Amorphous silicon nitride (a-SiN<sub>x</sub>) thin films are deposited at low temperature by remote-type inductively coupled plasma enhanced chemical vapor deposition (ICP-CVD) using N<sub>2</sub>/SiH<sub>4</sub> gases as reactant gases to obtain low hydrogen content in the films. Refractive index, deposition rate, stoichiometry, hydrogen content, and hydrogen configuration in the films are analyzed with the variation of deposition parameters. As RF power and N<sub>2</sub> flow rate increase, refractive index decreases due to the decrease of Si/N ratio, total hydrogen content is constant with N-H changing hydrogen bond configurations (Si-H, N-H) reversely. However, as substrate temperature increases, refractive index increases due to the reduction of Si/N ratio, and total hydrogen content as well as both hydrogen bond configurations (Si-H, N-H) decrease. In remote-type ICP-CVD using N<sub>2</sub>/SiH<sub>4</sub> gases, N-rich a-SiN<sub>x</sub> films with low refractive index and density are deposited due to efficient dissociation of N<sub>2</sub> gas by high density plasma, and hydrogen content in the films is greatly reduced.
ma without an external magnetic field than do conventional parallel-type PECVD.

In this system, the intense degree of ionization and dissociation is established in a region away from the substrate in the deposition chamber. The plasma stream is a fluid dynamically transported with the reaction of source gases to the substrate where the deposition occurs. Thus, this remote-type ICP-CVD process allows the deposition of dense high quality thin film without heating and damage to the substrate.

The silicon nitride films were deposited on (100) p-type Si substrate using SiH₄/N₂ as reactant gases, and Ar as the diluent gas. N₂ and Ar gases were premixed in a gas mixing box, and the gas mixtures pass through the plasma chamber. On the other hand, SiH₄ passes through by ejecting from the gas ring located just under the plasma chamber. Thus, N₂ gas is directly dissociated by the RF power while SiH₄ is indirectly dissociated. Gases were introduced after evacuating the chamber and lines to the base pressure of 10⁻⁶ Torr, and the deposition was done at the pressure of 10⁻¹ Torr. The substrate is rotated at 5 rpm for uniform deposition. Deposition characteristics have been examined with the variation of process parameters. The substrate temperature, RF power, and SiH₄/N₂ gas flow rate ratio were systematically changed while the rest were held constant. The experimental deposition condition and process parameters used in this study are listed in Table I.

We performed thin film X-ray diffraction (TXRD, Rikagai Inc., Cu target and Ni filter) analysis to confirm the amorphous phase of the films. The relative N/Si ratios of the films were analyzed using Auger electron spectroscopy (AES, Perkin-Elmer SAM 4300) with electron acceleration voltage of 5 keV and current of 300 nA. In the depth profile of AES analysis, Ar sputtering voltage and current density were 3 kV and 250 μA/cm², respectively.

The thickness and reflective index of the films were simultaneously obtained using an ellipsometer (Rudolph, Auto-EL2). Hydrogen content in the films was analyzed by Fourier transformed infrared spectroscopy (FTIR, Bomem 3000 Series) spectrum of the films. Also, scanning electron microscopy (SEM, Philips 535M) was used for the observation of surface morphology.

### Results and Discussion

All the films deposited in this study are confirmed to be amorphous by XRD analysis. As a consequence of the large temperature difference between the reactive species in the plasma (~10³ K) and the substrate temperature (~600 K), the deposition can be regarded as a quenching process. Thus, they form an amorphous phase since the deposited atoms do not have enough time to migrate to the stable site. Also, the SEM images of the films show smooth surfaces representing no surface damage by activated species and heterogeneous deposition process.

**Compositional analysis.**—We deposited the a-SiNₓ films with the variation of N₂ flow rate from 10 to 40 sccm under the condition of RF power of 200 and 300 W, deposition temperature of 300 °C, SiH₄ flow rate of 1 sccm, working pressure of 0.1 Torr.

