Controlling Fluorine Concentration and Thermal Annealing Effect on Liquid-Phase Deposited $SiO_{2-x}F_x$ Films

Ching-Fa Yeh and Chun-Lin Chen

Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Hsinchu, Taiwan

ABSTRACT

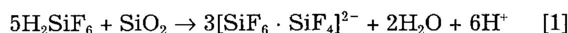
Silicon oxide ($SiO_{2-x}F_x$) with fluorine naturally incorporated can be prepared by the liquid-phase deposition (LPD) method at 15°C. The fluorine is uniformly distributed in the bulk of the LPD oxide. The fluorine incorporation as well as the qualitative properties can be accurately controlled by varying the amount of H_2O added. A high temperature process has considerable effect on the low temperature fluorinated oxide. FTIR and XPS spectra show that Si—F and SiO—H bonds can restructure with densification at higher thermal annealing temperature, and that restructuring is a function of temperature. Film densification with increasing temperature is also discussed in terms of Si—O—Si bond angle and Si—Si bond length.

As a gate insulator, silicon oxide incorporating a small amount of fluorine has the following merits; (*i*) it can enhance resistance to the hot-carrier effect,[1-5] (*ii*) it drastically reduces the density of radiation-induced oxide charges and interface traps, and (*iii*) it can reduce the dielectric constant for multilevel interconnection. Several methods of incorporating fluorine into silicon oxide have been suggested, such as immersing Si wafers in dilute HF solution prior to the oxidation process,[1] F ion implantation into the polycrystalline silicon (poly-Si) gate followed by annealing,[2,3] and addition of NF_3 to the oxygen ambient during furnace oxidation.[4] Inoue *et al.* applied F_2 to the Si surface and irradiated the surface with ultraviolet light prior to chemical vapor deposition of SiO_2 films.[5]

Fluorine can be naturally incorporated into silicon oxide by liquid-phase deposition (LPD).[6] The resulting LPD oxide has been represented as $SiO_{2-x}F_x$, however, accurate control of how much fluorine is incorporated in the LPD $SiO_{2-x}F_x$ has not yet been studied. In this paper, the mechanism of fluorine incorporation as well as the mechanism of LPD is described first. Then, based on these chemical reaction mechanisms, we describe how fluorine atoms can be incorporated quantitatively. Generally, an as-deposited oxide always has occasion to be exposed to high temperature processes (HTP) for reasons such as thermal annealing, reflow, or densification. Therefore details of the changes in film properties and fluorine incorporation owing to HTP are concerned here. Thus the effect on LPD $SiO_{2-x}F_x$ of thermal annealing in N_2 ambient is discussed. In addition, we have tried to analyze the changes in bond structures and film properties owing to thermal annealing in terms of bond intensity and F concentration.

Experimental

The following reactions recapitulate our previous studies of the growth mechanism of LPD $SiO_{2-x}F_x$.[6] The immersion solution was prepared by dissolving silica in hydrofluorosilicic acid (H_2SiF_6) solution; the resulting reaction is shown in Eq. 1



$$5H_2SiF_6 + SiO_2 \rightarrow 3[SiF_6 \cdot SiF_4]^{2-} + 2H_2O + 6H^+ \quad [1]$$

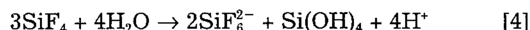
and yields a species of fluosilicic complex $[SiF_6 \cdot SiF_4]^{2-}$. Adding H_2O to the solution produces the reaction shown in Eq. 2

$$[SiF_6 \cdot SiF_4]^{2-} + 2H_2O \rightarrow SiF_4(OH)_2^{2-} + SiF_4 + 2HF \quad [2]$$

The reaction of $SiF_4(OH)_2^{2-}$ with H^+ in the acidic immersion solution is shown in Eq. 3

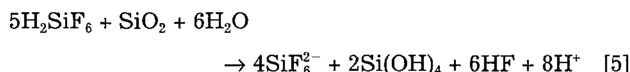
$$SiF_4(OH)_2^{2-} + 2H^+ \rightarrow SiF_4 + 2H_2O \quad [3]$$

However, the hydrolysis of SiF_4 in aqueous solution, as expressed in Eq. 4, yields SiF_6^{2-}, H^+; and the silicic monomer $Si(OH)_4$



$$3SiF_4 + 4H_2O \rightarrow 2SiF_6^{2-} + Si(OH)_4 + 4H^+ \quad [4]$$

The net reaction produced by adding H_2O to the immersion solution can be thus represented as in Eq. 5



$$5H_2SiF_6 + SiO_2 + 6H_2O \rightarrow 4SiF_6^{2-} + 2Si(OH)_4 + 6HF + 8H^+ \quad [5]$$

