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# Fluorinated silicon nitride film for the bottom antireflective layer in quarter micron optical lithography

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**Abstract.** Fluorinated silicon nitride thin film as a bottom antireflective layer (BARL) material, being suitable for line-patterning in 0.25 $\mu$m KrF excimer laser (248 nm) lithography, has been studied by film fabrication/characterization and computer simulation. Three-dimensional reflectance simulation process suggests that the 0% reflectance between photoresist (PR) and BARL can be achieved by selecting proper combinations of film optical properties such as refractive index (*n*), extinction coefficient (*k*) and thickness (*d*). For the PR/300 Å BARL/c-Si or PR/300 Å BARL/W-Si structure at a wavelength of 248 nm, the simulation process reveals that nearly 0% reflectance could be obtained when the *n* and *k* values of the film are 2.109 and 0.68 or 2.052 and 0.592 respectively. The fluorinated silicon nitride films prepared by ICP enhanced CVD have been evaluated with the variations of $NF_3$ flow rates under the two conditions of $SiH_4$:$N_2$ = 2 : 15 and 3:20 (sccm). The film *n* and *k* values at 248 nm vary in the ranges of 1.665–2.352 and 0.007–0.695 respectively, depending on gas flow ratio. As it is very sensitive to the film thickness, the reflectance could be reduced, using compoter simulation, to almost 0% by changing the film thickness. Furthermore, the ARL performance for 0.25 $\mu$m line/space processed by the KrF excimer laser stepper and the stripping ability/selectivity show this material to be a superior candidate for deep-UV microlithography applications.

## 1. Introduction

The circuit density in ultra-large scale integration (ULSI) is rapidly increasing, and the feature size is becoming smaller and smaller; for example the required mean feature size in the 256 M DRAM is as small as 0.25 $\mu$m. Generally, higher resolution can be obtained by using a shorter wavelength in the optical lithographic process. For these reasons, the KrF excimer laser (248 nm) stepper [1] for quarter micron lithography is attracting attention as a substitute for the i-line (365 nm) stepper widely used at present in mass production of ULSI devices. However, with adoption of the KrF excimer laser stepper in photolithography, the increased reflectivity at the interface between photoresist (PR) and substrate causes disparities in the linewidth due to the multiple interference effect (MIE) within the PR. That is, swing and notching effects occur in the lithographic process. ‘Swing’ is the effect by which the linewidth varies due to thin film interference effects caused by variation in resist thickness or variation in the thickness of transparent layers, such as oxide or nitride, underneath the resist layer. ‘Notching’ is the effect by which light reflected from the substrate topography becomes concentrated at certain positions, so that local linewidth narrowing or broadening occurs. One way to solve these problems is to apply a bottom antireflective layer (BARL) with appropriate optical constants, i.e. refractive index (*n*) and extinction coefficient (*k*), and thickness beneath the photoresist [2–5]. Although the use of this extra layer in the fabrication process was initially unappealing to process engineers, the current industry consensus is that the benefits of the antireflective layer outweigh its added cost and process complexity.

We have searched for a practical material to be used as a BARL whose refractive index and extinction coefficient are close to the optimum conditions. Among several candidate materials, we studied fluorinated silicon nitride films as a novel and practical BARL material for deep-ultraviolet (DUV) optical lithography. Fluorinated silicon nitride films have been fabricated by an inductively coupled plasma (ICP) [6] enhanced chemical vapour deposition (CVD)

