

The Physicochemical Properties and Growth Mechanism of Oxide (SiO_{2-x}F_x) by Liquid Phase Deposition with H₂O Addition Only

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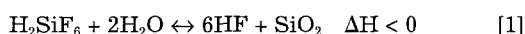
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ABSTRACT

Silicon oxide formation was studied by a novel liquid phase deposition (LPD) method with H₂O addition only at 35°C. The deposition rate could be controlled by varying the quantity of H₂O added. The LPD-oxide was lightly oxygen-deficient. FTIR spectra and AES depth profiles indicate that a small amount of fluorine was incorporated into the oxide. The composition of LPD-oxide can be represented as SiO_{2-x}F_x. The physicochemical properties of LPD oxide were investigated, as was the behavior of fluorine in the oxide and the chemical reaction. A model for the LPD mechanism is proposed that satisfactorily explains all of the experimental phenomena observed.

In microelectronics, silicon dioxide (SiO₂) is widely used as an insulator including the gate dielectric, isolation, and passivation layers. Conventional methods of preparing SiO₂ films, such as thermal oxidation or CVD techniques, are subject to several problems, such as thermal stress, dopant redistribution, and material interaction. To solve these problems, we suggest replacing conventional techniques with a room-temperature method that grows an SiO₂ film with similar quality.

Liquid phase deposition (LPD) is a room-temperature method for SiO₂ formation. To date, LPD-oxide films have been obtained by adding either H₃BO₃¹⁻⁵ or Al⁶ to hydrofluosilicic acid (H₂SiF₆) solution saturated with silica. In this approach, however, owing to the number of additional parameters, the deposition reaction in LPD is complicated. Moreover, this method does not consider the contamination from the chemicals, but rather merely assumes that such contamination is minimal. The LPD method with H₂O addition was first attempted by Yoshitomi *et al.*⁵ According to Ref. 5, the chemical reaction for SiO₂ growth in the treatment solution can be represented by the following equilibrium reaction



In fact, however, this equation represents only the chemical reaction in the solution and does not explain the growth of LPD-oxide on the substrate at all. In addition, Yoshitomi

et al. concentrated mainly on investigating the electrical properties of the as-deposited and the annealed LPD-oxide, such as current *vs.* voltage and capacitance-voltage. Basic phenomena such as the effects on the deposition process of adding different quantities of H₂O and the physicochemical properties of LPD-oxide were not clarified. Furthermore, the behavior of fluorine incorporated in the LPD oxide and the mechanism of the method are still unknown. In this study, we investigate these issues.

Experimental

Figure 1 shows the experimental flow diagram for the LPD process, including the preparation of the chemical solution and samples. First, 35 g of silica (SiO₂) powder (99.999%) were added to 1 liter of hydrofluosilicic acid (H₂SiF₆, 4 mol/l). The solution became saturated with silicic acid [Si(OH)₄] after being stirred at 23°C for 17 h. Before the substrates were immersed, the solution was filtered to remove the undissolved silica, and deionized water (H₂O) was added to the saturated solution as it was stirred. The H₂O enabled the solution to become supersaturated with silicic acid. The titration rate of H₂O was about 1 ml/min, and the quantity of H₂O added was 15 ~ 67 ml per 100 ml of the immersing solution.

The substrates used in this experiment were n-type (100) silicon wafers. After initial cleaning, the native oxides formed on the substrates in the HCl + H₂O₂ mixed solution

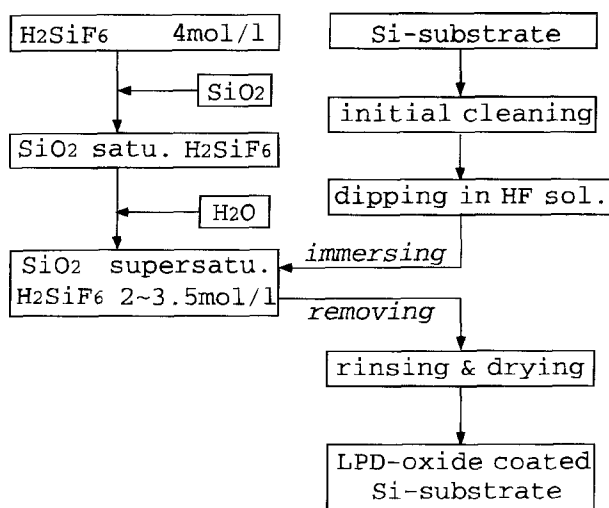


Fig. 1. Experimental flow diagram of the LPD solution and sample preparation.