The compositional analysis of a-SiNₓ film deposited at N₂ flow rate of 30 sccm was performed by AES, as shown in Fig. 2. Figure 2a is an AES spectrum of the SiNₓ film at a certain depth. The Si, N, Ar, and O elements were detected in the spectrum. Compositional uniformity is found in the depth profile of the AES analysis. Compared with Si and N, the oxygen content in the film can be neglected. The peak to peak height ratio of Si/L₁/Si/Sii is taken as a relative composition ratio of N/Si. The measured N/Si ratios at the N₂ flow rate of 10 and 30 sccm are 0.69 and 0.62, respectively. Certainly, the increase of N₂ flow rate results in the decrease of Si/N ratio of the film. Existence of oxygen incorporated in the film is believed to be due to moisture released from the inner wall of the reactor by the plasma.

The relative Si/N ratio with the variation of RF power is shown in Fig. 3a. As RF power increases, the Si/N ratio decreases from 1.0 to 0.62. In general, the radical has higher generation than the ion since the dissociation energy of gas molecule is lower than ionization energy. Also, neutral radicals have longer lifetime than ions since positive ions meet electrons easily near the surface and chamber wall. Therefore, the concentration of radicals is much higher than that of ions, and major deposition agent is a neutral radical. With a very crude approximation, the molecular dissociation probability is exp(−ΔE/kTₑ), where ΔE is a dissociation energy and Tₑ is an electron temperature. If Tₑ is raised, the concentration of the reactant gas having larger ΔE is changed more widely. It results in a change in the composition stoichiometry of the film. In the N₂/SiH₄ plasmas system, the dissociation energy of N₂ gas is 9.0 eV and SiH₄ is 3.1 eV. Therefore, as power is increased, the electron temperature increases and Si/N ratio decreases. This represents the RF power variation results in similar composition variation in the film to N₂ flow rate variation in remote-type ICP-CVD.

Si content in the films increases with increasing substrate temperature as shown in Fig. 3b. The less activated SiH₄ gas rather than N₂ gas, due to the indirect plasma dissociation, participates in the surface reaction more actively at high temperature. Thus, more Si is incorporated in the film at higher substrate temperature.

**Refractive index and deposition rate.**—The deposition rates and refractive indexes of a-SiNₓ films as a function of N₂ flow rate, RF power, and substrate temperature are shown in Fig. 4, 5, and 6, respectively. Generally, the deposition rate grows with increasing N₂ flow rate since more

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**Table I. Deposition conditions and process variables.**

<table>
<thead>
<tr>
<th>Deposition variables</th>
<th>Power (W)</th>
<th>N₂ (sccm)</th>
<th>SiH₄ (sccm)</th>
<th>Ar (sccm)</th>
<th>Temperature (°C)</th>
<th>Pressure (mTorr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ flow rate</td>
<td>200, 300</td>
<td>10, 20</td>
<td>30, 40</td>
<td>1</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>Power</td>
<td>200, 300, 400, 300, 600</td>
<td>10</td>
<td>1</td>
<td>150</td>
<td>300</td>
<td>140</td>
</tr>
<tr>
<td>Temperature</td>
<td>200</td>
<td>1</td>
<td>1</td>
<td>150</td>
<td>25, 100, 200, 300</td>
<td>140</td>
</tr>
</tbody>
</table>
activated N	extsubscript{2} gas is generated as shown in Fig. 4. The deposition rate is saturated since no more nitrogen is dissociated above 20 sccm due to the limitation of dissociability of 300 W RF power. The refractive index decreases from 2.20 to 1.90 at 300 W RF power, and from 2.00 to 1.83 at 200 W RF power with increasing N	extsubscript{2} flow rate as shown in Fig. 4. This is due to the decrease in Si/N ratio of the film with increasing N	extsubscript{2} flow rate according to AES compositional analysis. In a-SiN	extsubscript{x} films, it is well known that a large Si/N value gives a large refractive index due to more absorptive Si-Si bonds in the film.

