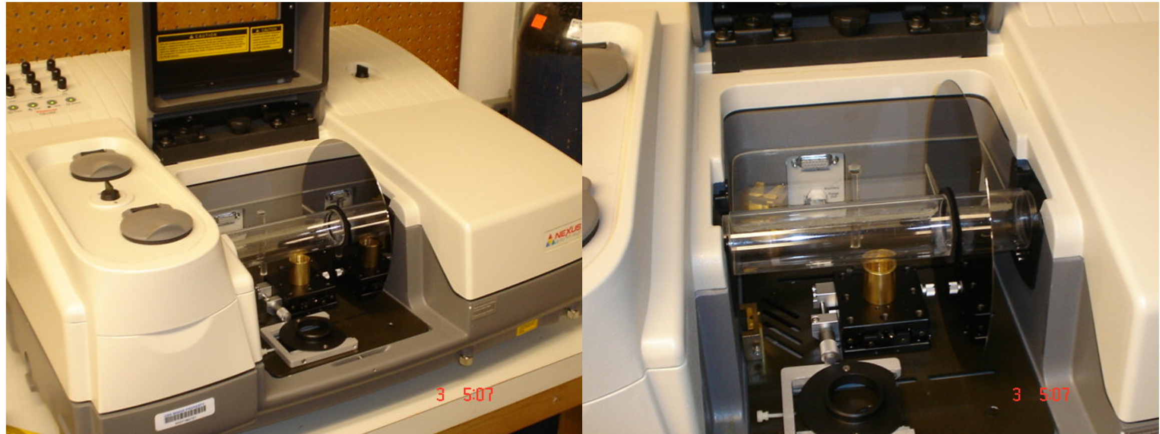

Figure 13. Sample in the measurement compartment.

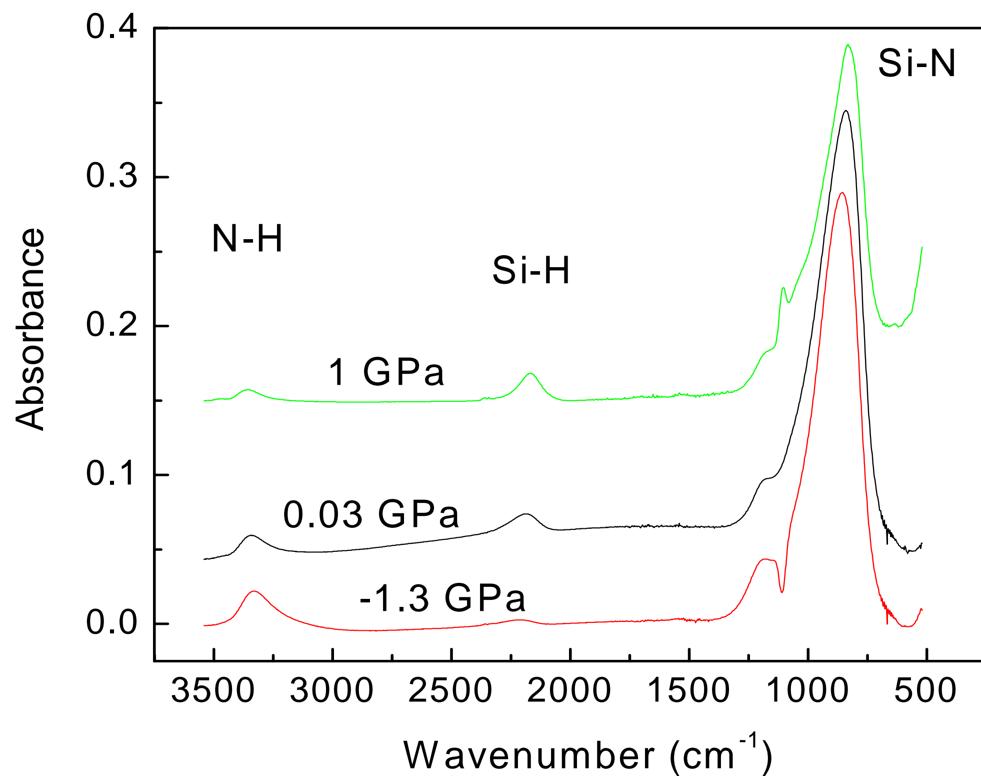

Figure 14. FTIR Spectra of three samples with high tensile stress to high compressive stress. Note that the spectra are shifted vertically for clarity.

2. FTIR Spectra

To understand the dependence of peak position and absorption strength for different stress, we have analyzed the spectra for all the eight samples. The absorption spectra for each peak (Si-N, Si-H and N-H) are shown in Figures 17, 18 and 19, respectively. It can be seen from the Figures 17-19 that the absorption strengths (peak areas) as well as the peak positions are affected by the amount of stress in the SiN film. The peak positions and area under each peak is extracted using the software provided by Nicolet and the results are summarized in Table 2.