Our Si wafers were cleaned using the standard RCA process, which leaves a thin native-oxide layer on the surface. The wafers were then dipped in HF solution to remove the native oxide in HCl + H_2O_2 mixed solution during initial cleaning. Many efforts have been focused on the HF-treated silicon surface, and it was concluded that the surface is almost all terminated with hydrogen.[7-9] Reoxidation occurs if this silicon surface is exposed to water. That is, the hydrides (Si—H) on the surface can react with water molecules with a certain time constant and be transformed to hydroxyls (Si—OH). This hydrogen on the silicon surface then is replaced by hydroxyl through the chemical reaction revealed in Eq. 6

$$Si{-}H + H_2O \rightarrow Si{-}OH + H_2 \quad [6]$$

Therefore, on the basis of the reaction equations above, we can conclude that the growth mechanism of LPD $SiO_{2-x}F_x$ is as follows.

An intermediate polysilicic acid is formed by the polymerization of the silicic monomer $Si(OH)_4$ (the product of Eq. 5) and adsorbed onto the substrate surface. An acid-catalytic dehydration occurs between the adsorbed polysilicic acid and Si—OH existing on the substrate, followed by Si—O—Si bond formation. Because some HF is always present in the system (Eq. 5), the surface of the as-deposited film and the Si—OH on the substrate are subject to HF attack according to the reaction

$$\equiv Si{-}OH + HF \rightarrow \equiv Si{-}F + H_2O \quad [7]$$

Hence, film-etching occurs simultaneously with film-deposition, however, deposition of LPD $SiO_{2-x}F_x$ on the substrate surface is the predominant result because of the continual adsorption of intermediate polysilicic acid. Following film deposition, fluorine incorporation into the bulk of the LPD oxide and Si/SiO_2 interface occurs naturally. From this mechanism, it is easy to understand how LPD $SiO_{2-x}F_x$ is grown and how fluorine atoms can be incorporated into the grown film.

According to Eq. 5, H_2O is a main reactant in the LPD $SiO_{2-x}F_x$ chemical reaction. It is therefore necessary to examine what effect addition of H_2O has on fluorine incorporation and growth rate. Figure 1 shows the experimental flow diagram for preparing the immersion solution and LPD samples. Silica (SiO_2) powder was dissolved into H_2SiF_6 to form the fluosilicic complex $[SiF_6 \cdot SiF_4]^{2-}$. Then H_2O was added supersaturating the solution with silicic

Downloaded on 2014-04-28 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

acid $Si(OH)_4$. The quantity of H_2O added in this study varied in the range of 25 to 150 ml per 100 ml of immersion solution.

The cleaned Si substrates, with 10 to 20 Ω-cm were then placed into the immersion solution at 15°C, until a ~1200 Å thick LPD oxide film formed on the substrate surface. The oxide thickness was set to about one-half of an ellipsometric period (1200 Å) for reliable refractive index and sample thickness measurement. To examine the fluorine incorporation in LPD oxide, Fourier transform infrared spectroscopies (FTIR, Bomen, DA 3.002) for all the samples were examined. The oxide composition depth profile was further investigated by Auger electron spectroscopy (AES, Perkin-Elmer, SAM Φ 650).

After deposition with 50 ml of H_2O added, a portion of the wafers were annealed in N_2 ambient for 1 h at various temperatures in the range of 300 to 1000°C. The refractive index and the P-etch rate of the LPD oxide were determined by ellipsometer before and after annealing. The bond-structure changes in the LPD oxides resulting from annealing were analyzed with FTIR and x-ray photoelectron spectroscopy (XPS, Perkin-Elmer Model 1600 spectrometer equipped with a 250 W monochromated Mg-k_α (1253.6 eV) x-ray source).

Results and Discussion

Since H_2O is a main reactant in the chemical reaction in Eq. 5, the reaction rate is a function of the quantity of H_2O added. As shown in Fig. 2, oxide deposition rate (D.R.) plotted as a function of the quantity of H_2O added indicates that the D.R. increases as the quantity of H_2O added increases. The result is approximately consistent with the growth mechanism described above. Figure 2 also shows the refractive index (n) plotted as a function of the quantity of H_2O added. The n value decreases as the quantity of H_2O added increases. This decrease implies that films prepared with differing quantities of H_2O added have slight changes in density. The film density (ρ) can be evaluated by means of the Lorentz-Lorenz relationship,[10] $\rho = K \cdot (n^2 - 1)/(n^2 + 2)$

