



Thermal Stability of Fluorinated Amorphous Carbon Thin Films with Low Dielectric Constant

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Fluorinated amorphous carbon (a-C:F) thin films were deposited by inductively coupled plasma enhanced chemical vapor deposition and annealed with increasing annealing temperature (100, 200, 300, 400°C). The evolution of composition, dielectric constant, and bonding configuration were investigated during the thermal annealing process. As the annealing temperature increased, the dielectric constant varied from 2.4 to 3.6; the atomic ratio of F varied from 25 to 10%, and that of C varied from 75 to 85%; in the C-F_x bonding configurations, the C-F bondings decrease and the C-F₂ and C-F₃ bondings are almost constant. Thus, the C-F₂ and C-F₃ bonding configurations are thermally more stable than the C-F bonding configuration. The structure of the film changes to a crosslinked structure by an increase in the C-C bonding and a decrease in the C-F bonding.

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The growth of the integrated circuit (IC) technology is primarily based on the continued scaling of devices to ever smaller dimensions. Smaller devices give higher packing density as well as higher operating speed. As a result, interconnect technology is getting more complicated with each device generation. For advanced logic chips, it is now the interconnect rather than transistors that is limiting the packing density and operating speed. Long interconnects also contribute significantly to the power consumption of chips. Thus, the need has increased for developing new low dielectric materials to replace conventional intermetal dielectric materials, such as the high dielectric ($k \approx 3.9$) SiO₂.

The conventional chemical vapor deposition (CVD) SiO₂ can be doped with fluorine to decrease its dielectric constant. The minimum k value, about 3.0-3.2, is obtained with about 10% fluorine in SiO₂,¹ but the decrease in dielectric constant is relatively small because the amount of fluorine that can be incorporated into SiO₂ is limited. Another candidate material is polymer thin films since they have low dielectric constants (below 3). Most studies on organic dielectrics are based on spin-on coatings followed by a curing process, including; $k = 2.4$ - 2.6 for fluorinated poly(arylenethers), $k = 2.6$ - 2.8 for fluorinated polyimides and $k = 2.4$ for perfluorocyclobutane (PFCB).² Another method is to use vapor deposition which is solvent free and can provide a uniform coating over a large area. Some vapor deposited polymeric films are:³⁻⁷ $k = 2.6$ for Parylene-N,⁵ $k = 2.2$ for Parylene copolymers, $k = 2.3$ for Parylene-F,⁶ and $k = 1.9$ for polytetrafluoroethylene (PTFE), (Teflon-AF). In particular, PTFE is a promising material since it may be the lowest dielectric constant material with reasonable mechanical strength. However, polymer thin films have problems satisfying some of the characteristics required for integration processing in microelectronics, such as thermal stability, adhesion, glass transition temperature, mechanical strength, and gap-filling property. These problems have reduced the candidates a few fluorocarbon materials.

One of such candidate materials is the fluorinated amorphous carbon (a-C:F) thin film, since it has excellent electrical and mechanical properties. However, the poor thermal stability of a-C:F thin films have hindered their use in microelectronics. Recently, a-C:F films with better thermal stability have been developed using plasma enhanced chemical vapor deposition.⁸⁻¹³ However, the thermal evolution of composition and the thermally stable bonding configuration are not known. In particular, it is not known whether the film satisfies both the low dielectric constant and thermal stability criteria.

In our previous study,¹⁴ we identified the mechanism for the

reduction of the dielectric constant of a-C:F thin films. In this paper, the thermal evolution of composition, dielectric constant, bonding configuration and structure are investigated and the thermally stable condition of the a-C:F thin film is identified. Finally, we present the optimal conditions to obtain a low dielectric constant and thermal stability.

Experimental

The samples were prepared by inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) at room temperature and radio frequency (rf) power of 400 W as shown in Table I. The a-C:F thin films were deposited on (100) p-type Si substrates using CH₄/CF₄ as reactant gases, and Ar as a diluent gas. Deposition characteristics were examined with the variation of CF₄:CH₄ flow rate ratio in our previous study.¹⁴ The a-C:F thin films deposited with 1:1 and 10:1 CF₄:CH₄ flow rate ratio were chosen for the annealing process since they had the lowest and the highest dielectric constant, respectively. The two samples were annealed under vacuum for 30 min with increasing annealing temperature (100, 200, 300, and 400°C), as shown in Table I. Remote-type ICP-CVD was used to deposit high quality films without heating or damaging the substrate, since the intense degree of ionization and dissociation is established in a region away from the substrate in the deposition chamber.