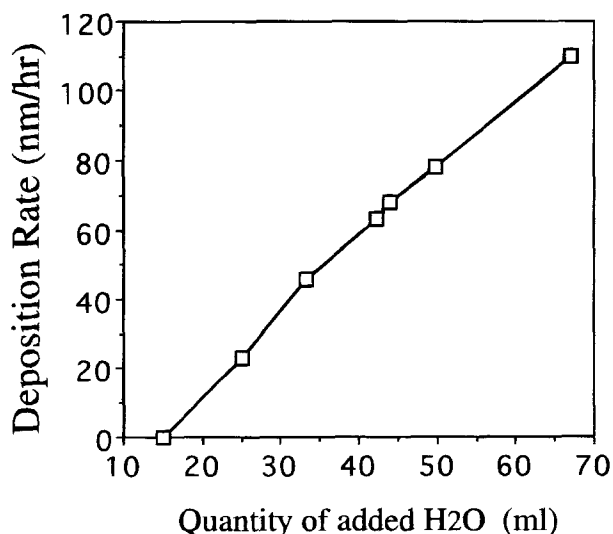


Fig. 2. Dependence of deposition rate on added H₂O volume.

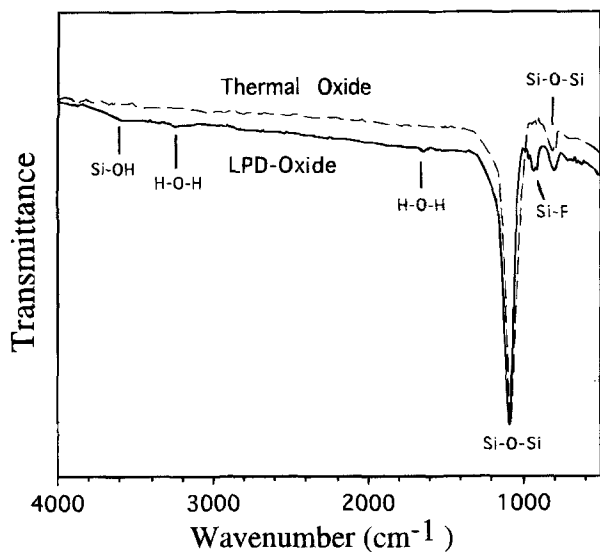


Fig. 3. Typical FTIR spectra of thermal oxide thickness: 1100 Å and LPD oxide thickness: 1020 Å.

during cleaning were removed by dipping in HF solution. The cleaned substrates were then placed into the immersing solution at 35°C, until a ~110 nm thick LPD-oxide film formed gradually on the substrate surface. The substrates were then removed from the solution, rinsed with deionized water, and spin-dried.

The thickness and refractive index of the LPD-oxide were determined by ellipsometer. The film structure and chemical resistance were evaluated by using Fourier transform infrared spectroscopy (FTIR) and the P-etch rate test,⁷ respectively. The depth profile of composition was investigated by using Auger electron spectroscopy (AES). To verify the correctness of the proposed LPD mechanism, the

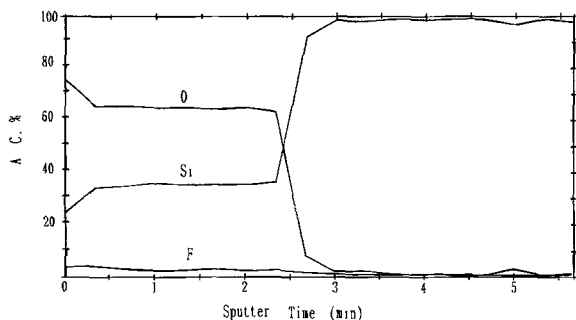


Fig. 4. AES depth profile of LPD oxide.