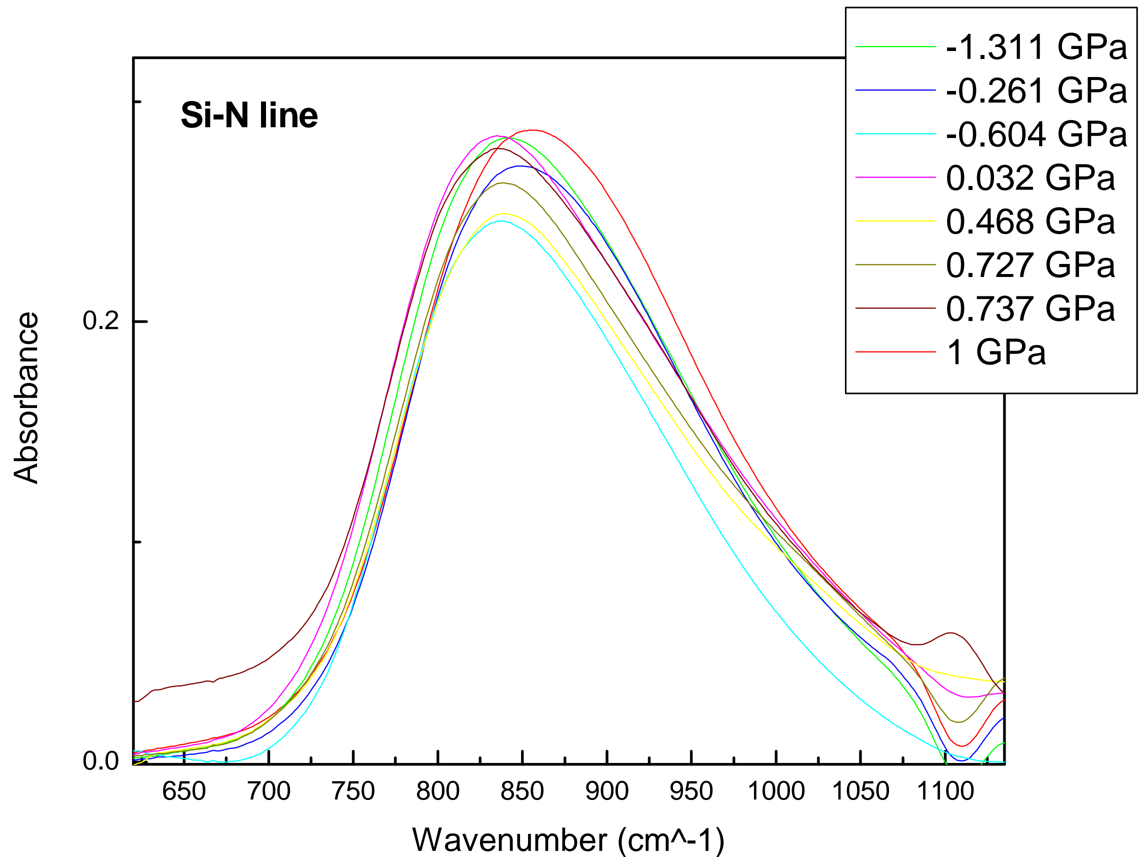

Figure 15. Absorption spectra of Si-N peak for different stress values.

