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Stabilizing dielectric constant of fluorine-doped SiO_2 film by N_2O and NH_3 plasma post-treatment

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Abstract

Fluorine doped oxide ($SiO_{2-x}F_x$) films have been found to exhibit a low dielectric constant. However, the critical issue about $SiO_{2-x}F_x$ is its low resistance to moisture which causes the dielectric constant of the film to increase with time. In this work, N_2O and NH_3 plasma post-treatments are applied to as-deposited $SiO_{2-x}F_x$ films. It has been observed that NH_3 plasma post-treatments of $SiO_{2-x}F_x$ are quite efficient at blocking moisture. The dielectric constant and stress values of the $SiO_{2-x}F_x$ films after the N_2O and NH_3 plasma post-treatments are very stable. The disadvantage of N_2O plasma post-treatment is that the dielectric constant of the $SiO_{2-x}F_x$ film increases from 3.21 to 3.6 due to fluorine desorption from the $SiO_{2-x}F_x$ network. On the other hand, NH_3 plasma post-treatment is more efficient at blocking moisture and keeping the low dielectric constant unchanged due to surface nitridation of the $SiO_{2-x}F_x$ film. © 1997 Elsevier Science S.A.

Keywords: Fluorine dope oxide; Low dielectric; Plasma post-treatment

1. Introduction

A continuous reduction in chip size and an increase in chip complexity are shifting the interconnection technology towards multilevel metallization. However, RC delay from multilevel interconnection becomes an important issue in limiting the performance of very large scale integration (VLSI). A lower dielectric constant insulator is needed to counter the problems of parasitic capacitance delays and cross talk across layers. Recently, numerous candidates for low-*k* dielectric films have been proposed and investigated. Among them, fluorine-doped silicon dioxide films receive considerable attention and have been fabricated by various techniques, such as room-temperature catalytic chemical vapor deposition (RT-CVD) using fluorotriethoxysilane (FTES) and H_2O [1], dual-frequency plasma enhanced CVD using tetraethoxysilane (TEOS)-C_2F_2-O_2 [2,3] and electron cyclotron resonance (ECR) plasma CVD using tetrafluorosilane (SiF_4)-SiH_4-O_2 [4]. A dielectric constant of 3.0 and a much enhanced device speed have been demonstrated for this particular type of film. However, the critical issue in fluorine-doped SiO_2 is the low resistance to moisture. If fluorine-doped SiO_2 is left in the clean room ambient, $SiO_{2-x}F_x$ absorbs moisture easily which results in an increase in the dielectric constant, because H_2O is a polar molecule. Besides, water absorption causes the degradation of device reliability. Therefore, some kind of post-treatment for fluorine-doped oxides to resist moisture is needed before they can be integrated into the multilevel interconnection scheme.

In this work, N_2O and NH_3 plasma post-treatments are applied to as-deposited $SiO_{2-x}F_x$ films. Moisture resistance and dielectric constant stability are investigated. We find that N_2O and NH_3 plasma post-treatments are quite efficient at enhancing the moisture absorption resistance of $SiO_{2-x}F_x$.

2. Experimental

The substrates used in this study were 4-in. p-type (11–25 Ω-cm) single crystal silicon wafers with (100) orientation. Before deposition, they were boiled in H_2SO_4+ H_2O_2 (heated

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Table 1

Deposition conditions of $SiO_{2-x}F_x$ films

	Gas flow rate (sccm)			Temperature (K)	Pressure (Pa)	RF power (W)
	TEOS	O_2	CF_4			
Samples for N_2O post-treatment	10	300	0, 300	573	27	200
Samples for NH_3 post-treatment	10	400	0, 200, 600	573	27	300

to 120°C) for 20 min followed by a 100:1 HF dip to remove the native oxide on the silicon surface. The depositions of $SiO_{2-x}F_x$ films were performed with a standard parallel-plate-type plasma CVD reactor. Its lower electrode had a built-in resistance heater which can be operated at up to 300°C. The plasma was enhanced using a radio frequency (RF) of 380 kHz. F-doped SiO_2 films were deposited by adding CF_4 as a fluorine source to tetraethylorthosilicate (TEOS)/O_2 based chemistry. TEOS was evaporated and mixed with O_2 gas before it was admitted into the chamber. The deposition conditions and plasma post-treatment conditions are listed in Tables 1 and 2, respectively.