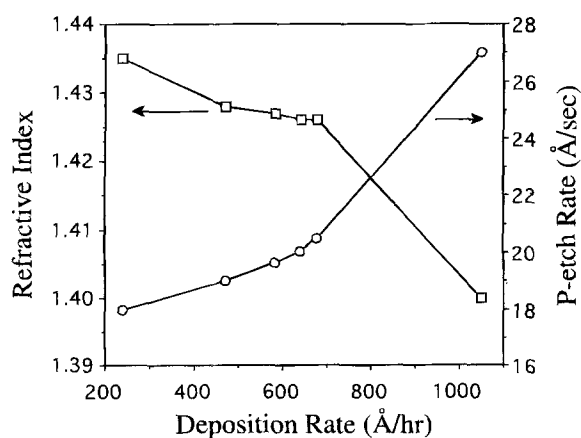


Fig. 5. Changes in refractive index and P-etch rate for LPD oxide films prepared with different deposition rates.

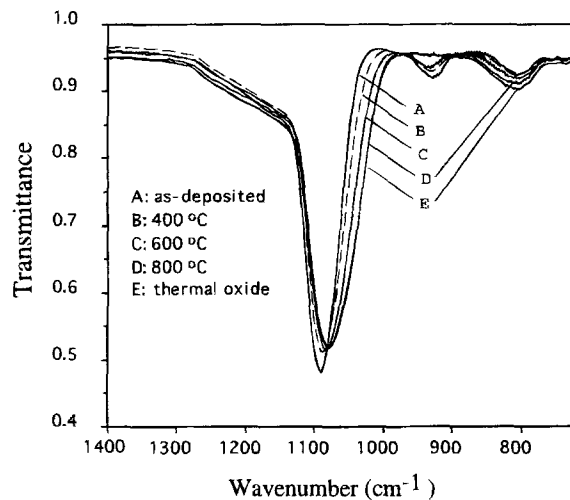


Fig. 6. Typical changes in FTIR spectra in the region of 700 ~ 1400 cm^{-1} for 1020 Å thick LPD-oxide films annealed at various temperatures for 1 h.

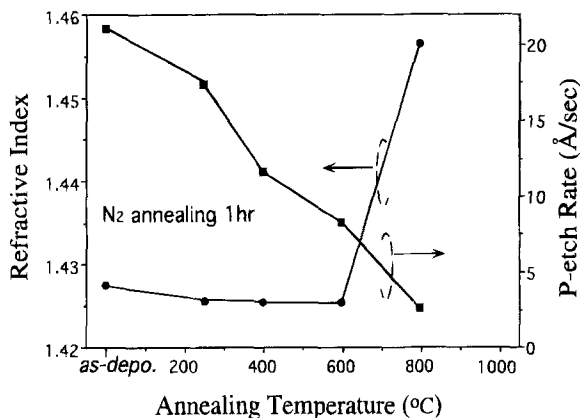


Fig. 7. Dependence of refractive index and P-etch rate on annealing temperature. The LPD-oxide films were annealed in N_2 ambient for 1 h.

changes in the chemical composition of the immersing solution were investigated using the FTIR method.

Results and Discussion

Physicochemical properties.—LPD-oxide was successfully formed in the solution with H_2O addition only. Moreover, the quantity of H_2O added had a significant effect on the LPD-oxide deposition rate (D.R.). As shown in Fig. 2, the plot of the oxide D.R. as a function of the quantity of H_2O added indicates that the D.R. can be controlled in the range of 0 ~ 110 nm/h by adding 15 ~ 67 ml of H_2O per 100 ml of the immersing solution. This D.R. range is similar to that of the LPD method with H_3BO_3 addition.⁴ The figure clearly shows that the D.R. can be enhanced by increasing the amount of H_2O added, and in fact the D.R. can be controlled by adding more or less H_2O . In the Discussion we explain this phenomenon after we propose a mechanism for the LPD process.