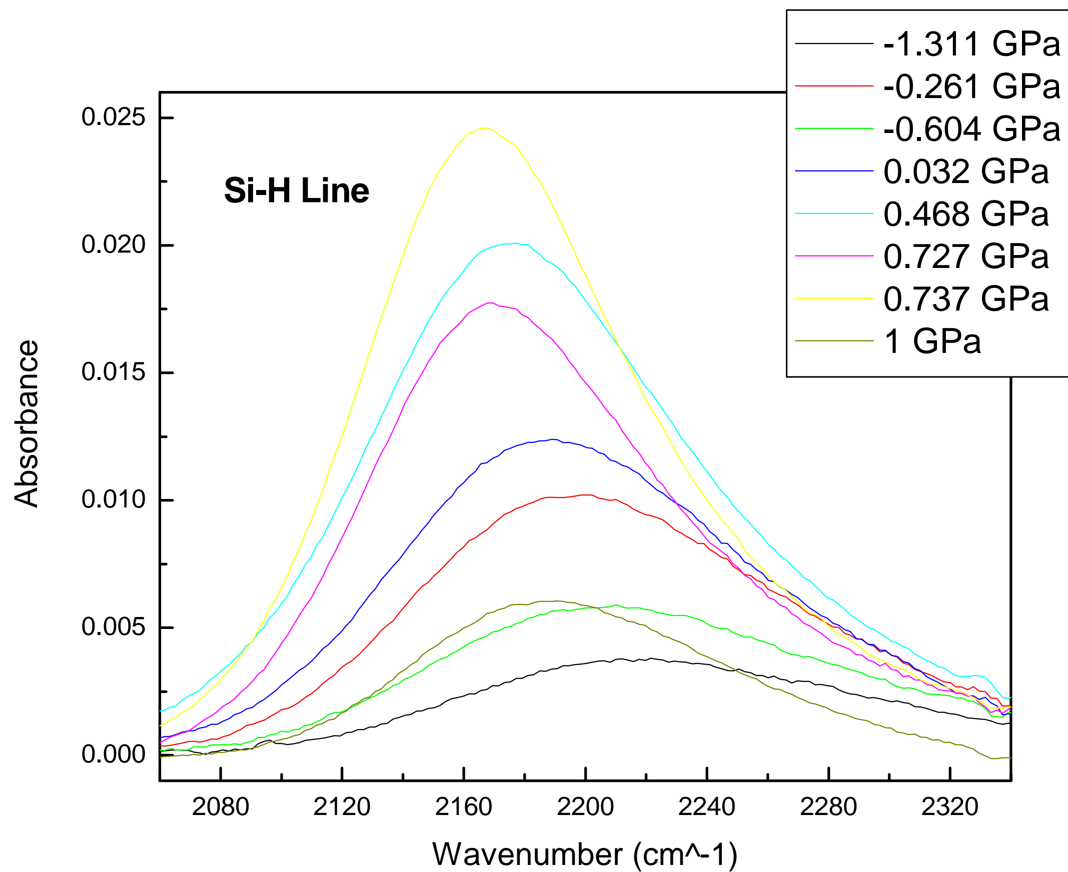

Figure 16. Absorption spectra of Si-H peak for different stress values.

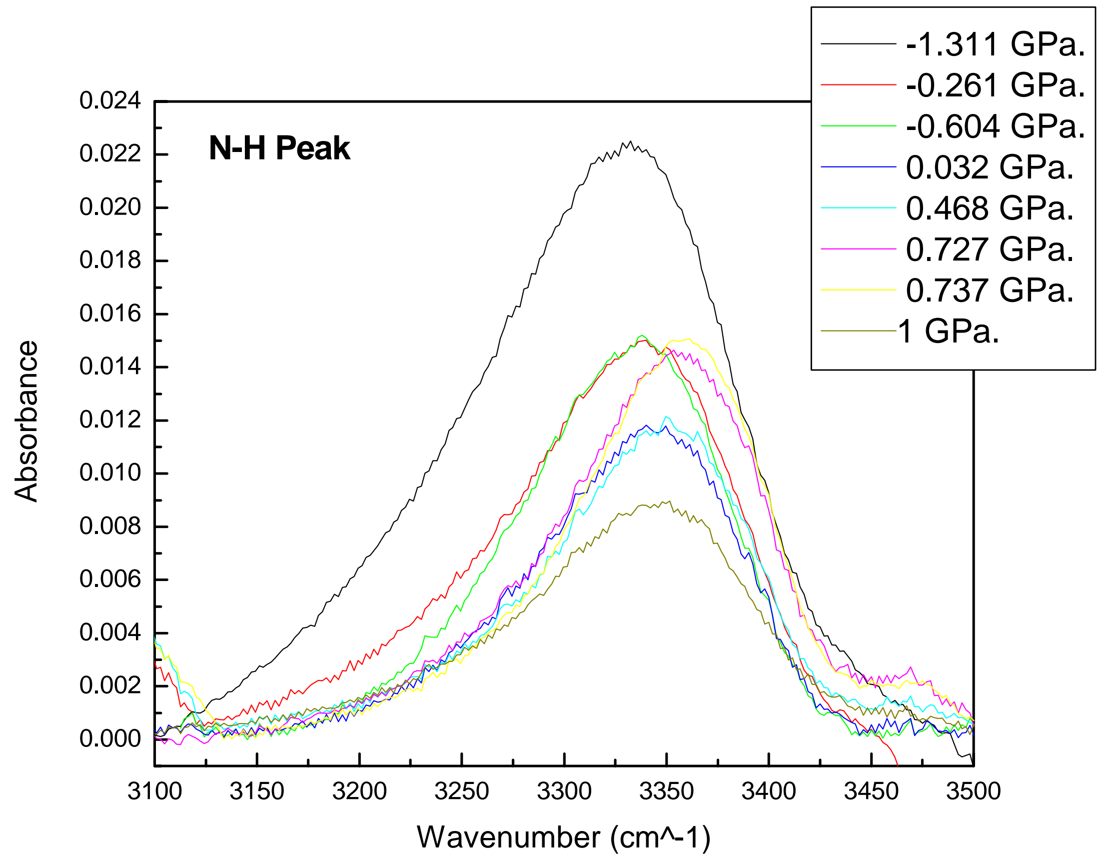

Figure 17. Absorption spectra of N-H peak for different stress values.