The refractive index and film thickness were measured by a Nanometrics 210XP thickness measuring system. Film stress was calculated from measured wafer curvature based on Stoney's equation using a Tencor FLX2320 thin film stress measurement system. The infrared spectrometry was performed from 4000 to 400 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer calibrated to an unprocessed wafer, for studying the chemical structure of the $SiO_{2-x}F_x$ films. A series of plasma post-treatments were performed on these sample. The composition and fluorine content of the $SiO_{2-x}F_x$ films before and after plasma treatment were determined by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The dielectric constant of the films was investigated by measuring capacitance-voltage (C-V) characteristics using a metal insulator semiconductor (MIS) capacitor structure at 1 MHz.

3. Results and discussion

3.1. N_2O plasma treatment

The property changes of $SiO_{2-x}F_x$ films between as-deposited and N_2O plasma post-treated films are listed in Table 3. The dielectric constant increases with plasma treatment time. Fig. 1 shows FTIR spectra of the $SiO_{2-x}F_x$ films before and after N_2O plasma treatment. After N_2O plasma treatment, the Si-F peak reduces whereas the Si-O peak becomes larger. The ratios of Si-F to Si-O bonds are listed in Table 3. This change is caused by oxidation and surface fluorine desorption of the $SiO_{2-x}F_x$ films during the N_2O plasma treatment. As a result of that, the dielectric constant of the $SiO_{2-x}F_x$ film increases. Fig. 2a,b shows the XPS data for the as-deposited and N_2O plasma post-treated $SiO_{2-x}F_x$ films, respectively. The N peak is not evident. There is only about 1 at.% of nitrogen on the surface of the $SiO_{2-x}F_x$ film after N_2O plasma treatment. It is suggested that the temperature and RF power are not high enough to form nitride during the N_2O plasma post-treatment. Only oxidation and surface fluorine desorption occur during the N_2O plasma post-treatment.

Fig. 3 shows the changes in dielectric constant values of the $SiO_{2-x}F_x$ film as a function of time with and without N_2O plasma treatment for 10 and 30 min. The dielectric constant of the $SiO_{2-x}F_x$ film without N_2O plasma annealing quickly increases with time. However, the increase of the dielectric constants of the $SiO_{2-x}F_x$ films with N_2O plasma post-treatment is much smaller than that of as-deposited $SiO_{2-x}F_x$ samples. In other words, the dielectric constant of $SiO_{2-x}F_x$ films becomes much more stable after N_2O plasma post-treatment. As for the increase in dielectric constant with time, it is suggested that it is due to absorbing moisture. It is reported that nitrogen atoms in the plasma play an important role in making the $SiO_{2-x}F_x$ film highly resistant to moisture [5]. In this study, the concentration of nitrogen

Table 2

Plasma post-treatment conditions

	Gas flow rate (sccm)	Plasma power (W)	Substrate temperature (K)	Chamber pressure (Pa)
N_2O	300	100	573	67
NH_3	300	100	573	40

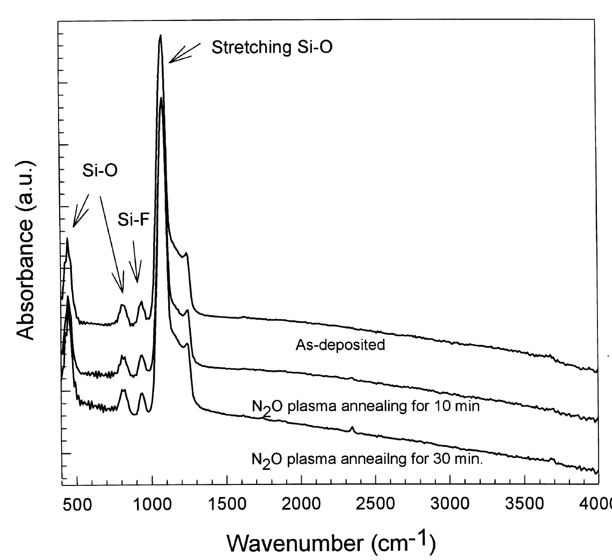

Fig. 1. FTIR spectra of $SiO_{2-x}F_x$ films before and after N_2O plasma treatment.