Figure 3 shows a typical FTIR spectrum of 1020 Å thick LPD-oxide. It is nearly the same as that of LPD film deposited with the addition of H_3BO_3 .⁸ The absorption bands around 1090 cm^{-1} and 810 cm^{-1} are due to the Si-O-Si vibration. These absorption bands, which are similar to those found in the spectra of thermal oxide, indicate that LPD oxide is amorphous in structure. Another main absorption band around 930 cm^{-1} found in the LPD spectra may be due to Si-F.⁸ The reason fluorine is incorporated into the oxide is explained when we discuss our model of the LPD mechanism later. The concentration and the distribution of fluorine incorporated in the oxide were investigated by AES measurement. As shown in Fig. 4, the AES depth pro-

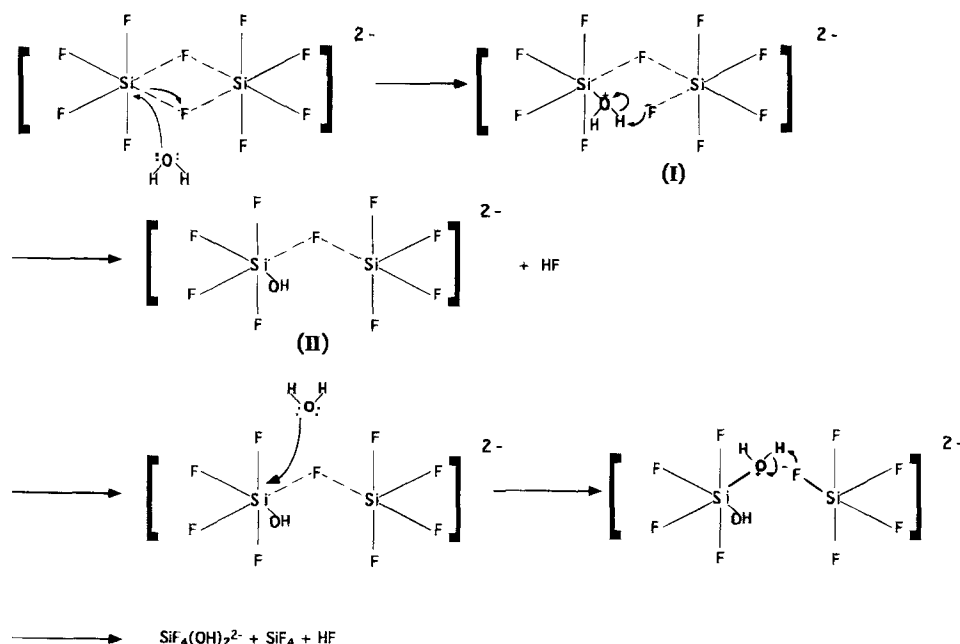


Fig. 8. Detailed chemical reaction and composition of immersing solution when H_2O was added.

file of an LPD-oxide film reveals that the atomic concentration ratio of Si: O: F is 32.88: 65.20: 1.92. The fluorine is uniformly distributed in the LPD-oxide. These results imply that the LPD-oxide is a lightly oxygen-deficient film. On this basis, the composition of LPD-oxide can be represented as $\text{SiO}_{2-x}\text{F}_x$.

On the other hand, a few absorption bands related to water are also found in the LPD spectrum. O-H stretching due to H_2O is exhibited in the absorption bands around 3300 cm^{-1} and 1640 cm^{-1} , while O-H stretching due to Si-OH is exhibited in the band around 3600 cm^{-1} . These bands reveal that the LPD film may contain a small amount of water. However, the intensity of these peaks is faint, indicating that the amount of water contained in the film is small.