Table 2. Area POSITIONS of the three peaks as a function of stress.

STRESS	**N-H LINE**		**Si-H LINE**		**Si-N LINE**		**THICKNESS IN ANGS.**
GPa	AREA	FREQ	AREA	FREQ	AREA	FREQ	-
0.0320	1.43	3340	1.795	2189	47.17	836	3000
-0.2610	1.97	3338	1.57	2197	60.84	840	3000
-0.6040	1.85	3333	0.95	2206	56.57	849	3000

-1.311	3.59	3328	0.61	2220	58.9	856	3000
0.468	1.44	33.47	2.90	2175	67.26	835	3000
0.727	1.31	3353	2.26	2169	57.11	838	3000
0.737	1.25	3358	3.12	2167	48.59	839	3000
1	1.3	3345	0.54	2188	61.00	836	3000

The peak wave number versus stress data in Table 2, are plotted as a function of the stress for each of the lines in Figures 20, 21 and 22, respectively. The objectives of these plots are to show the stress dependence of the different peaks positions (Si-N, Si-H, and N-H), and the area under them. The peak position as a function of stress for Si-N, Si-H and N-H peaks, respectively, are shown in these figures.

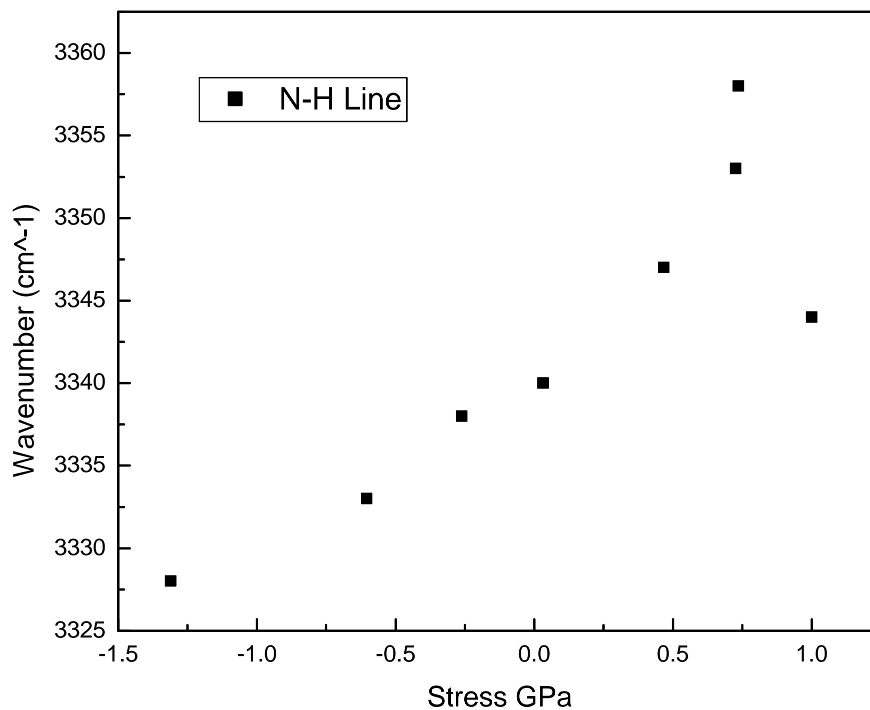

Figure 18. Peaks positions for N-H absorption.