Also, more N	extsubscript{2} gas is dissociated and Si/N ratio in the film reduces with increasing RF power as mentioned earlier. Thus, the deposition rate increases and the refractive index decreases widely from 2.20 to 1.73 with changing RF power as shown in Fig. 5. The refractive index values of the films deposited at high RF power is lower than those of the films deposited at high N	extsubscript{2} gas flow rate. Also, it is found that the variation of refractive index depending on RF power is larger than that depending on the N	extsubscript{2} flow rate. Because only N	extsubscript{2} gas is dissociated directly by RF power in the plasma chamber while SiH	extsubscript{4} gas is dissociated indirectly by activated N	extsubscript{2} gas outside the plasma chamber in the remote-type ICP-CVD used in this experiment. Therefore, the reaction chemistry can be controlled more widely by RF power rather than N	extsubscript{2} flow rate since the high RF power generates more activated N	extsubscript{2} gas rather than SiH	extsubscript{4} gas. The controllability of reaction chemistry in remote-type ICP-CVD is able to deposit the N-rich a-SiN	extsubscript{x} films having low refractive indexes.

Figure 6a shows that the surface reaction is more activated resulting in fast deposition at high substrate temperature. The greater the Si/N ratio in the film at higher substrate temperatures results in higher refractive index as shown in Fig. 6b. Also the denser film at higher substrate temperature contributes to produce the higher refractive index of the film.

**FTIR spectroscopy.**—Figure 7 presents the FTIR spectra of a-SiN	extsubscript{x} films deposited at various RF power. As RF power increases, the Si-N peak (890 cm	extsuperscript{-1}) becomes broader, the Si-H peak (2160 cm	extsuperscript{-1}) disappears, and the N-H peak (3340 cm	extsuperscript{-1}) is distinguishable. The increase of N-H intensity is proportional to N content according to the random network model.

The broad Si-N peak shape reflects the broad distribution of Si-N stretching vibration energies owing to the large vibration in binding energies in the amorphous films. The increase in N concentration induces the shift of Si-N peak to higher frequency. The existence of electronegative neighboring atoms like F or N in Si-Si bond strength of back bond by changing its polarization. Thus, the more N atoms in the a-SiN	extsubscript{x} films create more Si-N back bonds resulting in lower bond strength. This allows the absorption band of the Si-N bond to shift to a higher wavenumber. Also, if the Si,N	extsubscript{2} molecule in the film is diatomic, the allowed energy levels for the vibration of a Si-N diatomic molecule, as given by quantum mechanical theory, is

$$E_{v} = \left(\frac{v + \frac{1}{2}}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{u}} \quad v = 0, 1, 2 \ldots$$

where $k$ is the force constant that measures the force required to stretch a bond by a given distance (that is, the stiffness of the chemical bond) and $u$ is the reduced mass for the two atoms, Si, N; $u = (x_{m_{n}} + y_{m_{n}})/(x_{m_{n}} + y_{m_{n}})$, $x + y = 2$. As the N concentration grows in the films, $y$ increases creating lower $u$ in eq 1 since $m_{n}$ is considerably smaller than $m_{n}$. Thus, the Si-N peak shifts to a higher frequency due to the increase of allowed vibration energy levels with increasing N content in the films.
The Si-H absorption band in amorphous Si films is observed around 2000 cm$^{-1}$. The fact that the absorption bands due to Si-H stretching vibration in a-SiN$_x$ films shifted to higher wavenumbers compared with those of a-Si films is caused by the inductive effect due to incorporation of N atoms whose electronegativity is greater than that of Si atoms.

Prediction of the density and Si/N ratio.—The densities of a-SiN$_x$ thin films and absolute Si/N ratio cannot be analyzed easily. However, the theoretical density and Si/N ratio can be calculated from the refractive index and the nitrogen concentration. The nitrogen concentration [N] can be obtained from the Si-N absorption band in FTIR spectrum:

$$[N] = 9.2 \times 10^4 \int \frac{\alpha(w)}{w} dw$$

$$\alpha(w) = \frac{1}{t} \ln \left( \frac{T_o}{T} \right)$$

where $w$ is the wavenumber and $\alpha(w)$ is the absorption coefficient, $T_o$ and $T$ are the incident and transmitted light intensity, $t$ is the film thickness, and $9.2 \times 10^4$ is the absorption cross section of nitrogen in a-SiN$_x$ thin films.