Table 3
The $SiO_{2-x}F_x$ film properties as a function of N_2O-plasma post-treatment time

Post-treatment time (min)	Dielectric constant	Refractive index (n)	ρ^a (g/cm^3)	Surface F concentration (at.%)	Si-F/Si-O ratio	Stress (10^9 dyne/cm^2)
0	3.21	1.441	2.125	2.7	0.03606	–0.36
10	3.53	1.447	2.15	0.6	0.03566	–0.30
30	3.6	1.456	2.187	0.4	0.02812	–0.30

[a]The density of SiOF(ρ) is determined from an n-value using the Lozentz-Lorentz relationship [4]: $\rho = K(n^2 - 1)/(n^2 + 2)$ where K = 8.046. The density of SiO_2 is 2.212 (g/cm^3).

atoms is too low to play such a role. The main reason for the stabilization of the dielectric constant of $SiO_{2-x}F_x$ is the reduction of Si-F bonds during N_2O plasma post-treatment. The Si-F bond which reacted easily with H_2O [6] will enhance moisture absorption which increases the dielectric constant of $SiO_{2-x}F_x$.

Fig. 4 shows the variation of stress of the $SiO_{2-x}F_x$ films as a function of time before and after N_2O plasma post-treatment. Compared with as-deposited films, the $SiO_{2-x}F_x$ films become less compressive in nature after N_2O plasma post-treatment. This result is due to fluorine desorption and silanol reduction of the $SiO_{2-x}F_x$ film by N_2O plasma post-treatment. $SiO_{2-x}F_x$ films become more compressive in nature with the increase in fluorine content and moisture absorption in the $SiO_{2-x}F_x$ film. The $SiO_{2-x}F_x$ film without N_2O plasma treatment became more compressive with time. This result indicates that the as-deposited $SiO_{2-x}F_x$ film has a poor resistance to moisture. In the case of samples with N_2O plasma post-treatment, the stress shift is much smaller than that of as deposited samples. In addition, the $SiO_{2-x}F_x$ film stress values become more stable with increasing N_2O plasma post-treatment time.

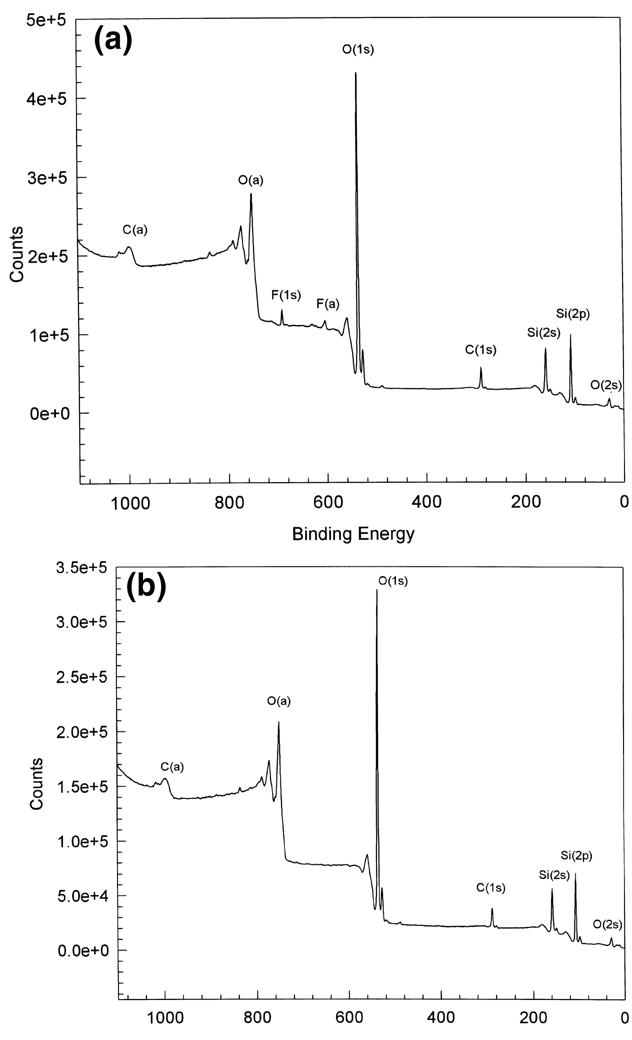

Fig. 2. XPS measurements of (a) as-deposited and (b) N_2O plasma treated $SiO_{2-x}F_x$ films.