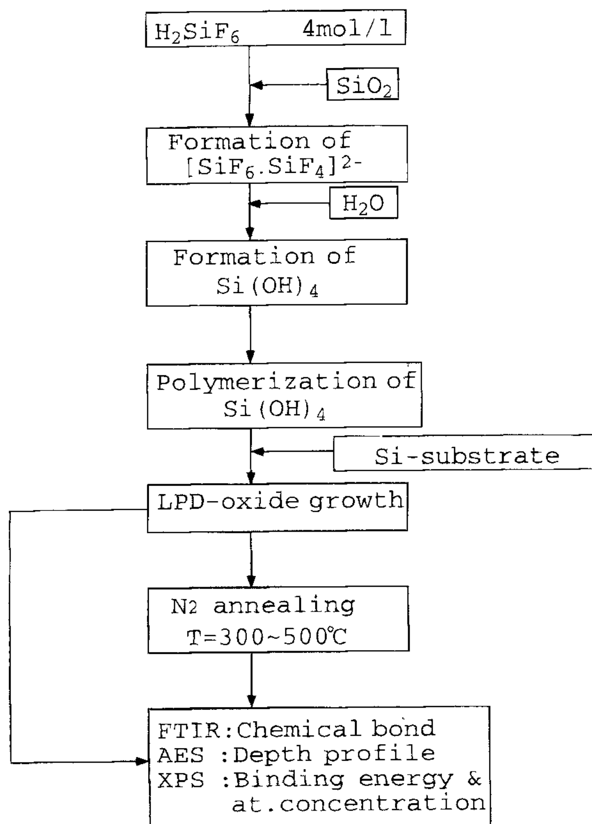
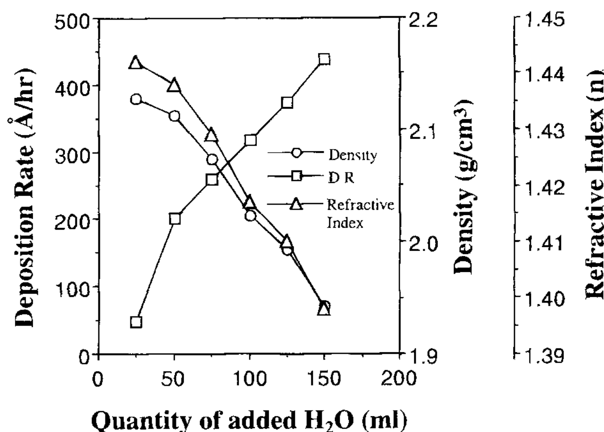


Fig. 1. Experimental flow diagram for preparing immersion solution and LPD samples.



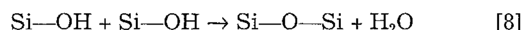


Fig. 2. Changes in deposition rate, refractive index, and density for LPD oxide films prepared with different quantities of H_2O added.

where K is 8.046 and n is the refractive index from ellipsometer. The plot of density as a function of the quantity of H_2O added is also shown in Fig. 2. The result reveals that the density of the films can be controlled in the range of 1.942 to 2.128 g/cm³ by adding 25 to 150 ml H_2O per 100 ml of immersion solution. These values are lower than those of thermal SiO_2 (2.212 g/cm³). The lower density implies more nonbridging oxygen in the LPD oxide.[11] The greater the quantity of H_2O added, the greater the concentration of $Si(OH)_4$ (Eq. 5) is, thus the silanol (Si—OH) elimination reaction, as expressed in Eq. 8

$$Si—OH + Si—OH \rightarrow Si—O—Si + H_2O \quad [8]$$

cannot occur sufficiently to condense the film bulk.[12] Figure 3 shows the FTIR spectra of LPD oxides with 50, 75, and 100 ml H_2O added, respectively. In general, LPD oxide including a higher Si—OH concentration gives rise to strong absorption in the FTIR spectra. The transmittance band around 3200 to 3700 cm^{-1} being O—H stretching due to Si—OH obviously shows that adding more H_2O increases the concentration of Si—OH groups. The higher the concentration of Si—OH groups, the lower the density of the LPD oxide is (Fig. 2).

In the typical LPD oxide FTIR spectrum, as shown in the inset of Fig. 3, the main transmittance band around 930 cm^{-1} due to Si—F indicates that fluorine has been incorporated into the oxide. The precise quantity of fluorine incorporated was further investigated by AES measurement. Figure 4 shows a typical AES depth profile of film prepared by adding 125 ml of H_2O to 100 ml immersion solution. It reveals that the atomic concentration ratio of Si:O:F is 33.77:64.37:1.86. Fluorine atomic concentration is 1.86% and uniformly distributed in the LPD oxide. Thus, the LPD oxide can be represented as $SiO_{2-x}F_x$. However, we found that the fluorine concentration could be changed. As shown in Fig. 5, a linear increase of atomic fluorine concentration (from 1.86 to 6.25%) can be obtained by decreasing the H_2O quantity (from 125 to 25 ml) per 100 ml of immersion solution. The reason why fluorine concentration can be controlled by varying the H_2O quantity is as follows: although H_2O in Eq. 5 is a reactant in the LPD system, it also acts as a dilutent since the quantity of H_2O added exceeds the mole fraction needed in Eq. 5. The more H_2O added, the lower the concentration of HF is, and the lower the tendency of the as-deposited film coming under HF attack is (Eq. 7). In that case, fluorine incorporation thus correspondingly decreases.