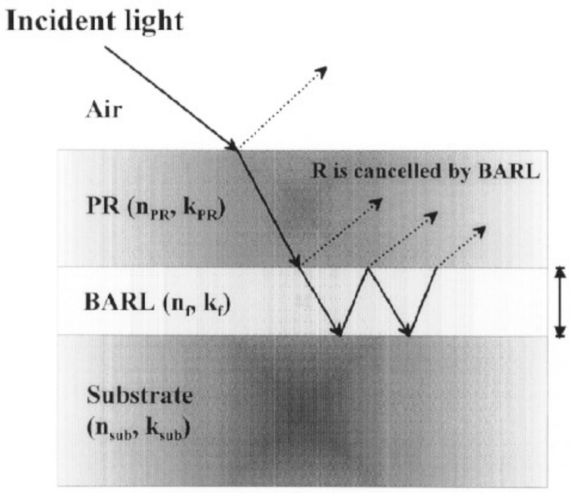

**Figure 1.** Schematic structure of bottom antireflective layer.

system which can offer improved process control as well as a considerable reduction in surface damage imposed on the substrate. In this paper, the effects of deposition parameters such as gas flow ratio on the optical constants at the wavelength of 248 nm will be studied. A BARL design and simulation program developed here will be employed to predict the optimum condition of 0% reflectance for the films on both Si and W-Si (tungsten silicide) substrates at 248 nm and to apply a reflectance calculation for the deposited films. Then, the applicability of fluorinated silicon nitride film as a BARL in the 0.25 $\mu$m optical lithography process will be demonstrated by investigating the lithographic performance and wet etch characteristic.

## 2. Physical model and BARL simulation

A considered physical ARL model is shown in figure 1. The reflectance ($R$) at the interface between PR and BARL, assuming a normal incident beam on a uniform and isotropic thin film and a multilayer structure, can generally be expressed by the following equations [7]:

$$R = \left| \frac{(n_{PR} - \mathrm{i}k_{PR})E - H}{(n_{PR} - \mathrm{i}k_{PR})E + H} \right|^2 \tag{1}$$

$$\begin{bmatrix} E \\ H \end{bmatrix} = \begin{bmatrix} \cos\delta & \frac{\mathrm{i}\sin\delta}{n_f - \mathrm{i}k_f} \\ \mathrm{i}(n_f - \mathrm{i}k_f)\sin\delta & \cos\delta \end{bmatrix} \begin{bmatrix} 1 \\ (n_{sub} - \mathrm{i}k_{sub}) \end{bmatrix} \tag{2}$$

where $n_{PR}$ and $k_{PR}$ are the optical constants of the photoresist, $n_f$ and $k_f$ are the optical constants of the BARL, $n_{sub}$ and $k_{sub}$ are the optical constants of the substrate, $E$ is the standardized electrical field at the incident boundary plane, $H$ is the standardized magnetic field at the incident boundary plane, and $\delta$ is the optical phase thickness ($= 2\pi$ $(n_f - \mathrm{i}k_f)d/\lambda$) where $d$ is the physical BARL thickness and $\lambda = 248$ nm.

The structure of PR (XP89131, negative type; $n_{PR} =$ 1.8 and $k_{PR} = 0.011$ at 248 nm)/300 Å BARL/crystalline Si (c-Si) substrate ($n_{Si} = 1.57$ and $k_{Si} = 3.565$ at 248 nm) or W-Si substrate ($n_{W\text{-}Si} = 1.763$ and $k_{W\text{-}Si} = 2.546$ at 248 nm; actually, W-Si film on c-Si bulk) is considered for the reflectance calculation between PR and BARL. Usually, the W-Si film is used as a bit-line or gate material in DRAM. Other applications of BARL are in structures such as PR/BARL/insulating film/W-Si or poly-Si and PR/insulating film/BARL/W-Si or poly-Si in gates and PR/BARL/Al in contact holes. When the optical constants and film thickness in the above multilayer structures are known, the reflectance at the interface between the PR layer and the layer beneath the PR can be calculated with the reflectance simulator.