3.2. NH_3 plasma treatment

The properties of $SiO_{2-x}F_x$ films before and after NH_3 plasma treatment are summarized in Table 4. It is shown that the surface fluorine concentration determined by XPS decreases by about 15% after 10 mins of NH_3 plasma post-

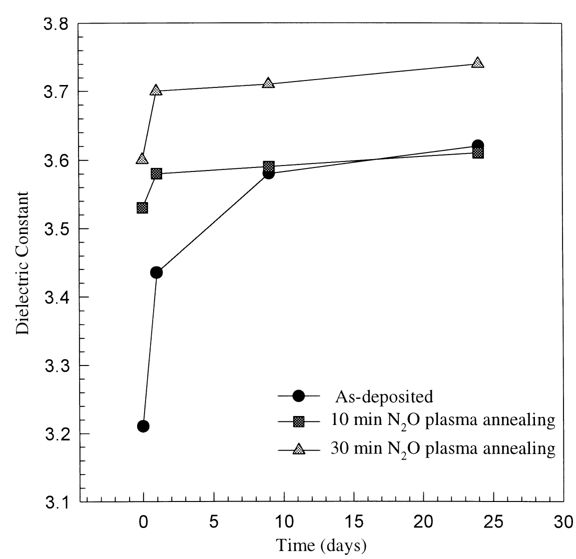

Fig. 3. Dielectric constants of $SiO_{2-x}F_x$ films as a function of time with and without N_2O plasma treatment for 10 and 30 min.

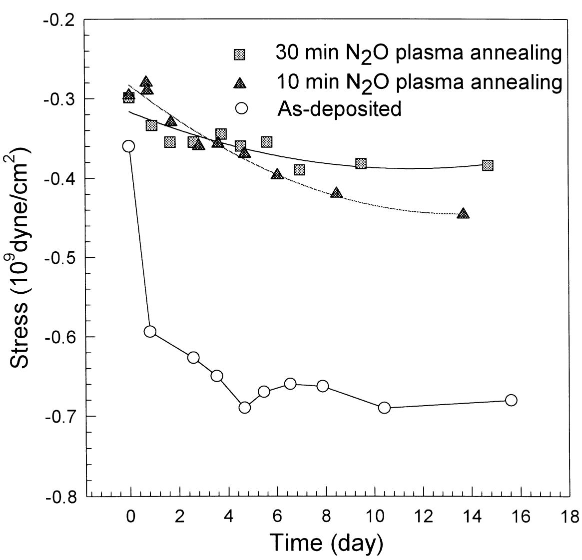

Fig. 4. Stresses of $SiO_{2-x}F_x$ films as a function of time before and after N_2O plasma treatment.

treatment. However, the surface concentration of $SiO_{2-x}F_x$ film has been found to decrease to as low as 22% during the N_2O plasma post-treatment. Fig. 5a,b shows the XPS data for as-deposited and NH_3 plasma post-treated $SiO_{2-x}F_x$ films, respectively. A nitrogen peak is observed in Fig. 5b. However, no nitrogen peak is found in Fig. 5a. As a result, the surface of the $SiO_{2-x}F_x$ film is nitrided during the NH_3 plasma post-treatment which is confirmed by the AES depth profile, as shown in Fig. 6.

Fig. 7 shows the dielectric constants of the as-deposited and post-treated $SiO_{2-x}F_x$ films as a function of exposure time in ambient conditions. The dielectric constant of as-deposited $SiO_{2-x}F_x$ film increases quickly with an increase of

