

# Annealing Effects in Hydrogenated Silicon Nitride Films during High Energy Ion Beam Irradiation

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## ABSTRACT

The annealing effects during energy recoil detection (ERD) analysis on the structure of hydrogenated silicon nitride film have been investigated by using Fourier transform infrared (FTIR) spectroscopy. Hydrogenated silicon nitride films were prepared by plasma enhanced chemical vapor deposition with various substrate temperatures. A 2.5 MeV  $^4\text{He}^{++}$  ion beam was irradiated onto the film in a vacuum chamber at room temperature. The ERD signal was measured after various ion doses in order to determine the loss of hydrogen counts induced by the ion beam. The IR absorption spectrum was obtained in order to follow the film structural change which occurred due to the ion beam. The films deposited at 200 and 300°C show a significant decrease in the ERD count with increasing ion beam dose, while the film deposited at 400°C, shows no significant changes. The IR absorption peak position for Si—N stretching ( $830\text{ cm}^{-1}$ ) shifted to smaller wave numbers after ion beam irradiation, while the Si—H stretching ( $2160\text{ cm}^{-1}$ ) shifted to the opposite direction. The peak position for N—H ( $3360\text{ cm}^{-1}$ ) shows no noticeable changes. Normalized peak area for the Si—N ( $830\text{ cm}^{-1}$ ) stretching increased after ion beam irradiation. The Si—H peak ( $2160\text{ cm}^{-1}$ ) area decreased slightly. The N—H peak ( $3360\text{ cm}^{-1}$ ) area decreased significantly. A recombination mechanism of the N and H radicals with excess Si radical coming from Si—Si bonds in Si-rich silicon nitride films has been suggested to explain the IR absorption spectral changes which have occurred due to ion beam irradiation.

## Introduction

Silicon nitride thin film deposited by plasma enhanced chemical vapor deposition (PECVD) is one of the most promising materials for semiconductor device technologies. Because of its hardness, chemical inertness, and low temperature adaptability, it can be used as passivation layers, intermetallic dielectrics, diffusion barriers, and thin gate dielectric materials in microelectronics.<sup>1-3</sup> The film properties depend on the details of the deposition process and condition, *i.e.*, reaction chamber design (direct or remote plasma system), reactant species, gas flow rates, chamber pressure, and substrate temperature, etc.<sup>4-9</sup>

Generally, the PECVD silicon nitride films are referred to hydrogenated amorphous silicon nitride ( $\text{a-Si}_x\text{N}_y\text{H}_z$ ). Rutherford backscattering (RBS) can be used to determine atomic density<sup>10</sup> and infrared (IR) absorption spectroscopy can be used to analyze the bond structure.<sup>11-13</sup> They are useful methods to study the hydrogenated amorphous silicon nitride films.<sup>9,14</sup> Other techniques such as energy recoil detection (ERD) and nuclear reaction analysis (NRA) are used for the quantitative analysis of hydrogen atom that is difficult to analyze using most traditional methods.<sup>15</sup> The number of hydrogen atoms in films obtained by these MeV ion beam techniques can be used for calibrating the IR absorption cross sections of the hydrogen-related bonds in the IR spectrum.<sup>16,17</sup>

It is known that MeV ion beams break hydrogen related bonds such as Si—H and N—H.<sup>16</sup> However, the details of the changes in chemical structure during high-energy ion beam irradiation to the hydrogenated silicon nitride film has not been reported previously. We have found that similar bond breaking effects, particularly the loss of hydrogen, occurred due to the irradiation of ion beam and electron beam during ERD and Auger analysis, respectively. These undesirable losses of the hydrogen count during exposure of a high energy probe lead to a serious analytical error. The bond breaking and annealing effects due to ion beam irradiation for PECVD silicon nitride films during ERD analysis are presented based on detailed information on the chemical bond changes obtained using Fourier transform infrared (FTIR) spectroscopy.

## Experimental

Hydrogenated silicon nitride films were deposited on Si and GaAs wafers by using a parallel plate PECVD reactor (IPL, 3000). Substrate temperatures used for the film deposition were 200, 300, and 400°C. Flow rates of the  $\text{SiH}_4$ ,

$\text{NH}_3$ , and  $\text{N}_2$  gases were 10, 30, and 50 SCCM, respectively. The  $\text{SiH}_4$  gas was diluted by ten times in volume ratio with argon. The RF power and RF frequency were 300 W and 13.56 MHz, respectively. The chamber pressure for film deposition was 700 mTorr. Initial thickness of the films deposited at 200, 300, and 400°C, were measured as 2511, 2118, and 1740 Å, respectively, using an ellipsometer (Rudolph, AutoEL-3).