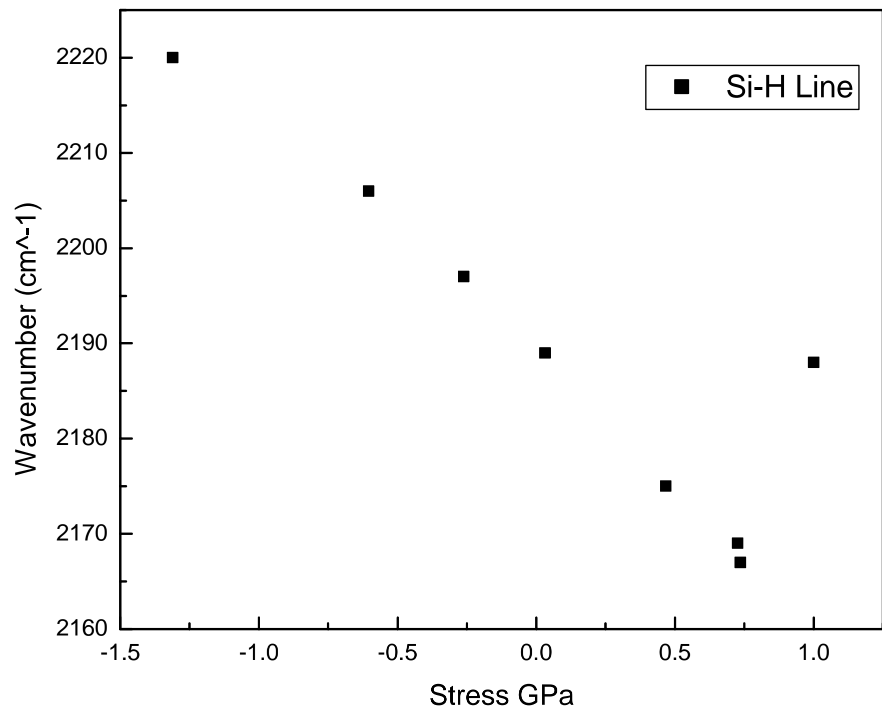

Figure 19. Peaks positions for Si-H absorption.

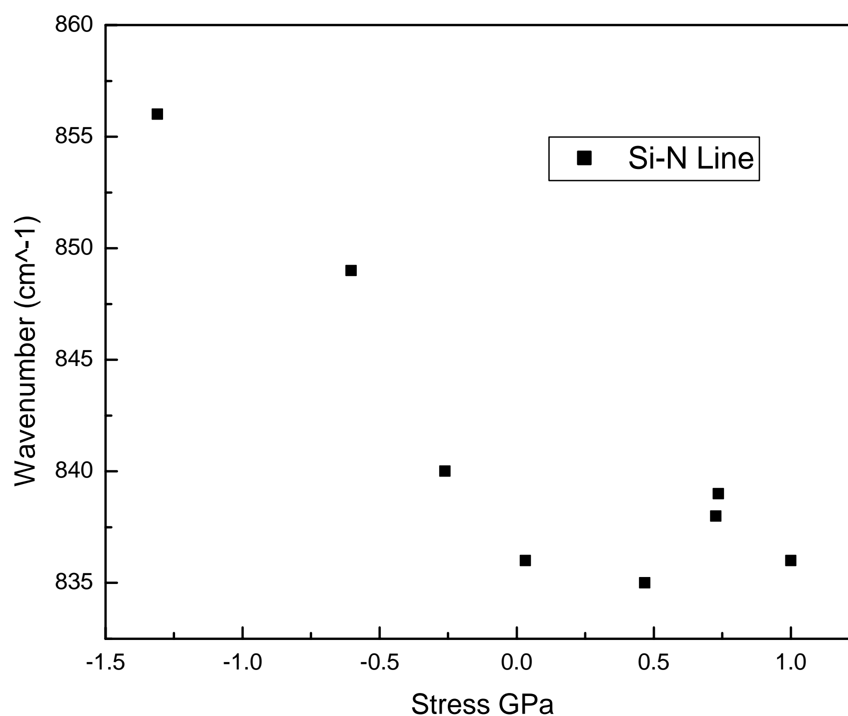

Figure 20. Peaks positions for Si-N absorption.

It can be seen from the Figures 20 and 21 that the peak position in wave number (or peak energy) decreases as the stress of SiN film changes from compressive to tensile. This indicates that both Si-N and Si-H bond strengths become weaker for tensile stress SiN films compared to compressive stressed ones.

On the other hand, the N-H peak strength becomes stronger as the film becomes more tensile. Figures 23, 24 and 25 show the variation of absorption strength (area under peak) for Si-N, Si-H and N-H peaks, respectively.