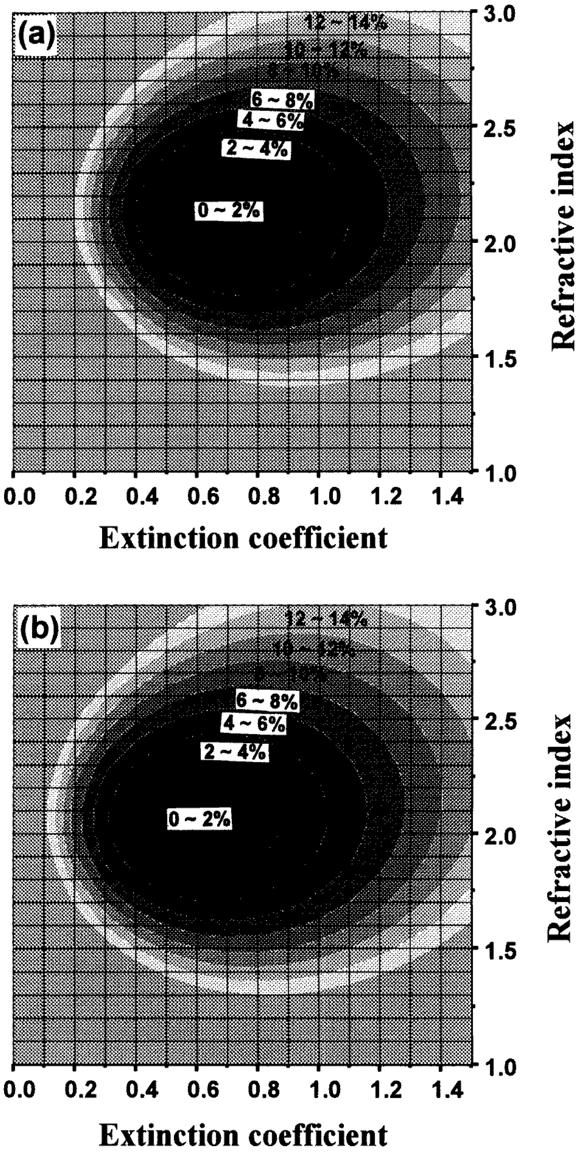

**Figure 2.** Reflectance contours simulated at a wavelength of 248 nm: (*a*) PR($n_{PR} = 1.8$, $k_{PR} = 0.011$)/300 Å, BARL/c-Si ($n_{Si} = 1.57$, $k_{Si} = 3.565$); (*b*) PR($n_{PR} = 1.8$, $k_{PR} = 0.011$)/300 Å, BARL/W-Si ($n_{W\text{-}Si} = 1.763$, $k_{W\text{-}Si} = 2.546$).

The three-dimensional simulated reflectance contours for $n$ and $k$ with Si and W-Si substrates in the PR/BARL/substrate structure are shown in figure 2. Supposing a film thickness of 300 Å, the reflectance

**Table 1.** Deposition conditions of fluorinated silicon nitride film (Substrate p-type (100) Si; base pressure 3 mTorr; working pressure about 250 mTorr; RF power 250 W; deposition temperature 300 °C; Ar 150 sccm).

| $SiH_4$:$N_2$ ratio (sccm) | $NF_3$ flow rate (sccm) |
|---|---|
| 2:15 (for BARL) | 0.65, 1, 1.5, 2, 3 |
| 3:20 (for BARL) | 1, 2, 2.5, 3 |
| 2:15 (for etching) | 0, 0.5, 0.65, 0.75, 1, 1.5, 2 |

becomes nearly zero at 248 nm when the BARLs have approximate values of $n = 2.109$ and $k = 0.68$ on Si substrate and when $n$ and $k$ are 2.052 and 0.592 on W-Si substrate.

## 3. Film preparation and optical properties

We have grown fluorinated silicon nitride films of 300–400 Å thickness for ARL, and thick ones of about 1000 Å for testing the stripping ability on a p-type (100) silicon substrate using $SiH_4$, $N_2$, Ar and $NF_3$ gases by an ICP enhanced CVD system producing a plasma density of $10^{11}$–$10^{12}$ $cm^{-3}$ as a kind of remote plasma enhanced chemical vapour deposition (RPECVD). In order to reduce the hydrogen content, $N_2$ gas instead of $NH_3$ gas was selected as the nitrogen source. The optical characteristics such as the optical constants and reflectance at a wavelength of 248 nm and the wet etch properties were investigated using various gas ratios. The deposition conditions are listed in table 1.

Thin film x-ray diffraction (TFXRD) analysis showed that all deposited films had amorphous phases required for optical isotropic characterization. The film composition determined by an Auger electron spectroscope (AES) included oxygen. As the $NF_3$ flow rate increased, the oxygen and fluorine contents in the film increased. Study of this phenomenon will be performed later.