The ERD and RBS measurements were performed with an RBS spectrometer (CE&A, RBS 400) equipped with an ion accelerator (NEC, 3SDH). A 2.5 MeV  $^4\text{He}^{++}$  ion beam with the beam current of 10 nA was irradiated through a  $3 \times 10^{-2}\text{ cm}^2$  slit into the target. The target was located in a vacuum chamber of  $1 \times 10^{-6}$  Torr at room temperature. The sample was placed at an angle of 15° to the beam. Two detectors were placed at 30 and 165° to detect forward scattered protons and backscattered He ions, respectively. The primary  $^4\text{He}^{++}$  ion dose was  $500\text{ }\mu\text{C}/\text{cm}^2$ . The ERD and RBS signals were recorded every  $10\text{ }\mu\text{C}/\text{cm}^2$  of the ion dose to observe the loss of hydrogen counts induced by the ion beam. The numbers of Si, N, and H atoms per unit area

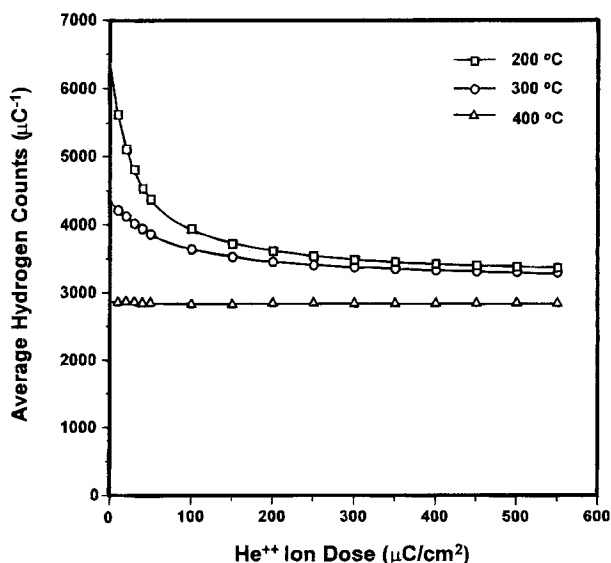


Fig. 1. Average ERD counts for the hydrogenated silicon nitride films deposited at 200, 300, and 400°C. The film thicknesses are 2511, 2118, and 1740 Å, respectively.

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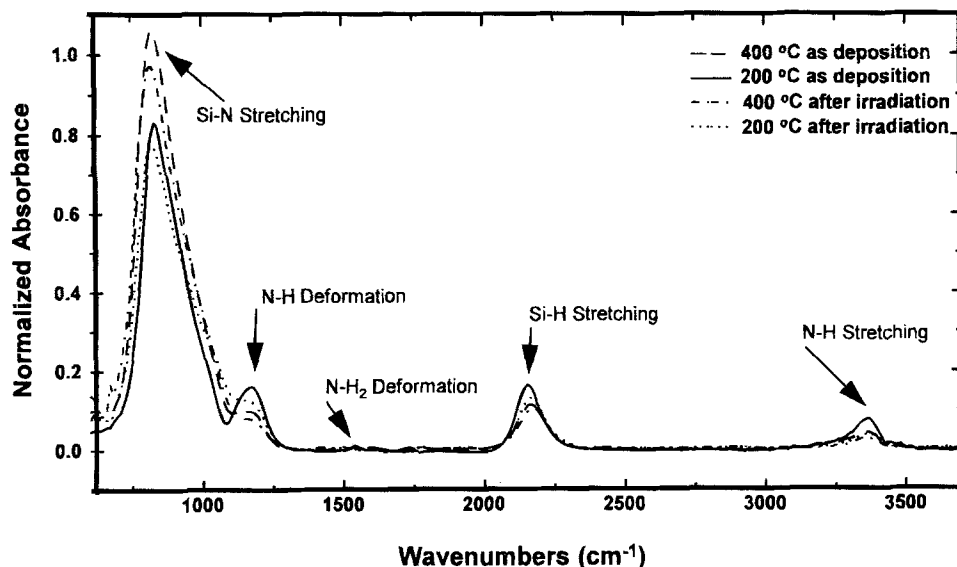


Fig. 2. IR absorption spectra for the hydrogenated silicon nitride films before and after ion beam irradiation.