The effects of thermally annealing LPD oxide in N_2 ambient between 300 and 1000°C has been studied with FTIR.[6] The FTIR spectra indicated that there were characteristic IR bands in the Si—O—Si groups, Si—F, and Si—OH stretching vibration. Among them the dominant changes, as shown in Fig. 6 are associated with the Si—O—Si and Si—F stretching vibration. The Si—F stretching vibration band gradually decreases with annealing tempera-

Downloaded on 2014-04-28 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

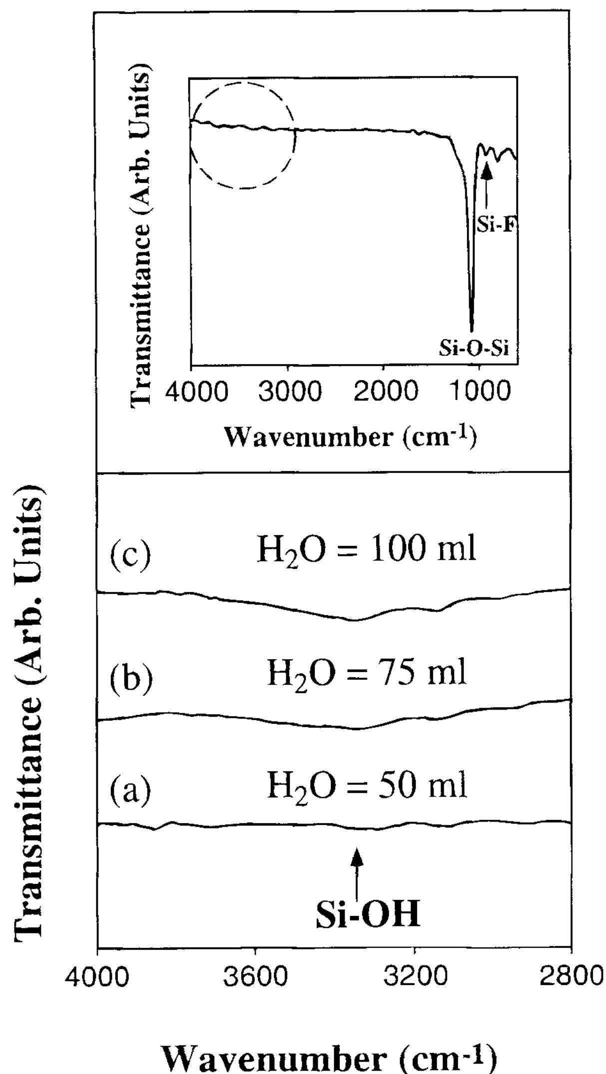


Fig. 3. Typical FTIR spectra in higher wave number region for LPD films (thickness: 1050 Å) formed with different quantities of H_2O added; (a) 50, (b) 75, and (c) 100 ml per 100 ml immersion solution.

ture and finally disappears at 700°C, while the Si—O—Si stretching vibrational frequency (ν) shifts from 1083 cm^{-1} (unannealed to 1075 cm^{-1}, and full width at half-maximum

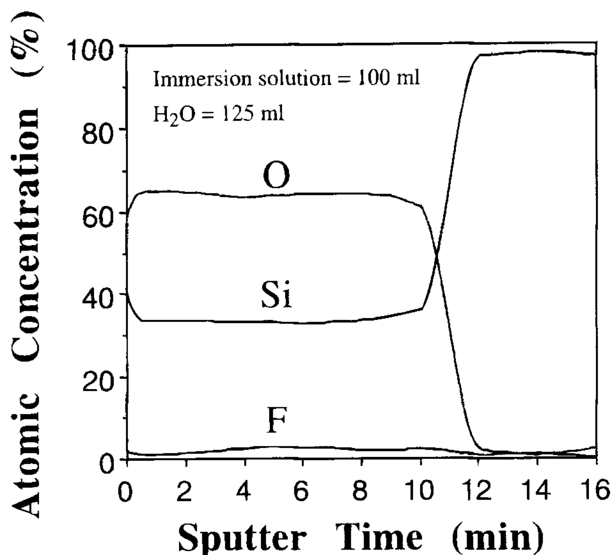


Fig. 4. A typical AES depth profile for atomic fluorine concentration in LPD oxide.