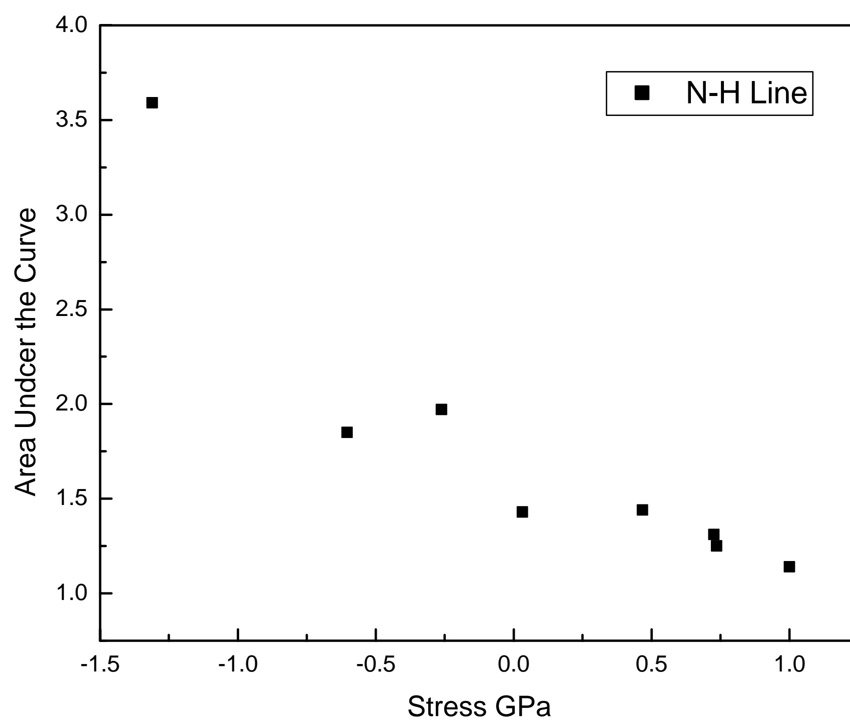

Figure 21. Area under the curve for N-H absorption peak.

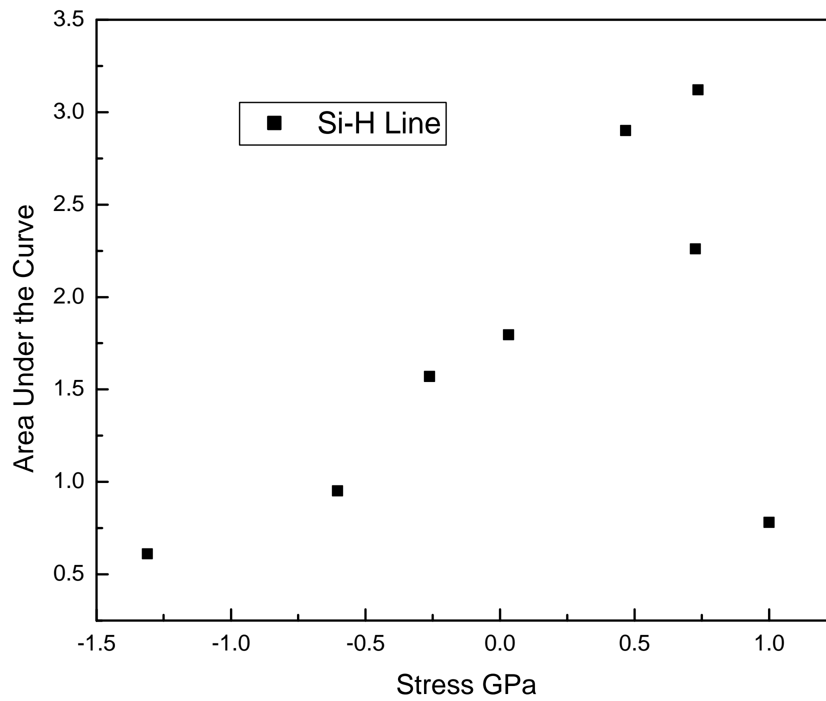

Figure 22. Area under the curve for Si-H absorption peak, the deviation of the last point could be due to difference of film thickness or growth parameters.

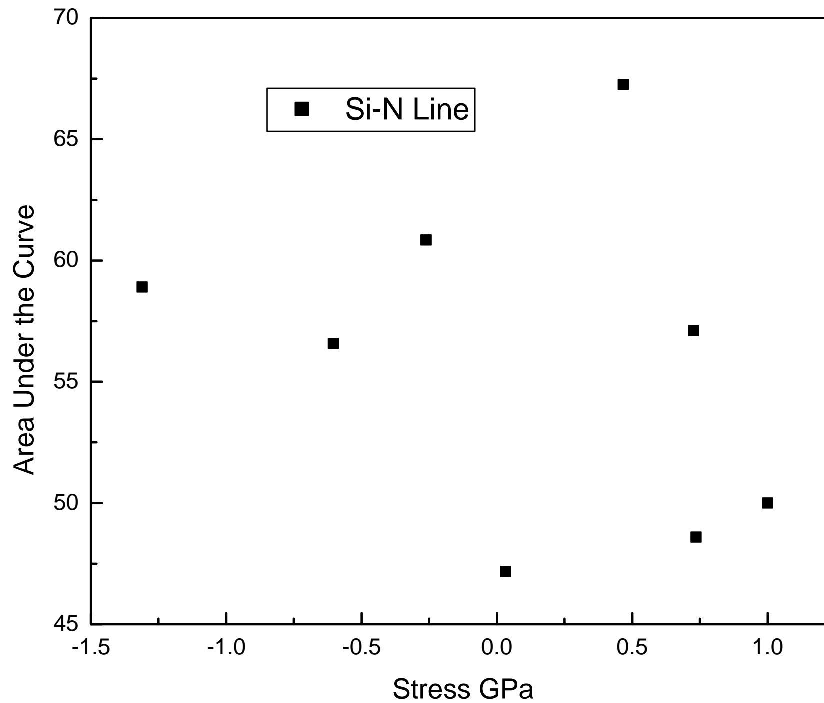

Figure 23. Area under the curve for Si-N absorption peak.