Figure 3 shows the variation of the film optical constants at a wavelength of 248 nm depending on the $NF_3$ flow rate. The films of 300–400 Å thickness deposited under two BARL deposition conditions in table 1 were measured. These optical constants at 248 nm and the film thickness were evaluated by a spectroscopic ellipsometer (Sopra SE ESVG). The refractive index decreases from 2.285 to 1.665 continuously as the $NF_3$ flow rate increases from 0.65 to 3 sccm in case of $SiH_4$:$N_2$ = 2:15 (sccm) and decreases from 2.352 to 1.99 with increase in the $NF_3$ flow rate from 1 to 3 sccm in $SiH_4$:$N_2$ = 3:20 (sccm). Similarly, with the increase in the $NF_3$ flow rate, the extinction coefficient decreases from 0.551 to 0.007 in $SiH_4$:$N_2$ = 2:15 (sccm) and from 0.695 to 0.26 in $SiH_4$:$N_2$ = 3:20 (sccm). The refractive index decreases with increase in the $NF_3$ flow rate since the increase in the bonding strength and electronegativity due to oxygen and fluorine atoms causes a smaller polarization than nitrogen. The extinction coefficient also decreases with increase in the $NF_3$ flow rate, since electron transition through the bandgap becomes more difficult due to the higher bonding strength and electronegativity of oxygen and fluorine. The $n$ and $k$ values of the fluorinated silicon nitride films for the selected $NF_3$ flow rates shown in figure 3 are well matched with the optimum conditions for the antireflective coating in KrF excimer laser lithography.

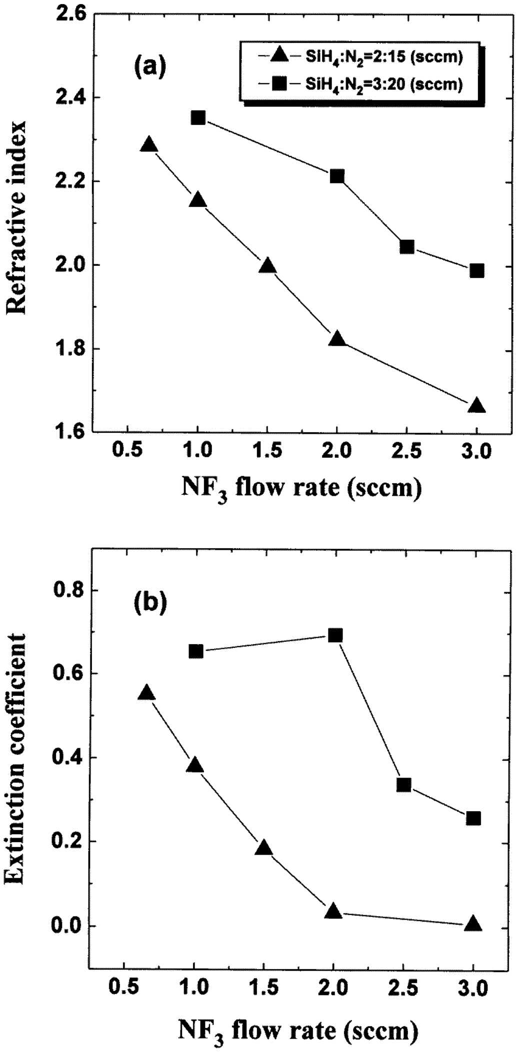

**Figure 3.** Effect of $NF_3$ flow rate on the optical constants at 248 nm of fluorinated silicon nitride film (250 W, 300 °C and Ar:150 sccm): (*a*) refractive index, (*b*) extinction coefficient.

## 4. Calculation of reflectance

Based on the optical parameters at a wavelength of 248 nm displayed in figure 3, the simulated reflectances at the interface between PR and the film for the PR/300 Å $SiN_x$:F film/c-Si and PR/300 Å $SiN_x$:F film/W-Si structures depending on the $NF_3$ flow rate under two deposition conditions are shown in figures 4 and 5 respectively. The films deposited at $SiH_4$:$N_2$ = 2:15 (sccm) and $NF_3 \leq 1$ sccm display reflectances of less than 5% for both substrates and those deposited at $SiH_4$:$N_2$ = 3:20 (sccm) and $NF_3 \leq 2.5$ sccm exhibit reflectances of below 7% for these two substrates. Obviously, the above films in both structures can be used as the antireflective coating in the practical lithographic process. In particular, the