The electronic polarizability of SiN$_x$, $P_{\text{SiN}}$, electronic polarizability of Si atom $P_{\text{Si}}$, and N atom $P_{\text{N}}$ and Si/N ratio $R$ are given by:

$$P_{\text{SiN}} = \frac{(P_{\text{Si}} R + P_{\text{N}})/R}{1 + 1} \quad (\text{cm}^3)$$

$$P_{\text{SiN}}^{\text{SiN}} = (1.67 + 1.39R) \times 10^{-24} \quad (\text{cm}^3)$$

$$R = \frac{[\text{Si}]}{[\text{N}]}$$

The Lorentz-Lorentz equation is:

$$\frac{(n^2 - 1)}{n^2 + 2} \rho = \frac{4n}{3} AP_{\text{SiN}}$$

$$M = \frac{(28R + 14)/(R + 1)}{1}$$

where [Si] and [N] are atomic densities of Si and N atoms, respectively, $n$ is refractive index, $M$ is the molecular
We can obtain an equation in \( R \) by substituting eq 4, 5, 6, 9, and 10 into eq 8

\[
1.39R^2 + 1.67R + 0.35 - \left( \frac{3}{4\pi} \right) \times \left( \frac{n^2 - 1}{n^2 + 2} \right) \left( \frac{10^{14}}{[N]} \right) = 0 \quad [11]
\]

\[
R = -0.60 + 0.36 \left( 0.84 + 1.33 \left( \frac{n^2 - 1}{n^2 + 2} \right) \times \frac{10^{-11}}{[N]} \right)^{1/2} \quad [12]
\]

Thus, \( \text{Si/N ratio} \) \( R \) can be calculated from the nitrogen concentration \([N]\) and refractive index \(n\). Figure 8 shows the variation of calculated \( \text{Si/N ratio} \) with RF power. The calculated \( \text{Si/N ratio} \) variation which decreases with increasing RF power agrees well with the experimental data of AES as shown in Fig. 3a. Thus, the calculated density by eq 11 would be reliable data. The variation of the calculated density depending on RF power is shown in Fig. 8. The density of the film decreases consistently with increasing RF power due to the reduction of the \( \text{Si/N ratio} \) in the films.

**Hydrogen content.**—The hydrogen content and the hydrogen bond configuration (Si-H, N-H) depend on the precise parameters, and have a great influence on film properties. It has been known that the hydrogen content in...
a-SiN$_x$ films is mainly determined by substrate temperature, and the hydrogen bond configuration depends on the gas flow ratio at a given substrate temperature.$^{32,33}$ Absorption FTIR spectroscopy has been used for hydrogen analysis of the films deposited on Si substrate.$^{24,32,33}$ The main absorption peak due to Si-N stretching vibration appears around 890 cm$^{-1}$, and the absorption peaks due to the Si-H stretching vibration and the N-H stretching vibration appear at 2180 and 3340 cm$^{-1}$, respectively. The hydrogen content can be analyzed quantitatively by using the Beer-Lambert's law:$^{19}$

$$C_n = \delta \int \frac{\alpha(w)}{w} dw$$

where, $A$ is an absorbance, $t$ is a film thickness, $T$ is a transmittance, and $\delta$ is a proportionality constant representing vibrational strength. The absorption cross section $\delta$ of hydrogen is $7.4 \times 10^{-18}$ cm$^2$ for N-H and $5.3 \times 10^{-18}$ cm$^2$ for Si-H in a-SiN$_x$ films which were obtained in the Lanford and Rand's result.$^{33}$

Figure 9 shows the variation of the hydrogen content and hydrogen bonding configuration with varying N$_2$ flow rate. The total hydrogen content is almost constant about $3 \times 10^{11}$ atom/cm$^2$ regardless of N$_2$ flow rate. However, the Si-H bond decreases but N-H bond increases with increasing N$_2$ flow rate since Si/N ratio is reduced.