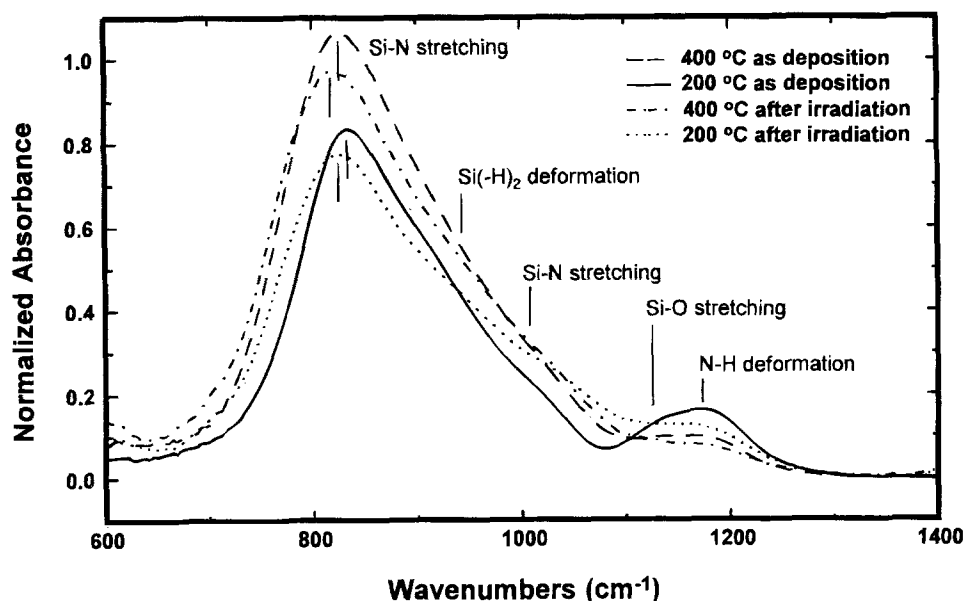


Fig. 3. Detailed IR absorption spectra for the samples in the range of 600-1400  $\text{cm}^{-1}$ .

were determined from the peak areas of the RBS and ERD spectra for the films deposited on Si wafer. A low pressure chemical vapor deposition (LPCVD) silicon nitride deposited on Si wafer was used for calibrating the cross sections of Si and N peak areas on the RBS spectrum. A spin-coated polystyrene film on Si wafer was used for calibrating H peak area on the ERD spectrum.

The IR absorption spectra of the samples before and after ion beam irradiation were obtained by using a vacuum-type single beam instrument FTIR spectrophotometer (Bomem, DA-8) with a mercury cadmium telluride detector. The IR absorbance was measured as a ratio of the transmitted beam intensities of the GaAs wafers with and without the silicon nitride film. The instrumental resolution was  $4 \text{ cm}^{-1}$  and the spectral range was  $400\text{--}4000 \text{ cm}^{-1}$ . All the IR spectra were manipulated by using a Bomem-Calc FTIR software (Spectra Calc. w2.21; Galactic Industries Corp.) which is capable of including background subtraction and peak deconvolution.

### Results and Discussion

Accumulated ERD counts for the hydrogenated silicon nitride film are observed during 2.5 MeV  $\text{He}^{++}$  ion beam irradiation. The results are plotted in Fig. 1 as a function of the ion dose. The films deposited at 200 and  $300^\circ\text{C}$ , show a significant decrease in the ERD count with increase of the ion dose, while the film deposited at  $400^\circ\text{C}$ , shows no significant changes. The ERD count decreased very rapidly at an

early stage of the ion beam irradiation (dose  $<5 \mu\text{C}/\text{cm}^2$ ), but the decrease was progressively slow as the beam dose was raised to  $30 \mu\text{C}/\text{cm}^2$ . The decrease in ERD count was not significant above  $30 \mu\text{C}/\text{cm}^2$ , where the hydrogen in the hydrogenated silicon nitride films was not affected by the ion beam irradiation. Thus, the films reached a limiting hydrogen concentration at which the structure seemed to be stable. The hydrogen loss did not follow a simple first-order decay kinetics, but the limiting hydrogen content was markedly dependent on the film deposition temperature. The film deposited at the lowest temperature had the highest concentration of hydrogen.

Among the samples, the one deposited at  $200^\circ\text{C}$ , shows the fastest initial decrease in hydrogen concentration. The hydrogenated silicon nitride film may be considered to consist of framework bonds such as  $\equiv\text{Si}-\text{N}=\text{}$  and  $\equiv\text{Si}-\text{Si}=\text{}$ , etc., and hydrogen-related terminal bonds such as  $\equiv\text{Si}-\text{H}$  and  $=\text{N}-\text{H}$ . Highly hydrogenated films may possess a coarse framework structure. For films that have such coarse framework structure, it is considered that the hydrogen atom can easily be diffused out of the film after released by the ion beam irradiation. The slow decrease of hydrogen content at high dose suggests that the film reaches more refined framework structures as the ion beam dose increases.