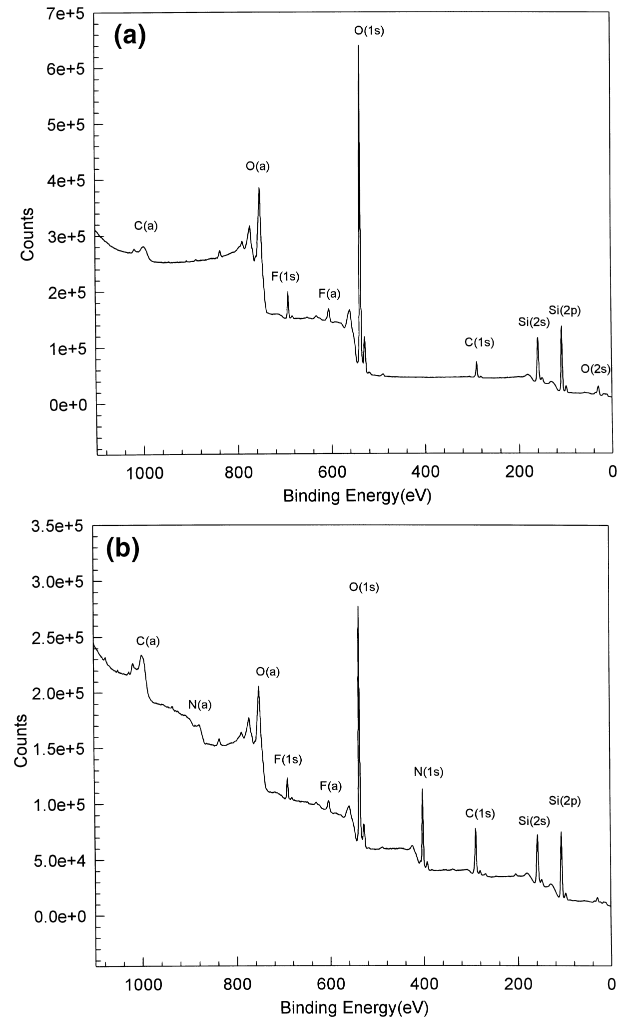

Fig. 5. XPS measurement for (a) as-deposited and (b) NH_3 plasma-treated $SiO_{2-x}F_x$ films.

Table 4
The $SiO_{2-x}F_x$ film properties as a function of NH_3-plasma post-treatment time

CF_4 flow rate (sccm)	Post-treatment time (min)	Dielectric constant	Refractive index (n)	ρ^a (g/cm^3)	Surface concentration (at. %)	
					Fluorine	Nitrogen
CF_4 = 0	0	3.86	1.468	2.237	0	0
	5	3.85	1.470	2.245	–	–
	10	3.91	1.475	2.265	0	17.971
	15	3.85	1.475	2.265	–	–
	20	3.86	–	–	0	22.408
CF_4 = 200	0	3.481	1.445	2.141	–	–
	5	3.425	1.449	2.158	–	–
	10	3.52	1.449	2.158	–	–
	15	3.54	1.400	2.162	–	–
	20	3.51	–	–	–	–
CF_4 = 600	0	3.35	1.430	2.078	3.520	0
	5	–	1.436	2.104	–	–
	10	3.35	1.436	2.104	2.966	15.056
	15	–	1.438	2.112	–	–
	20	3.35	–	–	2.215	17.542

[a]The density of SiOF(ρ) is determined from an n-value using the Lozentz-Lorentz relationship [4]: $\rho = K(n^2 - 1)/(n^2 + 2)$ where K = 8.046. The density of SiO_2 is 2.212 (g/cm^3).

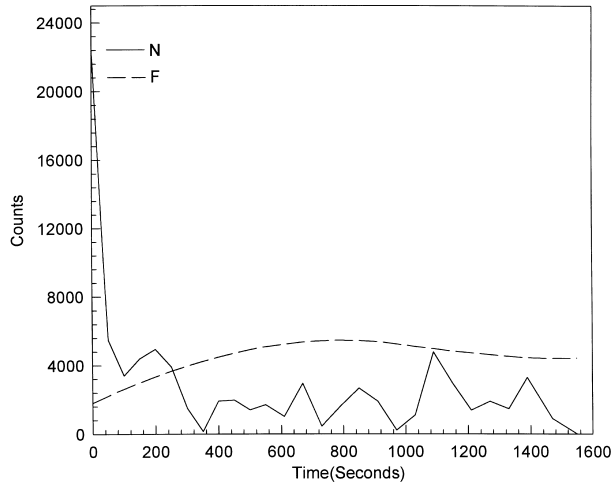

Fig. 6. AES depth profile of $SiO_{2-x}F_x$ films treated by NH_3 plasma.