For the LPD-oxide film prepared by this method, the refractive index is about $1.40 \sim 1.435$. As was reported,⁹ the refractive index of LPD-oxide film is lower than the value of 1.462 for thermal silicon dioxide.¹⁰ In general, the lower refractive index is due to the fluorine contained in the oxide.¹⁰ In fact, the AES measurement shows that the LPD-oxide film indeed contains fluorine. This conclusion is consistent with the properties of the P-etch rate. The P-etch rate of LPD-oxide in this study was about $18 \sim 27\text{ \AA/s}$, which is greater than that of thermal oxide ($2 \sim 8\text{ \AA/s}$).⁷ Moreover, our experiments also indicated that both the refractive index and the P-etch rate are highly dependent on oxide D.R. As shown in Fig. 5, the refractive index decreases as the D.R. increases, while the P-etch rate increases with the D.R. This result indicates that to control the film quality deposition conditions with a relatively low D.R. should be used. Although both the refractive index and the P-etch rate are dependent on the D.R., the electrical properties of the LPD-oxide do not vary with the D.R.

Since the AES results reveal that LPD-oxide contains fluorine, it is essential to investigate the behavior of fluorine in the annealed LPD-oxide. Figure 6 shows the typical changes in FTIR spectra in the region of $700 \sim 1400\text{ cm}^{-1}$ for the annealed 1020 \AA thick LPD-oxide films under different annealing temperatures in N_2 ambient. The spectrum of thermal oxide with a thickness of 1010 \AA is also shown (curve E) for comparison. The Si-F band around 930 cm^{-1} gradually decreases with annealing temperature. This phenomenon indicates that reduction in the Si-F bonds occurred during annealing at temperatures above 400°C . At temperatures above 800°C , the spectrum of the LPD film (curve D) is nearly indistinguishable from that of thermal oxide (curve E), and the Si-F bonds seem to have completely disappeared. After N_2 annealing, the absorption

band near 1090 cm^{-1} due to Si-O-Si vibration of LPD shifted toward lower wave numbers, and the width of the bands became broader. In addition, after N_2 annealing the water-related absorption bands, such as 3300 cm^{-1} (OH) and 3600 cm^{-1} (Si-OH), also disappeared at temperatures above 250°C . This implies that the composition and structure of LPD oxide became similar to that of thermal oxide after 800°C annealing. It also implies that the wave number of Si-O-Si bonds in as-deposited LPD-oxide is slightly higher than that in thermal oxide because of the high electronegativity of fluorine incorporated in LPD oxide.

The effect of annealing temperature on refractive index was also investigated. As shown in Fig. 7, after N_2 annealing the refractive index decreases slightly as the temperature increases until 600°C . This decrease can be ascribed to the release of water out of the LPD-oxide.⁷ On the other hand, after annealing at higher temperature ($>600^\circ\text{C}$) the refractive index increases dramatically. The increased refractive index is nearly the same as that of thermal oxide (1.46). The lower index found in LPD oxide may be due to the fluorine in the film. When the film is annealed at higher temperature ($>600^\circ\text{C}$), the Si-F bonds can be broken and may be changed into Si-O-Si bonds. This is the reason the refractive index increases after annealing at higher temperature. The dependence of the P-etch rate on annealing temperature is also shown in Fig. 7, which indicates that the P-etch rate of LPD-oxide decreases dramatically with higher temperature. For the LPD film annealed at 800°C , both the refractive index (~ 1.457) and the P-etch rate ($\sim 2.5\text{ \AA/s}$) are nearly the same as those for thermal oxide. This means that few large changes such as changes in bonding and the disappearance of fluorine from the LPD-oxide occur when the annealing temperature is as high as 800°C .

LPD mechanism.—To investigate the LPD mechanism, it is indispensable to clarify the chemical composition of the immersing solution and the details of the chemical reaction. In this section, we explain the composition and the chemical reaction and then propose a mechanism for the LPD process.