The ERD count can be extrapolated to zero dose. Since the hydrogen content is proportional to the ERD counts,

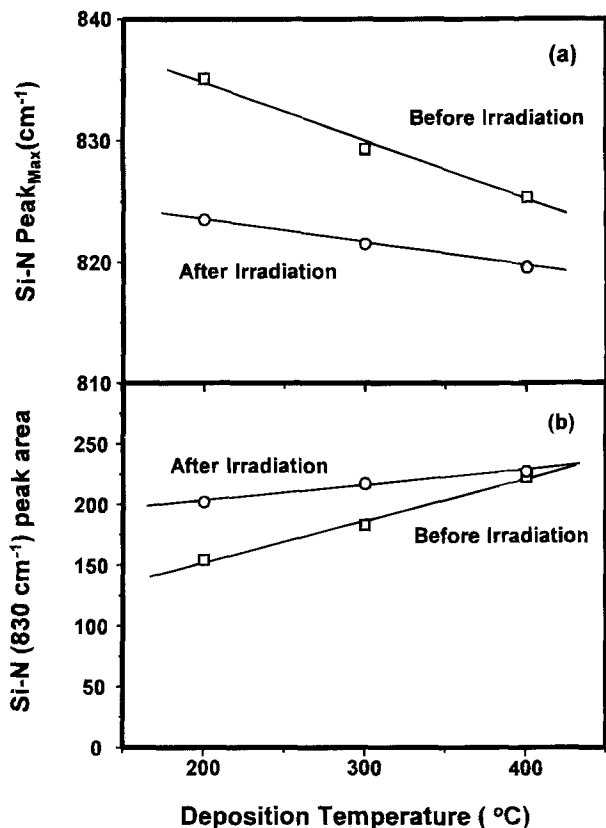


Fig. 4. (a) The maximum peak positions and (b) overall peak areas for the hydrogenated silicon nitride films, before and after ion beam irradiation, according to the deposition temperature.

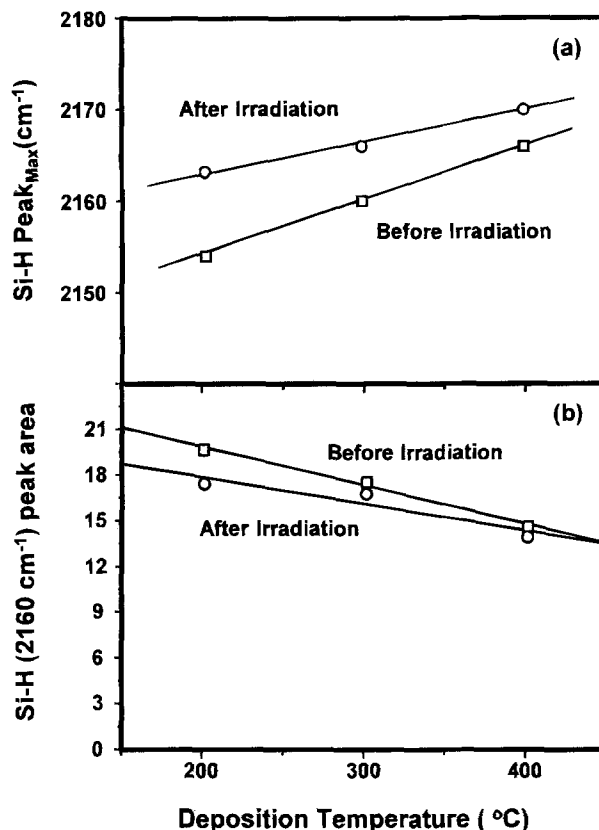


Fig. 6. (a) The maximum peak positions and (b) peak areas of the Si-H stretching bands for the hydrogenated silicon nitride films, before and after ion beam irradiation, according to the deposition temperature.

the number of hydrogen atoms present in the original sample can be determined by calibrating the zero dose ERD count with that of a standard sample with known hydrogen density and film thickness. In the present work, a polystyrene film with density  $4.99 \times 10^{22}$  H atoms/cm<sup>3</sup> and thickness 3410 Å has been used as standard for this purpose.

Figure 2 shows IR absorption spectra of the hydrogenated silicon nitride films deposited at 200 and 400°C. The spectra were background-subtracted and normalized by the initial film thickness. Five main absorption bands are observed: Si-N stretching (850 cm<sup>-1</sup>), N-H deformation (1170 cm<sup>-1</sup>), N(-H)<sub>2</sub> deformation (1530 cm<sup>-1</sup>), Si-H stretching (2160 cm<sup>-1</sup>), and N-H stretching (3350 cm<sup>-1</sup>).