Figure 10 represents the variation of the hydrogen content and the hydrogen configuration with variation of RF power. Since N content in the films is raised with increasing RF power, the N-H bond concentration increases, but the Si-H bond concentration decreases at high RF power. At a greater electron temperature, the SiH$_4$ would give up more hydrogen to produce more H$^+$ in the plasma and less Si-H bond in the film. The generation of N$^+$ ion increases and a more negatively biased surface field is induced as a consequence of greater electron energy and density. Thus, there are more H$^+$ and N$^+$ ions incorporated into the film to produce more N-H bond. Although the production of H$^+$ bond in the plasma is also possible, the chance is smaller compared to the surface recombination. However, the N-H bond concentration is saturated above 500 W RF power since available N$_3$ gas is almost dissociated. Also, the Si-H bond concentration is reduced to an undetectable value above 400 W RF power so that the N-H bond is dominant in the hydrogen configuration. Because the dissociated H from SiH$_4$ gas is more attractive to N dangling bond (which is more generated in N-rich films at higher RF power) than Si dangling bond due to the higher bonding energy of N-H bond than that of Si-H bond. Therefore, the total hydrogen content becomes the lowest at 300 W RF power where Si-H and N-H bond contents are similar. The composition variation of the film becomes close to stoichiometry at 300 W RF power producing the lowest number of dangling bond (which is attachable to H) and making the most stable film.

Figure 11 shows the variation of hydrogen content and the hydrogen bond configuration depending on substrate temperatures. As the substrate temperature increases,

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*Fig. 9. Variation of hydrogen content and hydrogen bond configuration as a function of N$_2$ flow rate. (300 W RF power, N$_2$: SiH$_4 = 10:1$ sccm.)*

*Fig. 10. Variation of hydrogen content and hydrogen bond configuration as a function of RF power. (300 °C, N$_2$: SiH$_4 = 10:1$ sccm.)*

*Fig. 11. Variation of hydrogen content and hydrogen bond configuration as a function of substrate temperature. (200 W, N$_2$: SiH$_4 = 10:1$ sccm.)*
Si-H and N-H bond concentrations as well as total hydrogen content decrease. At high substrate temperature, the hydrogen atom obtains more energy required to release from the surface than at low temperature. Thus, Si-H bond concentration as well as N-H bond concentration are reduced at high temperature although Si content increases with increasing the substrate temperature. The evolution of hydrogen in the N-H bond is faster than that of the Si-H bond with increasing the substrate temperature. Among the process parameters, the total hydrogen content depends mainly on the substrate temperature.

Total hydrogen content is about 3 to 5.5 \times 10^{21} \text{atoms/cm}^3 regardless of N2 flow rate and RF power when deposited at 300 °C. This value is an order lower than those which were reported in previous studies using SiH4/NH3 gases in conventional PECVD. For example, total hydrogen reported in previous studies using SiH4/NH3 gases in conventional PECVD using SiH4/NH3 gases is around 1.6 to 2 \times 10^{21} \text{atom/cm}^3. Thus, the hydrogen content of the a-SiN films can be greatly reduced by deposition using SiH4/N2 gases, which can be easily dissociated in ICP-CVD.

**Conclusion**

a-SiN films with low hydrogen content can be deposited by remote-type ICP-CVD using SiH4/N2 gases as the reactant gases. Refractive indexes of the a-SiN films are reduced by decreasing Si/N ratio obtained by increasing RF power and N2 flow rate, and decreasing substrate temperature. In particular, the unique advantage of remote-type ICP-CVD rather than conventional PECVD is the ability to deposit the N-rich a-SiN films containing low hydrogen content with relatively low N2/SiH4 flow rate ratio since stoichiometry of the film can be controlled extensively by the variation of RF power due to the direct dissociation of N2 gas in ICP-CVD.

The total hydrogen content in a-SiN films is almost constant with the variation of RF power and N2 flow rate at 300 °C of substrate temperature. The hydrogen content in a-SiN films is much less than those in other a-SiN films prepared by conventional PECVD using SiH4/NH3 gases. However, Si-H and N-H bond concentration vary reversibly with each other with the variation of RF power and N2/SiH4 flow rate ratio. As the substrate temperature increases, total hydrogen content and hydrogen bond configurations decrease due to the release of hydrogen at high temperatures.

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**REFERENCE**