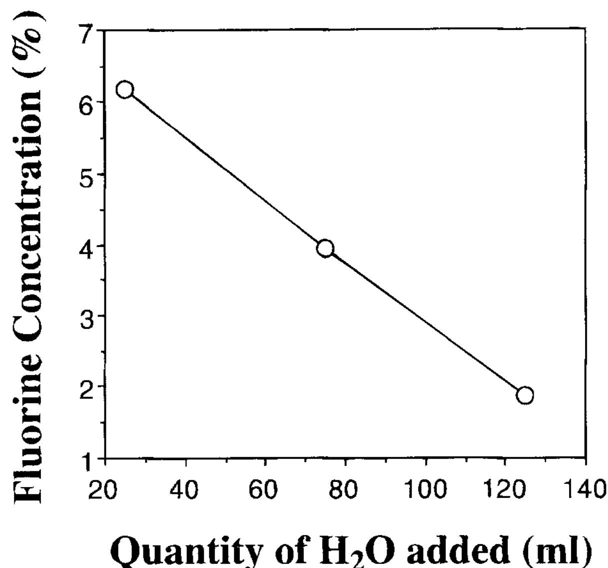


Fig. 5. Linearly decreasing relationship of fluorine concentration vs. quantity of H_2O added.

(FWHM) broadens from 63 cm^{-1} (unannealed) to 84 cm^{-1}. These results obviously indicate that increasing the annealing temperature effects gross changes in the chemical composition of the resulting LPD $SiO_{2-x}F_x$. In particular, annealing at 1000°C, results in a chemical composition similar to that of thermal oxide, which means that the structural density of LPD $SiO_{2-x}F_x$ is highly dependent on annealing temperature.

To aid in understanding how annealed LPD oxide comes to resemble thermal oxide, we illustrate the structure changes produced by annealing in Fig. 7. According to the LPD oxide and fluorine incorporation mechanism,[6] the structure of the as-deposited LPD oxide is as shown in Fig. 7a. Restructuring occurs during annealing because the hydrogen atoms (H) present between the fluorine (F) and oxygen (O) atoms are very electronegative, there exists a special hydrogen bond structure in SiO—H---F—Si. Since the SiO—H bond energy is 111 kcal/mol, while the Si—F bond energy is 143 kcal/mol. Annealing at temperatures between 300 and 500°C can break SiO—H bonds, forming SiO^-, but few Si—F bonds are broken (Fig. 7b). However when the annealing temperature is higher than 700°C, not only the SiO—H bonds but also most of the Si—F bonds are broken, and Si^+ is formed (Fig. 7c). The Pauling radii for the resulting ions are as follows: F^-, 1.33 Å; H^+, <0.37 Å. These sizes suggest that F^- and H^+ can be mobile, and diffuse out through interstitial channels in LPD oxide (Fig. 7c).[13,14] This is why FTIR spectra Si—F peak completely disappears at $T \geq 700°C$.[15] This restructuring, with Si—O—Si bond formation as well as Si—F peak disappearance suggests that LPD oxide has been densified and become similar to thermal oxide. This restructuring has been quantitatively evaluated by integrating the bond intensity from FTIR peaks, as summarized in Table I. With increasing annealing temperature, the Si—O—Si bond intensities gradually increase, while Si—F bond intensities decrease, finally becoming undetectable (less than 0.5%). With further detection for fluorine (F 1s) by XPS, the changes in F atom concentrations (Table I) obviously indicate that Si—F bond intensities are decreasing with annealing temperature. These quantitative results demonstrate that the restructuring is a function of temperature.

Assignment of stretching frequencies in Fig. 6 can be approximated by the application of Hook's law. The following equation, derived from Hook's law, states the relationship between frequency of oscillation, atomic masses, and the force constant of the bond

$$\nu = \frac{1}{2\pi c}\left[\frac{f}{(M_x M_y)/(M_x + M_y)}\right]^{1/2} \quad [9]$$