The peak heights represent relative densities of the corresponding chemical bonds in the film. Dividing the integrated band areas by the IR absorption cross sections, we estimate the numbers of Si-H and N-H bonds. According to our previous work,<sup>17</sup> the IR absorption cross sections for the Si-H (2160 cm<sup>-1</sup>) and N-H (3350 cm<sup>-1</sup>) are  $9.4 \times 10^{-18}$  cm<sup>2</sup> and  $6.0 \times 10^{-18}$  cm<sup>2</sup>, respectively. The atomic density obtained from RBS and the bond density from the IR spectrum are presented in Table I.

Figure 3 shows detailed IR absorption spectra in the range of 600-1400 cm<sup>-1</sup>. Four absorption bands for asymmetric Si-N stretching (830 cm<sup>-1</sup>, 1000 cm<sup>-1</sup>), N-H deformation (1170 cm<sup>-1</sup>), and Si(-H)<sub>2</sub> deformation (920 cm<sup>-1</sup>)

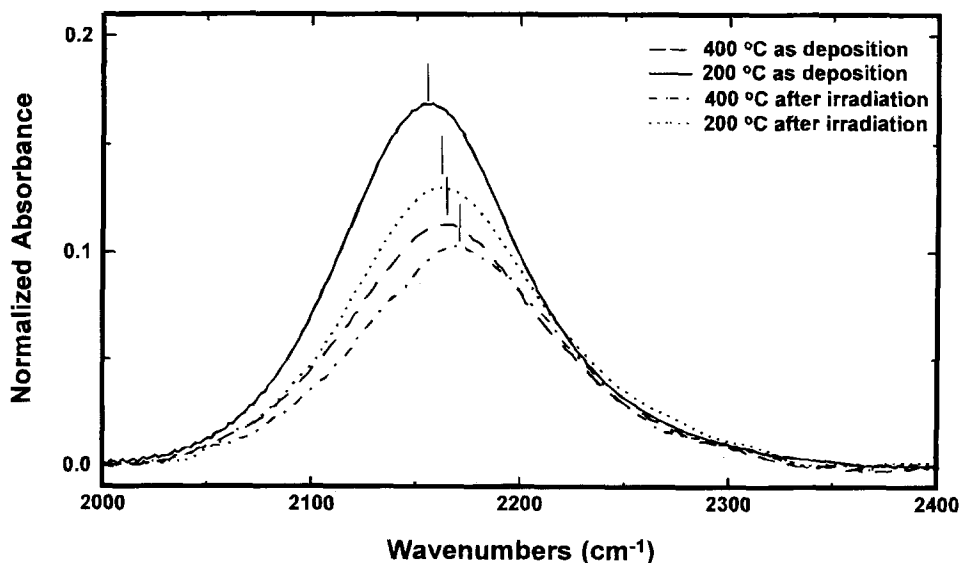


Fig. 5. Detailed IR absorption spectra for the samples in the range of Si-H stretching vibration band.

**Table I. Atomic and bond densities of the hydrogenated silicon nitride films before and after ion beam irradiation. All of the atomic and bond densities are estimated from the numbers of atoms and bonds in unit area, respectively, dividing by the initial film thickness.**

Deposition temperature	Before irradiation					Si/N	After irradiation		
	[Si] <sup>a</sup>	[N] <sup>a</sup>	[H] <sup>b</sup>	[Si-H] <sup>c</sup>	[N-H] <sup>c</sup>		[H] <sup>b</sup>	[Si-H] <sup>c</sup>	[N-H] <sup>c</sup>
	← 10 <sup>22</sup> /cm <sup>3</sup> →						← 10 <sup>22</sup> /cm <sup>3</sup> →		
200°C	3.10	3.12	4.09	2.09	1.89	0.99	2.09	1.51	0.53
300°C	3.28	3.23	3.23	1.86	1.42	1.02	2.40	1.53	0.42
400°C	3.74	3.33	2.49	1.55	1.13	1.12	2.49	1.43	0.45

<sup>a</sup> [Si] and [N]; measured by RBS.<sup>b</sup> [H]; measured by ERD.<sup>c</sup> [Si-H] and [N-H]; measured by FTIR.

can be identified. A small absorption band for asymmetric Si—O stretching also exists at 1125 cm<sup>-1</sup>, probably due to the presence of a surface oxide. According to the IR spectrum, the film as-deposited at 200°C, has lower Si—N stretching and higher N—H deformation peak intensity than the film deposited at 400°C. The peak heights of both the Si—N stretching and N—H deformation bands decrease after high energy ion beam irradiation. However, the overall peak area for the Si—N stretching bands increases because the band width increases more than the height decrease.