The immersing solution was prepared by dissolving silica in H_2SiF_6 solution. In relatively concentrated H_2SiF_6 solution, silica can be dissolved to an amount well beyond its solubility¹¹ with the formation of species such as fluosilicic complex $[\text{SiF}_6 \cdot \text{SiF}_4]^{2-}$.¹² This has been confirmed by analysis of UV absorption spectrum in which the peak density was found to be dependent on the H_2SiF_6 concentration and the quantity of SiO_2 in solution.^{12,13} The formation of the fluosilicic complex can be represented¹⁴ by

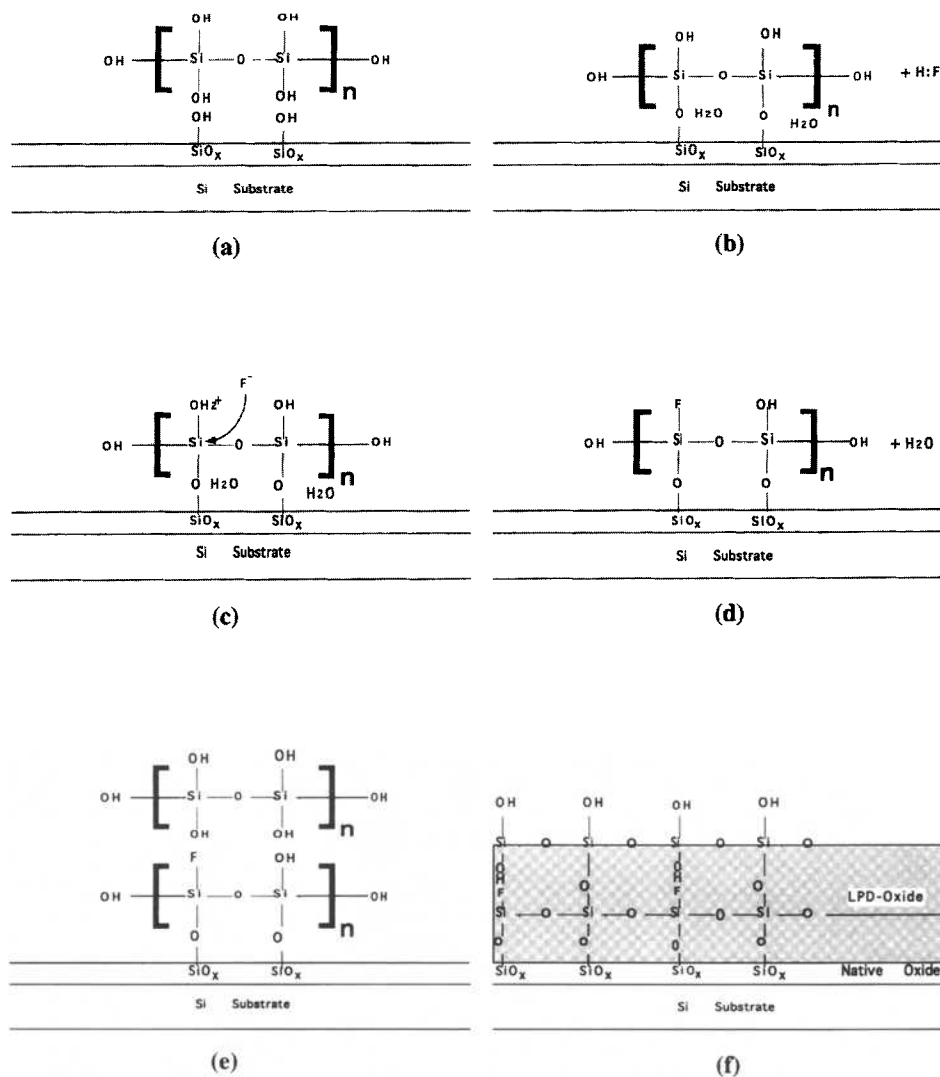
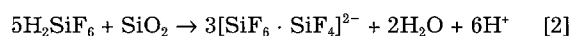


Fig. 9. Schematic illustrations of the proposed LPD mechanism.