Downloaded on 2014-04-28 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

where ν is the vibrational frequency (cm^{-1}), c is velocity of light (cm/s), f is force constant of bond, and M_x and M_y are mass (g) of atom x and atom y, respectively. To approximate the vibrational frequencies of bond stretching by Hook's law, the relative contributions of bond strength and atomic masses must be considered. Generally, functional groups that have a stronger dipole give rise to a higher force constant and the increase in the force constant from left to right across the first two rows of the periodic table has a greater effect than the mass increase.[16] FTIR spectra in Fig. 6 show that there are Si—F bonds. It is generally believed that SiO_2 forms a continuous random network with a nearly perfect AX_4 tetrahedral structure.[17] When an Si—O bond is replaced by an Si—F bond, the Si—O—Si bond stretching frequency (ν) increases to 1083 cm^{-1} for unannealed LPD oxide (Fig. 6), higher than the 1075 cm^{-1} of thermal SiO_2. This is because the dipole moment of Si—F is larger than that of Si—O. Similarly, because of the dipole moments: Si—F > Si—O^- > Si—O, the Si—O—Si bond-stretching frequencies around 1082, 1078, and 1075 cm^{-1}, as shown in Fig. 6, can be attributed to gradually increased annealing temperatures. After annealing at 1000°C, the Si—O—Si peak broadens, FWHM increases from 63 cm^{-1} (unannealed LPD oxide) to 84 cm^{-1}, which nearly equals the 85 cm^{-1} of thermal SiO_2.

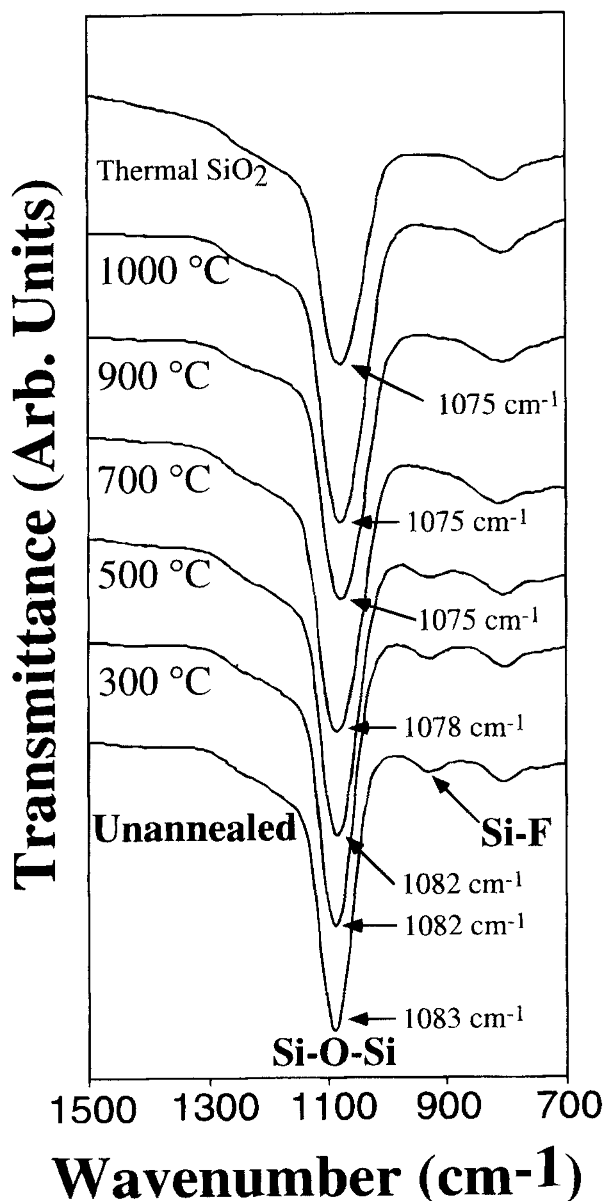


Fig. 6. Typical FTIR spectra in lower wave number region for LPD films annealed at different temperatures.

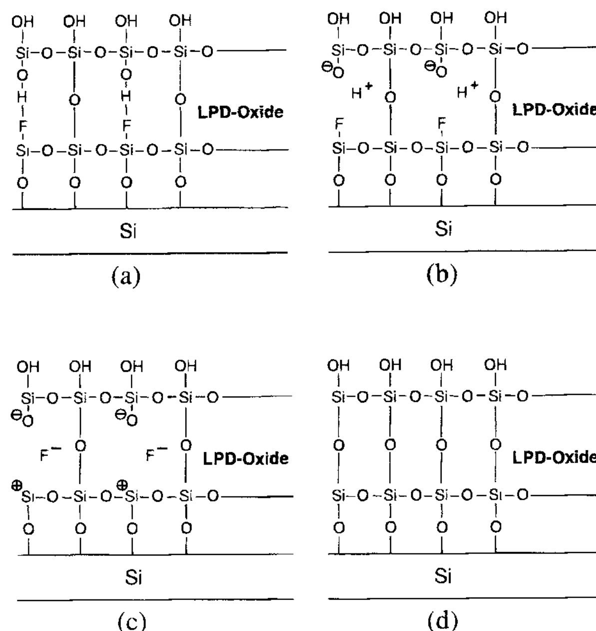


Fig. 7. Schematic illustrations of the proposed LPD restructuring mechanism.