From the IR absorption spectra shown in Fig. 3, the maximum peak positions near 830 cm<sup>-1</sup> and integrated peak areas of the Si—N stretching bands were obtained. The peak position and peak area for the samples before and after ion beam irradiation are plotted according to deposition temperature in Fig. 4.

The peak position of the Si—N stretching bands (Fig. 4a) decreases against the deposition temperature. This chemical shift seems to be caused by the differences in the film structure due to variation of the film composition, *i.e.*, the Si/N ratio and H content (see Table I). The peaks also shift to the smaller wave numbers after ion beam irradiation. It is noteworthy that the hydrogen content of the film after ion beam irradiation is lower than that of the as-deposited film.

The peak area in the range of 710–1080 cm<sup>-1</sup> is used to investigate differences of the Si—N bond density among various samples. Although the Si(—H)<sub>2</sub> deformation band overlaps in the same region, the effect of overall peak area due to the variation of this inseparable band intensity is very small. The overall peak area increases with increasing deposition temperature as shown in Fig. 4b. Since the film deposited at high temperature has high film density and a small amount of hydrogen atoms, the film is expected to have high density of Si—N bond. The Si—N peak area also increases after ion beam irradiation. The increase of peak area for the film deposited at low temperature is greater than that for the film deposited at 400°C. This is due to relatively high initial hydrogen content and a rapid loss of the hydrogen during ion beam irradiation. The formation of additional Si—N bonds seems to come from free Si and N radicals when Si—H and N—H bonds are broken during ion beam irradiation. Although the IR peak broadening induced by ion beam irradiation also appears for Si—N stretching band of the film deposited at 400°C, (see Fig. 3), the difference in the overall peak areas before and after ion beam irradiation is small as shown in Fig. 4b. Therefore, the number of Si—N bonds recombined in this film is same as that of the Si—N bonds broken due to ion beam. Moreover, the formation of additional Si—N bonds from the deformation of the hydrogen related bonds seems to be very small in this film. This result agrees well with the saturation feature in the ERD count during the ion beam irradiation for the film deposited at 400°C as shown in Fig. 1.

Detailed IR absorption bands for the Si—H stretching for our samples are shown in Fig. 5. Bustarret *et al.*<sup>18</sup> investigated the Si—H stretching band for hydrogenated silicon nitride films using summation of several Gaussian contributions which were assigned with first neighbor atomic configurations. They concluded that the Si—H stretching

bands for the heavily hydrogenated, and nearly stoichiometric a-Si<sub>x</sub>N<sub>y</sub>H<sub>z</sub> films could be described by three components such as N<sub>3</sub>Si—H (2220 cm<sup>-1</sup>), HN<sub>2</sub>Si—H (2175 cm<sup>-1</sup>), and SiN<sub>2</sub>Si—H and HSiNSi—H (2140 cm<sup>-1</sup>). As shown in Fig. 5, the maximum peak positions of the Si—H stretching bands for the samples are observed within the range of 2150–2170 cm<sup>-1</sup>. Therefore, it is believed that the major components existing in the samples are the three components as mentioned before. In addition, minor contributions from a high order of the silicon neighbor atomic configuration such as NSi<sub>2</sub>Si—H and HSi<sub>2</sub>Si—H, etc., are also considered to be present at the wave numbers below 2085 cm<sup>-1</sup>.