exposure time. On the other hand, the dielectric constant of $SiO_{2-x}F_x$ with NH_3 plasma post-treatment remains almost constant after being exposed to ambient. A comparison of Figs. 3 and 7 depicts that the dielectric constant of $SiO_{2-x}F_x$, after NH_3 plasma post-treatment, increases by less than 2%. However, the dielectric constant of $SiO_{2-x}F_x$ after N_2O plasma post-treatment increases by 12%. This is due to the fact that compared with N_2O plasma post-treatment, the NH_3 plasma post-treatment causes less F to evolve from the $SiO_{2-x}F_x$ network (Figs. 2 and 5). As mentioned above, the dielectric constant of the $SiO_{2-x}F_x$ film without post-treatment increases due to moisture absorption when the sample is exposed to air ambient. The dielectric constants of $SiO_{2-x}F_x$ films with NH_3 plasma post-treatment do not change. This indicates that the NH_3 plasma post-treatment is an efficient method to block moisture and to keep the dielectric constant low. Fig. 8 shows the stress variation of $SiO_{2-x}F_x$ films exposed in ambient air for one week as a

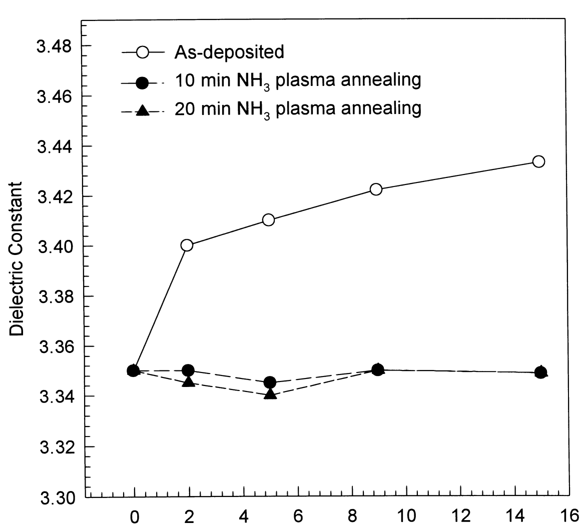

Fig. 7. Dielectric constants of as-deposited and post-treated $SiO_{2-x}F_x$ films with CF_4 = 600 sccm as a function of exposure time in ambient conditions.

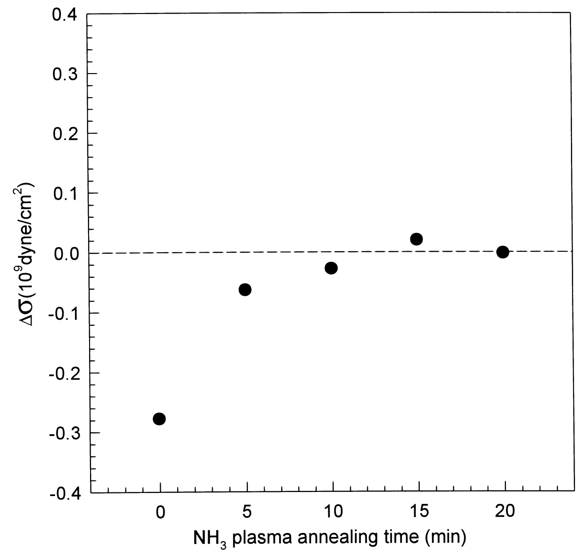

Fig. 8. Stress variation exposed in ambient for a week as a function of time of NH_3 plasma post-treatment.

function of time of NH_3 plasma post-treatment. The stress variation decreases with increasing time of NH_3 plasma post-treatment. This result also indicates that NH_3 plasma post-treatment is an efficient method to resist moisture absorption.

4. Conclusions

Both N_2O and NH_3 plasma post-treatment of $SiO_{2-x}F_x$ films can decrease the variation of dielectric constants and stresses after exposure to ambient. We proposed the mechanism of moisture-absorption resistance in these two plasma post-treatments. In the N_2O plasma post-treatment case, the reduction of fluorine concentration in the $SiO_{2-x}F_x$ film results in higher moisture resistance. In the NH_3 plasma post-treatment case, the formation of nitride on the surface of $SiO_{2-x}F_x$ film is the major reason for blocking moisture. The disadvantage of N_2O plasma post-treatment is that the dielectric constant of $SiO_{2-x}F_x$ will increase from 3.21 to 3.6 due to more fluorine desorption from $SiO_{2-x}F_x$ due to N_2O plasma post-treatment. On the other hand, NH_3 plasma post-treatment does not change the dielectric constant of the $SiO_{2-x}F_x$ film. Therefore, NH_3 plasma post-treatment is a more effective method to block moisture and maintain the low dielectric constant by only surface nitridation of $SiO_{2-x}F_x$ films.

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