**Table 2.** Optimum AR conditions for the selected films at 248 nm wavelength (RF power 250 W; deposition temperature 300 °C; Ar:150 sccm).

| $SiH_4$:$N_2$:$NF_3$ (sccm) | $n$ and $k$ at 248 nm | Optimum condition on Si substrate | Optimum condition on W-Si substrate |
|---|---|---|---|
| 2:15:0.65 | $n$: 2.285, $k$: 0.551 | $d$: 260 Å, $R$: 0.913% | $d$: 230 Å, $R$: 0.138% |
| 3:20:1 | $n$: 2.352, $k$: 0.654 | $d$: 240 Å, $R$: 0.124% | $d$: 220 Å, $R$: 0.034% |
| 3:20:2 | $n$: 2.214, $k$: 0.695 | $d$: 270 Å, $R$: 0.002% | $d$: 250 Å, $R$: 0.188% |

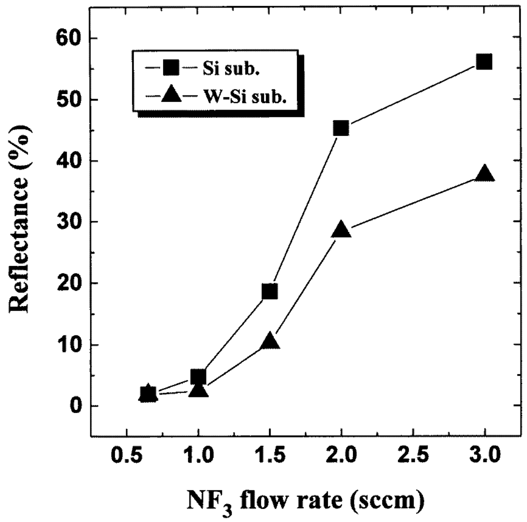

**Figure 4.** Dependence of the reflectance at 248 nm on the $NF_3$ flow rate for two structures (250 W, 300 °C, $SiH_4$:$N_2$:Ar = 2:15:150 (sccm) and film thickness 300 Å).

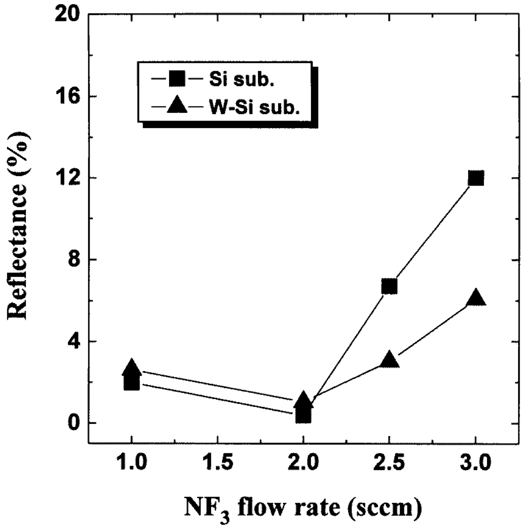

**Figure 5.** Dependence of the reflectance at 248 nm on the $NF_3$ flow rate for two structures (250 W, 300 °C, $SiH_4$:$N_2$:Ar = 3:20:150 (sccm) and film thickness 300 Å).

reflectance of the film deposited under the condition of $SiH_4$:$N_2$:$NF_3$ = 2:15:0.65 (sccm) for two substrates can be reduced to the lowest value of 1.8% and to below 1% in the case of $SiH_4$:$N_2$:$NF_3$ = 3:20:2 (sccm).

The reflectance at the interface between PR and the film is strongly influenced by film thickness and then it is calculated by a 3D simulation program by changing the film thickness. The optimum thickness was found below 500 Å which was preferred in the lithographic process. Supposing that these optical 'constants' are constant regardless of film thickness, the optimum AR conditions for the selected films at the wavelength of 248 nm are summarized in table 2.