As illustrated in Fig. 8, the fluosilicic complex $[\text{SiF}_6 \cdot \text{SiF}_4]^{2-}$ is a bridged intermediate, usually an anion. Because of high electronegativity of fluorine, the bonded Si is electron-deficient. However, the Si-F-Si bond is rather weak, so we propose that the Si-F-Si bond brings on an attack

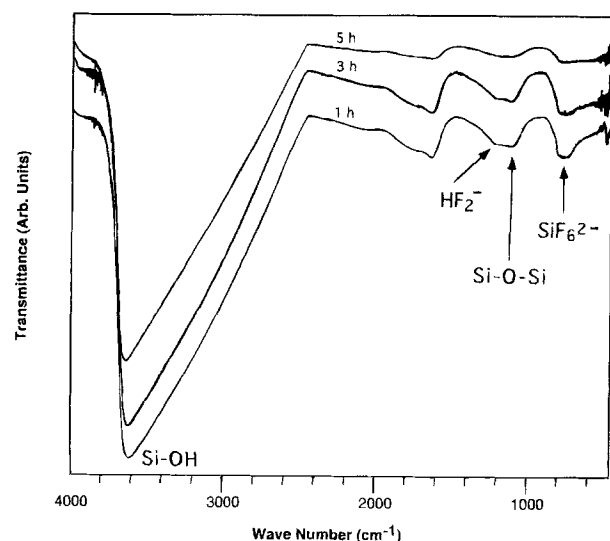
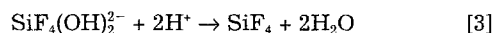
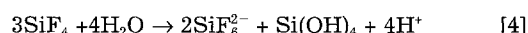


Fig. 10. Typical changes in FTIR spectra for the immersing solution after deposition for 1, 3, and 5 h.

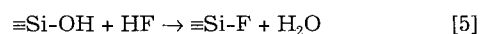
from an external nucleophile H_2O , yielding the product (I). Furthermore, the reaction of the Lewis base F^- with the proton yields the product (II) and HF. For the same reason, the product (II) can further react with H_2O to yield $\text{SiF}_4(\text{OH})_2^{2-}$, SiF_4 , and HF. Because the immersing solution is acidic, the reaction of $\text{SiF}_4(\text{OH})_2^{2-}$ and H^+ will occur as follows



However, the hydrolysis of SiF_4 in aqueous solution will yield SiF_6^{2-} , H^+ , and silicic monomer $\text{Si}(\text{OH})_4$, as follows



Thus, from the chemical reaction and the chemical composition discussed above, we hypothesize that the mechanism for the deposition of LPD-oxide can be described by the five steps shown in Fig. 9. (i) First, the intermediate polysilicic acid is formed by the polymerization of the silicic monomer $\text{Si}(\text{OH})_4$.¹⁵ (ii) Since the concentration of polysilicic acid in the system is very low, the polysilicic acid cannot form a spatial network throughout the volume, but is instead absorbed onto the substrate surface (the deposition phenomenon), as illustrated in Fig. 9a. (iii) Acid-catalytic dehydration occurs between the absorbed polysilicic acid and Si-OH present on the substrate surface, followed by Si-O-Si bond formation (Fig. 9b). (iv) Because some HF is present in the system, the surface of the as-deposited film will be subject to HF attack (Fig. 9c and d) according to the reaction



Hence etching also occurs simultaneously with deposition. (v) In summary, deposition of LPD-oxide film on the substrate surface is the predominant result, because of the continual absorption of polysilicic acid as described in step (ii) (Fig. 9e and f).

Discussion

To confirm the correctness of the model proposed above, we investigated the changes in the chemical composition of the immersing solution with FTIR after performing deposition for 1, 3, and 5 h. As shown in Fig. 10, FTIR spectra indicate that the peaks around 3600, 1202.5, 1090, and 732 cm^{-1} are due to the Si-OH bonds, HF_2^- functions, Si-O-Si bonds, and SiF_6^{2-} , respectively. This chemical composition is consistent with the reaction products entailed by the model presented above. Because the polysilicic acid in solution was absorbed onto the substrate surface, the Si-O-Si peak intensity, which is proportional to residual concentration, obviously decreased with deposition time. Although Si-F bonds were detected in the LPD-oxide (Fig. 3), they were not detected in the immersing solution. However, the results concerning the chemical reaction and composition support the LPD mechanism proposed above.