Figure 23 shows that the Si-N peak strength generally tends to go down as the film becomes more tensile. The scatter of data indicates that this is not very conclusive. However, the Si-H peak strength becomes weaker as the film becomes more tensile (see Figure 24) and the opposite is true for the N-H peak strength as shown in Figure 25. It is clear from the above data that hydrogen incorporation plays an important role in controlling the stress in SiN films. Towards the understanding of the role of hydrogen on stress SiN film stress; the following chapter presents some insights from quantum mechanical modeling.

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III. MOLECULE MODELING WITH SPARTAN WAVE FUNCTION SOFTWARE

The effect of hydrogen substitution onto Si films has been investigated by budhani and co-workers [ref. 10]. They showed systematic shift in the vibrational energy band of Si-H, between 1250 and 2190 cm^{-1}, with decreasing N/Si ratio.

Nearest neighbor representations of possible modifications in α-Si_xN_{1-x}: H film resulting from the infusion of chemical-bonded hydrogen was used by these workers to explain the observed vibrational shifts. These molecular are shown in Figure 26.

The effect of hydrogen substitution in the basic Si_3N_4 molecule (see Figure 26 (a)), was revisited in this thesis research using the equilibrium geometry and a Hartree-Fock/3-21G approximations in the Spartan Quantum Chemical code developed by Wave function Inc. [ref. 11]. Calculated bond lengths of Si-N, Si-H and N-H, in these four previously studied molecular arrangements by Budhani, are reported in Table 3.

Molecular structure (a), is a unit molecular cell representation of show us a Silicon Nitrate. Adjacent bonds directly connected to the central Si-N bond are absent of hydrogen. Molecules “b”, “c” and “d” is representative of stepwise hydrogen atom insertions across the central Si-N bond. The estimated Si-N bond length decreases as a result of each insertion: in particular “a” to “b”, “a” to “c”, “b” to “d”, and “c” to “d”. These estimates are entirely consistent with the interferences made by Budhani based on Si-N vibrational shifts.

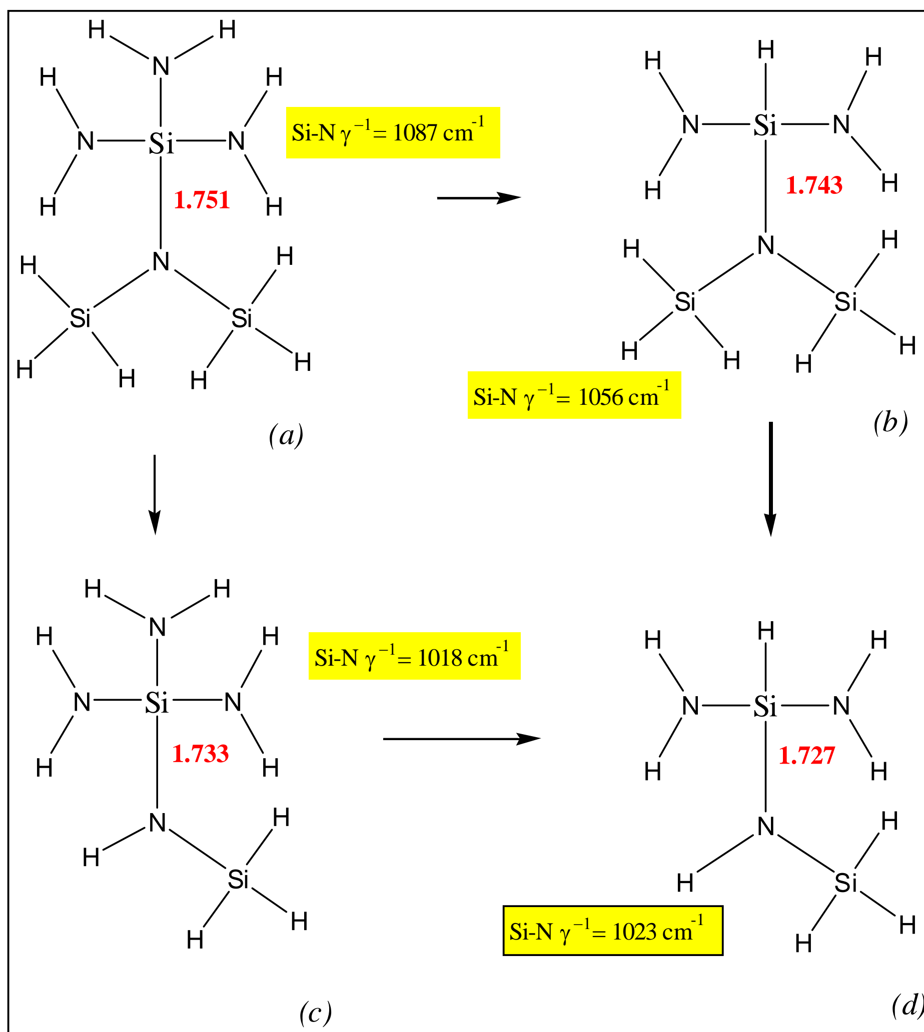

Figure 24. Nearest neighbor representations of possible modifications in α-Si_xN_{1-x}: H.