## 5. BARL performance (practical lithography and stripping ability)

The BARL performance of the lithographic process was investigated by the following procedures. In order to verify the BARL effect clearly, the step with 4000 Å height and 45° slope was patterned on an Si substrate by dry etching. The BARL of the fluorinated silicon nitride was deposited on the stepped substrate under the condition of $SiH_4$:$N_2$:$NF_3$ = 3:20:2 (sccm) and film thickness of 270 Å. Subsequently, a PR coating of 0.53 $\mu$m thickness was performed on this film. The exposure was done under a dose of 70 mJ cm$^{-2}$ with the KrF excimer laser stepper and then the PR developing was carried out. Figures 6(*a*) and 6(*b*) show the SEM morphologies of 0.25 $\mu$m L/S PR patterns at the steps without and with ARL respectively. The lithographic performance clearly shows that the pattern resolution in quarter micron lithography can be enhanced efficiently by employing a fluorinated silicon nitride BARL.

Generally, BARL stripping by wet etching after use is recommended in the lithographic process because the device size can be diminished after stripping and circuit performance can be enhanced by the removal of harmful effects which probably occur due to the defects in the film. For example, if we consider the PR/BARL/W-Si/Si structure already referred to, the lithographic procedures would be as follows. After PR patterning with a stepper, the BARL and W-Si layer can be dry etched continuously. Then, the PR and BARL should be stripped by boiling in $H_2SO_4$ or other wet etching solutions. Generally, PR can be easily removed by $H_2SO_4$. However, inorganic BARL etching with high selectivity should be considered. After those etchings, the final patterned W-Si structure is fabricated on an Si substrate. Thus, the ease of stripping of the BARL by wet etching is an important characteristic for practical application.

The fluorinated silicon nitride films prepared in this study could be etched by an 85% phosphoric acid ($H_3PO_4$) solution. Wet etching of the films with a thickness of about 1000 Å deposited under the conditions listed in table 1 was performed for 1 min at 160 °C. Variation of the wet

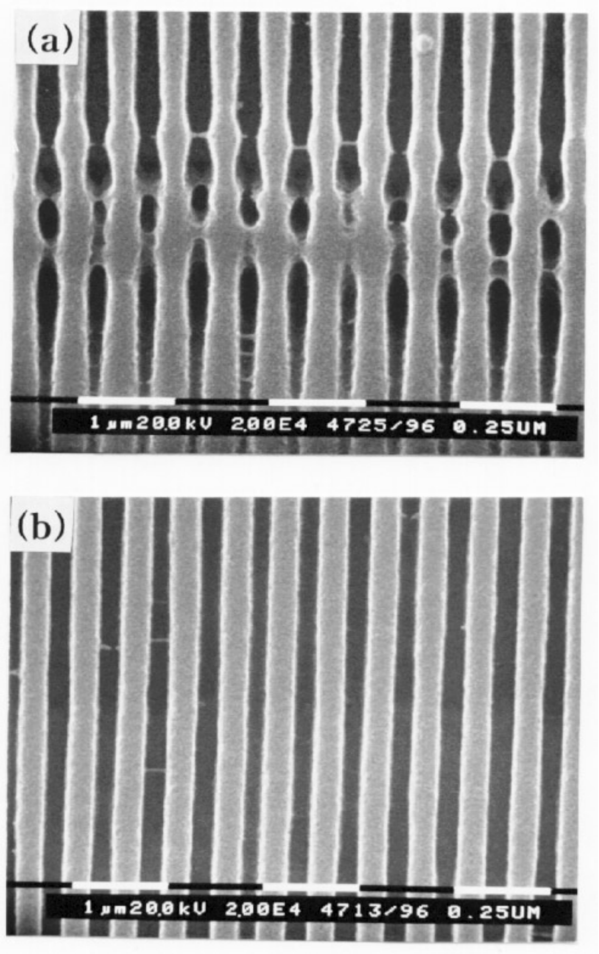

**Figure 6.** BARL performance for 0.25 $\mu$m line/space: (*a*) without BARL, (*b*) with BARL.

etch rate depending on the NF$_3$ flow rate is represented in figure 7. When the phosphoric acid is used as an etching solution, the fluorinated silicon nitride film has very high etch selectivity against silicon oxide. As mentioned before, the oxygen and fluorine contents in the film increase with increasing NF$_3$ flow rate. Therefore, as the NF$_3$ flow rate increases, the wet etch rate increases to about 420 Å min$^{-1}$ and then decreases. The film deposited at an NF$_3$ flow rate of 0.65 sccm whose optical constants satisfy the optimum AR condition has a high etch rate of about 350 Å min$^{-1}$. Thus, the fluorinated silicon nitride films with a high stripping ability prepared by the ICP enhanced CVD method could be used as the antireflective layer in KrF excimer laser lithography by controlling the film thickness as well as process parameters such as the gas flow ratio.