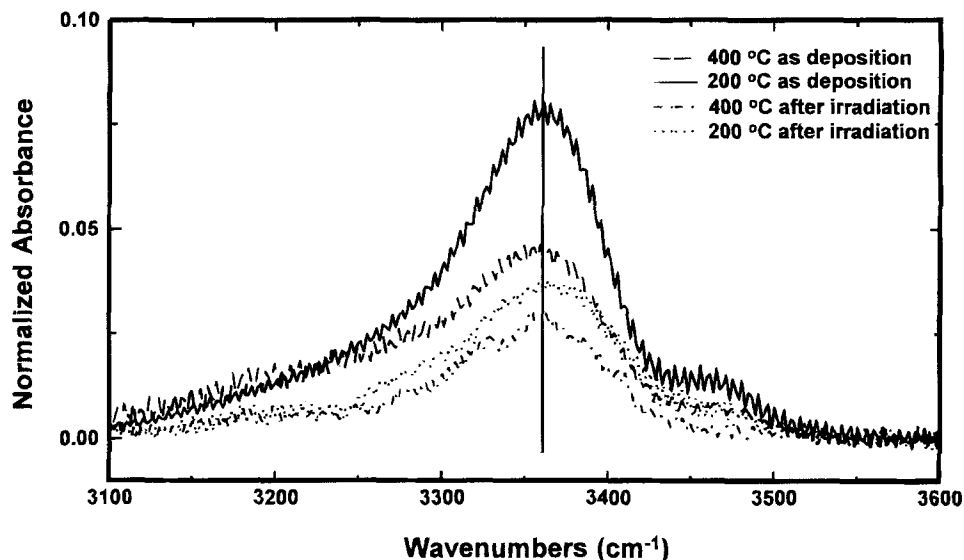
In general, for PECVD silicon nitride films, the wave number at maximum peak for the Si—H stretching band increases against decrease of the Si/N ratio and hydrogen content. Figure 6a compares maximum peak positions of the Si—H stretching band for the as-deposited films with those after ion beam irradiation. Although the Si/N ratio increases with the deposition temperature as in Table I, the Si—H stretching band shifts to higher wave numbers as the deposition temperature increases. This tendency may be caused by a considerable decrease of the hydrogen content in the film upon deposition at high temperature. The Si—H stretching band also shifts to the higher wave numbers following the ion beam irradiation. This is probably due to the formation of additional Si—N bond subsequent to the formation after the ion beam induced bond breaking.

The normalized Si—H peak areas for the films before and after ion beam irradiation are plotted according to deposition temperature in Fig. 6b. The peak areas for the as-deposited film decrease against the deposition temperature, but slightly decrease after ion beam irradiation. For the films deposited at 300 and 400°C, there is a considerable band shift due to ion beam irradiation. However, the peak area does not change, and the hydrogen content in the film deposited at 400°C does not change due to ion beam irradiation. The peak shift without variation of the Si—H bond density or the hydrogen content strongly indicates significant changes in the frame bond structure.

Figure 7 shows the IR absorption spectra in the range of 3100–3600 cm<sup>-1</sup>. The symmetric and asymmetric N—H stretching bands are observed at 3350 (medium intensity) and 3460 cm<sup>-1</sup> (weak intensity), respectively. The slow slope in the range of 3150–3320 cm<sup>-1</sup> is unusual and likely to be due to hydrogen bonding between the H atoms in the N—H bonds and lone-pair electrons on nearby N atoms. Even if there are variations in the hydrogen content and the film structure, the peak position and the band shape for the N—H stretching do not show any considerable changes.

The peak area for the N—H stretching bands significantly decreases against the film deposition temperature, as well as ion beam irradiation as shown in Fig. 8. The decrease of the N—H stretching band area after ion beam irradiation is much larger than that of the Si—H stretching band. Namely, a considerable number of the N—H bonds are removed from the film framework during ion beam irradiation, while the same amount of the Si—H bond exists nevertheless in the ion beam induced bond breaking. This difference cannot be completely explained by the differences in the bond strength.<sup>19,20</sup> Since the ion beam used in

Fig. 7. Detailed IR absorption spectra for the samples in the range of N—H stretching vibration band.



this experiment has enough energy to break such chemical bonds, the number of broken bonds would insignificantly vary with the bond strength. Hence, it can be suggested that this remarkable difference is due to the presence of excess Si—Si bonds in the silicon-rich silicon nitride film. When the excess Si—Si bonds are present in the film, Si radicals can be generated from both the Si—Si and Si—H bonds. At the same time, N and H radicals are likely to form during ion beam irradiation and subsequently recombine with the Si radicals. This may explain why the number of Si—N bonds increases while the number of Si—H bonds does not change and the number of N—H bonds significantly decreases.

### Conclusions

In order to investigate the annealing effects during ERD analysis, chemical bonds in a hydrogenated silicon nitride film have been studied using FTIR spectroscopy.

From a decrease in the ERD count with the ion beam dose, we conclude that the hydrogen atom in the films deposited at low temperature easily diffuses out of the film due to the annealing effects after the chemical bonds are broken.

The IR absorption peak positions and normalized peak areas for Si—N stretching ( $830\text{ cm}^{-1}$ ), Si—H stretching ( $2160\text{ cm}^{-1}$ ), and N—H stretching ( $3360\text{ cm}^{-1}$ ) bands were also observed for the films before and after ion beam irradiation. We have found significant changes in the peak position for Si—N and Si—H bands and peak area for N—H

band. On the contrary, the peak area for the Si—N band increases significantly while that of the Si—H band slightly decreases due to ion beam irradiation. This contradictory result can be explained by the recombination of broken bonds generated by the ion beam. In the case of the Si-rich silicon nitride film, the Si—N and Si—H bonds are likely to be regenerated by recombination of N and H radicals with excess Si radicals.