In the context of force constant models for the vibrational properties,[18,19] the frequency (ν) of the bond-stretching vibration in SiO_2 can be approximated by the equation $\nu = \nu_0 \sin(\theta/2)$, where ν_0 is 1117 cm^{-1},[20] and θ is the Si—O—Si bond angle. Simon[21] has shown that when SiO_2 is compacted with radiation, the Si—O bond length is essentially unchanged while the Si—Si distance (d_{Si-Si}) is decreased. The d_{Si-Si} is directly related to the Si—O—Si bond angle (θ) by the relationship;[22] $d_{Si-Si} = 2r_o \sin(\theta/2)$, where r_o is Si—O bond length (1.504 Å). This means that the changes in ν after thermal annealing can be explained in terms of the changes in θ at the oxygen atom site. Specifically, as θ is decreased, ν also decreases. We can relate change in the density to the change in the Si—O—Si bond angle by further assuming that the density of LPD oxide varies inversely as the cube of the Si—Si distance. On this basis, we can obtain the Si—O—Si bond angle (θ) and d_{Si-Si} from ν for each annealed LPD oxide. As summarized in Table II, θ is 155°, 151°, 149°, and 148° for the unannealed and the annealed at 300 to 500, 700, and 900 to 1000°C, respectively. Therefore the d_{Si-Si} is 2.937, 2.912, 2.898, and 2.891 Å for the unannealed and the annealed at 300 to 500, 700, and 900 to 1000°C, respectively. The shift of the Si—O—Si stretching frequency is related to a 7° reduction in the Si—O—Si bond angle with annealing at temperatures from 300 to 1000°C. The more the θ decreased, the shorter the Si—Si distance, and the higher the density became. The decrease in d_{Si-Si} obviously indicates that the thermal annealing surely caused the LPD oxide to grow more compact.

Chemical etching rate has been shown to be a sensitive measure for density of SiO_2 film.[17] Pliskin and Lehman[23] reported that a more dense SiO_2 can give a slower etching rate in an HF-based etchant. The etching rates of the LPD oxides annealed at different temperatures were examined with P-etch solution (48% HF: 70% HNO_3: H_2O = 3:2:60) at

Table I. Changes in Si—F, Si—O—Si bond intensity, and F concentration of $SiO_{2-x}F_x$ film due to thermal annealing.

N_2 annealing temperature (°C)	Si—F (FTIR) intensity	Si—O—Si (FTIR) intensity	F (XPS) (atom conc %)
Unannealed	1.177	46.12	3.18
300	1.128	47.57	3.00
500	0.541	49.22	2.76
700	—	52.43	0.45
900	—	54.18	0.26
1000	—	58.14	0.22

Downloaded on 2014-04-28 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

Table II. Changes in Si—O—Si bond bond angle and Si—Si bond length for $SiO_{2-x}F_x$ due to thermal annealing.

N_2 annealing temperature (°C)	Si—O—Si Bond angle (θ°)	d_{Si-Si} (Å)
Unannealed	155	2.937
300	151	2.912
500	151	2.912
700	149	2.898
900	148	2.891
1000	148	2.891
Thermal SiO_2	148	2.891

room temperature. As shown in Fig. 8, the P-etch rate decreased with increasing annealing temperature. This result is rather consistent with the densification found above.

Conclusion

Fluorine can be naturally incorporated into $SiO_{2-x}F_x$ by using LPD in conjunction with H_2O addition. The reaction rate is a function of the quantity of H_2O added since H_2O is a main reactant in the chemical solution. The deposition rate can be controlled in the range of 50 to 450 Å/h, while the film density (ρ) can be controlled in the range of 1.942 to 2.128 g/cm^3 by adding 25 to 150 ml of H_2O per 100 ml of immersion solution. In the same way, the atomic fluorine concentration is also linearly increased from 1.86 to 6.25% by decreasing the H_2O quantity from 125 to 25 ml per 100 ml of immersion solution. The more H_2O added, the higher the concentration of Si—OH groups, and the lower the density of the LPD oxide. The more H_2O added, the lower the concentration of HF, and the less fluorine incorporated.

Thermal annealing of LPD oxide results in densification with Si—F and SiO—H bonds restructuring. H^+ can diffuse out of the LPD oxide at $T \leq 500$°C, while F^- dramatically decreases at $T \geq 700$°C. This restructuring, with Si—O—Si bond formation is strongly temperature-dependent. LPD oxide annealed at 1000°C becomes similar to thermal SiO_2 in structure.