The proposed LPD-mechanism also explains all the phenomena observed in the experiment. First, the D.R. of the oxide can be determined by the quantity of H_2O added because a larger amount of H_2O increases the nucleophilic attack from H_2O in the solution. This increases the concentration of polysilicic acid and thus enhances the D.R. Next, the fluorine incorporation can be understood as a result of Si-F bond formation. The formation of Si-F bonds can be attributed to the fact that the as-deposited oxide is always attacked by HF. To explain the dependence of the refractive index and P-etch rate on the D.R. of the LPD-oxide, the relationship between the D.R. and the chemical reaction rate has to be taken into account. The increase in the D.R. is due to the increase in the chemical reaction rate of the system. When H_2O addition increases the reaction rate, the concentration of HF also increases. Because the as-deposited LPD-oxide is subjected to HF attack, the amount of Si-F bonds will also increase. Thus the higher the concentration of Si-F bonds, the lower the refractive index is, and the higher the P-etch rate will become.

Conclusions

This research investigated the formation of oxide by using liquid phase deposition in silica-saturated H_2SiF_6 solution with H_2O addition only. The LPD-oxide D.R. varied from 0 ~ 110 nm/h depending on the quantity of H_2O added. A larger amount of H_2O addition enhances the nucleophilic attack from H_2O in the solution, which increases

the concentration of polysilicic acid and in turn raises the D.R. The concentration ratio of Si: O: F is 32.88: 65.20: 1.92. The oxide can be represented as $\text{SiO}_{2-x}\text{F}_x$. Both the refractive index and the P-etch rate depend heavily on the oxide D.R. The higher the concentration of Si-F bonds, the lower the refractive index is, and the higher the P-etch rate will be. However, high temperature annealing in N_2 ambient results in a higher refractive index and lower P-etch rate. The model of the deposition mechanism proposed on the basis of chemical reaction and composition explains how H_2O addition enhances oxide deposition and how fluorine is incorporated into the oxide.

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REFERENCES

1. T. Goda, H. Nagayama, A. Hishinuma, and H. Kawahara, *Mater. Res. Symp. Proc.*, **105**, 283 (1988).
2. H. Nagayama, H. Honda, and H. Kawahara, *This Journal*, **135**, 2013 (1988).
3. T. Homma, T. Katoh, Y. Yamada, J. Shimizu, and Y. Murao, in *IEEE Symposium on VLSI Technology*, p. 3, IEEE (1990).
4. C. L. Chen, S. S. Lin, C. F. Yeh, and Y. W. Hu, *International Electron Devices and Materials Symp.*, p. 489 (1992).
5. S. Yoshitomi, S. Tomioka, and N. Haneji, *ibid.*, p. 22 (1992).
6. A. Hishinuma, T. Goda, and M. Kitaoka, *Appl. Surface Science*, **49**, 405 (1991).
7. W. A. Pliskin, *J. Vac. Sci. Technol.*, **14**, 1064 (1977).
8. C. F. Yeh, C. L. Chen, S. S. Lin, and Y. W. Hu, in *International Electron Devices and Materials Symp.*, p. 489 (1992).
9. C. F. Yeh, S. S. Lin, C. L. Chen, and Y. C. Yang, *IEEE Electron Device Lett.*, **14**, 403 (1993).
10. J. W. Fleming and D. L. Wood, *Applied Optics*, **22**, 3102 (1983).
11. R. H. Busey, E. Schwartz, and R. E. Mesmer, *Inorg. Chem.*, **19**, 758 (1980).
12. S. Deki, 56th Spring Meeting, *Jpn. Electrochem. Soc.*, p. 18 (1989).
13. S. Deki, 56th Spring Meeting, *ibid.*, 751 (1988).
14. S. M. Thomser, *J. Am. Chem. Soc.*, **74**, 1690 (1952).
15. N. I. Vorob'ev, O. B. Dormeshkin, and V. V. Pechkovskii, *J. Appl. Chem. USSR*, **62**, 1539 (1989).