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### REFERENCES

1. K. D. Mackenzie, A. J. Snell, J. French, P. G. Lecomber, and W. E. Spear, *Appl. Phys. A*, **31**, 87 (1983).
2. G. J. Valco and V. J. Kapoor, *This Journal*, **134**, 685 (1987).
3. D. Jousse, J. Kanicki, D. T. Krick, and P. M. Lenahan, *Appl. Phys. Lett.*, **52**, 445 (1988).
4. A. K. Sinha, H. J. Levinstein, T. E. Smith, G. Quintana, and S. E. Haszko, *This Journal*, **125**, 601 (1978).
5. H. Dun, P. Pan, F. R. White, and R. W. Douse, *ibid.*, **128**, 1555 (1981).
6. G. M. Samuelson and K. M. Mar, *ibid.*, **129**, 1773 (1982).
7. M. A. Khaliq, Q. A. Shams, W. D. Brown, and H. A. Naseem, *J. Electron. Mater.*, **17**, 5 (1988).
8. Q. A. Shams and W. D. Brown, *Microelectron. J.*, **20**, 49 (1989).
9. J. H. Souk, G. N. Parson, and J. Batey, *Mater. Res. Soc. Symp. Proc.*, **19**, 787 (1991).
10. J. Gyulai, O. Meyer, J. W. Mayer, and V. Rodriguez, *Appl. Phys. Letters*, **16**, 232 (1970).
11. S. V. Nguyen, W. A. Lanford, and A. L. Reiger, *This Journal*, **133**, 970 (1986).
12. Z. Yin and F. W. Smith, *Phys. Rev. B*, **42**, 3666 (1990).
13. M. M. Pradhan and M. Arora, *Jpn. J. Appl. Phys.*, **31**, Part 1, 176 (1992).
14. J. W. Lee, K. I. Cho, R. Ryoo, and M. S. Jhon, in *State-of-the-Art Program on Compound Semiconductor XVIII*, R. E. Enstrom, S. N. G. Chu, T. Kamijoh, J. P. Vilcot, and O. Ueda, Editors, PV 93-27, p. 201, The Electrochemical Society Proceedings Series, Pennington, NJ (1993).
15. W. A. Lanford, *Nucl. Instrum. Methods Phys. Res.*, **B66**, 65 (1992).
16. W. A. Lanford and M. J. Rand, *J. Appl. Phys.*, **49**, 2473 (1978).
17. J. W. Lee, K. I. Cho, R. Ryoo, and M. S. Jhon, *J. Phys. Chem. Solids*, **56**, 293 (1995).
18. E. Bustarret, M. Bensouda, M. C. Habrard, J. C. Bruyere, S. Poulin, and S. C. Gujrathi, *Phys. Rev. B*, **38**, 8171 (1988).
19. C. M. M. Denisse, K. Z. Troost, F. H. P. M. Habraken, W. F. van der Weg, and M. Hendriks, *J. Appl. Phys.*, **60**, 2543 (1986).
20. H. J. Schliwinski, U. Schnakenberg, W. Windbracke, H. Neff, and P. Lange, *This Journal*, **139**, 1730 (1992).

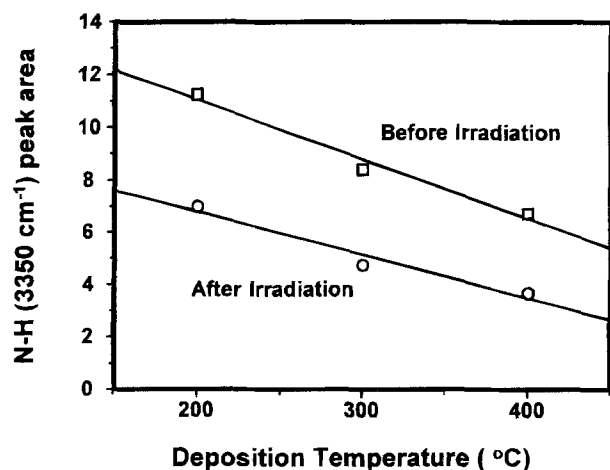


Fig. 8. The N—H stretching band areas for the hydrogenated silicon nitride films, before and after ion beam irradiation, according to the deposition temperature.