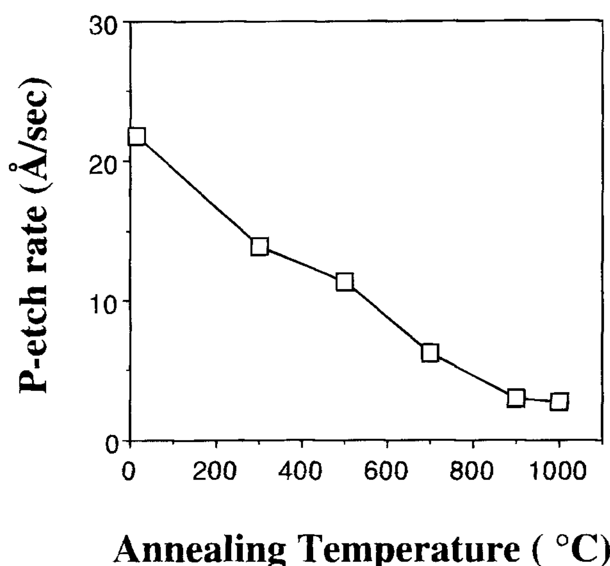


Fig. 8. P-etch rate for LPD films annealed at different temperatures.

In the FTIR spectra, the shifts of Si—O—Si stretching to a low wave number with increasing annealing temperature have been analyzed in terms of Si—O—Si bond angle and Si—Si bond length. The decrease in d_{Si-Si} also obviously indicates that the thermal annealing has surely caused the LPD oxide to become more compact.

Acknowledgment

This study was supported by the National Science Council, Republic of China, under Contract Number NSC 83-0404-E-009-121. A portion of the work was supported by the United Microelectronics Corporation.

Manuscript submitted March 21, 1995; revised manuscript received June 20, 1995.

Dr. Yeh assisted in meeting the publication costs of this article.

REFERENCES

1. Y. Nishioka, E. F. da Silva, Jr., Y. Wang, and T. P. Ma, *IEEE Electron Device Lett.*, **EDL-9,** 38 (1988).
2. Y. Nishioka, K. Ohyu, Y. Ohji, N. Natuaki, K. Mukai, and T. P. Ma, *ibid.*, **EDL-10,** 141 (1989).
3. P. J. Wright, M. Wong, and K. C. Saraswat, in *IEDM Tech. Dig.*, 574 (1987).
4. E. F. da Silva, Jr., Y. Nishioka, and T. P. Ma, *IEEE Trans. Nucl. Sci.*, **NS-34,** 1190 (1987).
5. K. Inoue, M. Nakamura, M. Okuyama, and Y. Hamakawa, *Appl. Phys. Lett.*, **55,** 2402 (1989).
6. C. F. Yeh, C. L. Chen, and G. H. Lin, *This Journal,* **141,** 3177 (1994).
7. S. Watanabe, N. Nakayama, and T. Ito, *Appl. Phys., Lett.*, **59,** 1458 (1991).
8. T. Konishi, K. Uesugi, K. Takaoka, S. Kawano, M. Yoshimura, and T. Yao, *Jpn. J. Appl. Phys.*, **32,** 3131 (1993).
9. J. S. Chau and S. C. Lee, *This Journal,* **141,** 3214 (1994).
10. E. Kobeda, M. Kellam, and C. M. Osburn, *ibid.*, **138,** 1846 (1991).
11. A. G. Revesz, *IEEE Trans. Electron Device,* **ED-12,** 97 (1965).
12. S. V. Nguyen, D. Dobuzinsky, D. Dopp, R. Gleason, M. Gibson, and S. Fridmann, *Thin Solid Films,* **193/194,** 595 (1990).
13. R. Williams and M. H. Woods, *J. Appl. Phys.*, **46,** 695 (1975).
14. C. G. van de Walle, F. R. McFeely, and S. T. Pantelides, *Phys. Rev. Lett.*, **61,** 1867 (1988).
15. C. F. Yeh, C. L. Chen, W. Lur, and P. W. Yen, *Appl. Phys. Lett.*, **66,** 938 (1995).
16. R. M. Silverstein, *Spectrometric Identification of Organic Compounds,* p. 94, John Wiley & Sons, New York (1991).
17. E. A. Irene, D. W. Dong, and R. J. Zeto, *This Journal,* **127,** 396 (1980).
18. P. N. Sen and M. F. Thorpe, *Phys. Rev.*, **B15,** 4030 (1977).
19. G. Lucovsky, *Philos. Mag.*, **B39,** 513 (1979).
20. J. T. Fitch and G. Lucovsky, American Vacuum Society, Fall Meeting, Anaheim, CA (1987).
21. I. Simon, in *Modern Aspects of the Vitreous State,* p. 120, J. D. MacKenzie, Editor, Butterworths, London (1960).
22. E. Kobeda and M. Kellam, *This Journal,* **138,** 1846 (1991).
23. W. A. Pliskin and H. S. Lehman, *ibid.*, **112,** 1013 (1965).

Downloaded on 2014-04-28 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).