According to the findings reported in the previous section, tensile strength should increase with Si-H increase and N-H decrease, assuming that the vibrational line intensities are direct indications of the population of these respective bonds in the SiN-Si films measured. The largest estimated changes in the model Si-N molecules (see Figure 24) occur between “a” to “c”, and “d” to “b”, which is also consistent with the influence of Si-H on tensile stress. The influence of Hydrogen substitution for the NH_2 group is much less and possibly in the range of uncertainty. Additional work is recommended to clarify this issue.

. The trends between other unions cannot be resolved and the code did not permit examinations near the far-IR spectra studied by Budhani [ref.10], which was also non-revealing.

Additional work is recommended to resolve the uncertainties regarding the effect of N-H bonding. Future investigations should also be directed towards assessing steric effects. For example, the effect of Si-H population in SiN might be largely a result of volumetric changes than deductive effects that were suggested by Budhani.

Bond Lengths (angstoms)

	$Si\text{-}N_{center}$	$Si\text{-}NH_2$	$Si\text{-}H_{subst}$	$N\text{-}SiH_3$	$N\text{-}H_{subst}$	Si-H	N-H	$N\text{-}N_{cross}$	$Si\text{-}Si_{cross}$	$Si\text{-}N_{cross}$
(a)	1.751	1.703		1.731		1.477	1.001	2.781(l)	3.034(l)	3.055
		1.708		1.737		1.477	1.002	2.824(l)		3.444
		1.715				1.478		2.814(l)		3.751
						1.476		2.770(d)	2.975(d)	3.921
						1.481		2.872(d)	3.026(d)	4.305
						1.475		2.779(d)		4.378
(b)	1.743	1.712	1.474		none	1.476	1.002	2.958(l)	3.078(l)	3.126(l)
						1.477	1.003			3.142(l)
						1.475				
						1.478		2.769(d)	2.986(d)	
						1.475			2.998(d)	4.355(d)
						1.476				
(c)	1.733	1.705	none	1.724	1.007	1.479	1.001	2.840(l)		3.143(l)
		1.710				1.477	1.002			
						1.483				
								2.726(d)	3.049(d)	4.344(d)
(d)	1.727	1.708	1.477	1.729	1.007	1.481	1.001	2.927(l)	none	none
		1.715				1.478	1.003			
						1.476				
								2.749(d)	3.058(d)	

Table 3. Calculated bond lengths for the configurations shown in Figure 26.

Substitution of hydrogen at either N or S site adjacent to the central Si-N bond in the molecules studied results in increasing the Si-N bond energy (decreasing bond distance). While these changes are affected by changes in electro negativity, there is also evidence of steric effects. That is the replacement of N and/or Si with hydrogen in these molecular arrangements reduces the spatial volume of electron-electron repulsion between adjacent atoms. For detail comparison of effects of hydrogen on the stress it is necessary to extend the model including the Si substrate which is beyond the present scope of the thesis.

IV. CONCLUSIONS

In this thesis, SiN films grown on Si substrates were characterized using Fourier transform infrared (FTIR) spectroscopy. The use of stress in SiN films grown on Si substrate to enhance of mobility of electrons and holes were analyzed using stress on Si band structure. The samples used in this study were prepared by Applied Materials using chemical vapor deposition (CVD) technique with different growth parameters. The stress of the samples varied from 1.3 GPa compressive to 1 GPa tensile depending on the growth conditions employed. The FTIR measurement showed three distinct absorption peaks associated with Si-N, Si-H and N-H vibrational modes. The hydrogen was unintentionally incorporated into the SiN film during the CVD process due to its use as the carrier gas for the precursors. It was found from the FTIR data that the area under Si-H and N-H peaks (amount of bonds) varies in opposite directions when the film stress changes from compressive to tensile. In addition, the peak position of the Si-H absorption shifted to higher energy while the opposite was true for N-H as the stress changes from compressive to tensile. The strength and the position of the Si-N absorption peak were found to be relatively insensitive to the stress of the film. This indicates that the amount of Si-H and N-H bonds in the film is responsible for controlling the stress of the film. The use of quantum calculation of SiN molecules with different amount of Si-H and N-H bonds was used toward understanding the experimental absorption spectra. The modeling of SiN along with the Si substrate is needed for developing a better understanding of the effects of hydrogen incorporation on stress.

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