## 6. Conclusions

Isotropic and amorphous fluorinated silicon nitride thin films were deposited with variation in the NF$_3$ flow rate under the two conditions of SiH$_4$:N$_2$:Ar = 2:15:150 (sccm) and SiH$_4$:N$_2$:Ar = 3:20:150 (sccm) at an RF power of 250 W and a deposition temperature of 300 °C by ICP enhanced CVD in order to examine their applicability as an antireflective layer in the KrF excimer laser optical lithography.

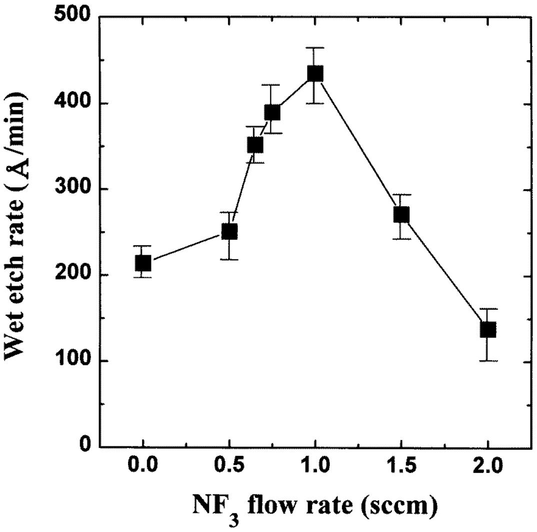

**Figure 7.** The effect of NF$_3$ flow rate on the wet etch rate (250 W, 300 °C, SiH$_4$:N$_2$:Ar = 2:15:150 (sccm); etching condition: 85% H$_3$PO$_4$ solution, for 1 min at 160 °C).

The refractive indices and the extinction coefficients of the fluorinated silicon nitride films at a wavelength of 248 nm lay in wide ranges from 1.665 to 2.352 and from 0.007 to 0.695 respectively, depending on the gas flow ratio of SiH$_4$:N$_2$:NF$_3$. A simulation process predicts that for a film thickness of 300 Å at a wavelength of 248 nm, the optimum conditions for nearly 0% reflectance are when $n = 2.109$, $k = 0.68$ and $n = 2.052$, $k = 0.592$ for Si and W-Si substrates respectively, which are included in the range of optical constants of the deposited films. The calculated reflectance values at the interface between PR and the film postulating the structures of PR/300 Å SiN$_x$:F film/c-Si and PR/300 Å SiN$_x$:F film/W-Si were less than 5% for NF$_3$ flow rates of 0.65–1 sccm in SiH$_4$:N$_2$ = 2:15 (sccm) and less than 7% for NF$_3$ flow rates of 1–2.5 sccm in SiH$_4$:N$_2$ = 3:20 (sccm). In addition, the reflectance is very sensitive to the film thickness, so that it could be reduced to almost 0% by changing the film thickness. As a representative example, for the film having $n = 2.214$ and $k = 0.695$ deposited at SiH$_4$:N$_2$:NF$_3$ = 3:20:2 (sccm), 0.002% and 0.19% reflectances could be obtained at film thicknesses of 270 Å and 250 Å for Si and W-Si substrates respectively.

Based on the above results, the BARL performance was verified from the actual KrF excimer laser lithographic process. The film satisfying the optimum AR condition showed high stripping ability with a high etch rate of about 350 Å min$^{-1}$ in 85% H$_3$PO$_4$ solution. Therefore, the fluorinated silicon nitride thin films are optically applicable as the bottom antireflective layer in 0.25 $\mu$m optical lithography.

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