The refractive indexes of the films were obtained using an ellipsometer (Rudolph, auto-EL2). The dielectric constants of the a-C:F films were calculated from the capacitance-voltage (C-V) plot measured at 1 MHz in the metal insulator semiconductor (MIS) structure (Al/a-C:F/Si). To make the ohmic contact between the probe and the back side of the Si substrates, Al films were deposited on the back side of the Si substrates by sputtering. Quantitative analyses for all elements, including hydrogen, in the films were performed by elastic recoil detection-time of flight (ERD-TOF) measurements. By the inverse reaction scheme, the recoil cross sections induced by <10 MeV ³⁵Cl ions have been measured. Therefore, we could obtain the energy counts spectra by plotting with different times of flight. Au-

Table I. Experimental conditions of a-C:F films for thermal annealing.

Experimental parameters	Conditions
Samples	Sample A : CF ₄ :CH ₄ = 1:1 Sample B : CF ₄ :CH ₄ = 10:1 Deposition conditions: 400 W, 25°C
Atmospheric pressure	Vacuum (10 ⁻² Torr)
Annealing temperature	100, 200, 300, 400°C
Annealing time	30 min

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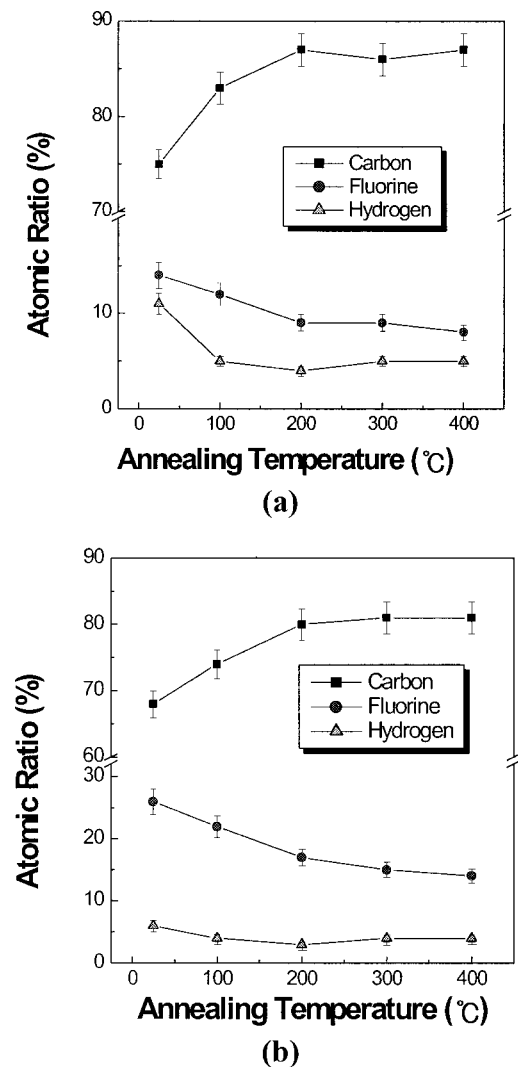


Figure 1. The atomic ratio measured from the ERD-TOF spectra of a-C:F thin films with various annealing temperatures. (a) $\text{CF}_4:\text{CH}_4 = 1:1$, (b) $\text{CF}_4:\text{CH}_4 = 10:1$.

ger electron spectroscopy (AES, Perkin-Elmer SAM 4300) was also used for certifying the compositional results of the ERD-TOF. The evolutions of the C-F bonding configurations were analyzed using hot-stage X-ray photoelectron Spectroscopy (XPS, VG ESCALAB 200R, Al $K\alpha$ radiation) with increasing annealing temperature. In particular, quantitative analysis of the C-F bonding configuration was done using the multiple Gaussian and peak integration method from the XPS data. Area densities of the films were calculated from the composition of the ERD-TOF, total number of atoms recoiled per unit area (cm^2) and the thickness of the film.

Results and Discussion

Compositional analysis.—Variation in the atomic ratios of the component elements during annealing are analyzed by the ERD-TOF method. Fig. 1a represents the variation in the atomic ratio of sample A (deposited at 1:1 $\text{CF}_4:\text{CH}_4$) with increasing annealing temperature. It is observed that the atomic ratio of carbon increases from 75 to 87% and the atomic ratios of the remaining elements (fluorine and hydrogen) decrease. The relative increase of carbon in the film is due to evolution of fluorine and hydrogen atoms to the atmosphere. Most of the increase occurs in the 25-200°C region. The atomic ratio of hydrogen decreases from 11 to 5% after annealing at 100°C and saturates at 5% above 100°C. This implies that

hydrogen atoms are loosely bonded with carbon and evolve into the atmosphere at 100°C. The atomic ratio of fluorine decreases from 15 to 9% in the 25-200°C range and saturates at 8% in the 200-400°C range. The fluorine content in the film has a great effect on the dielectric constant, as discussed earlier. Thus, it is assumed that the dielectric constant increases in the 25-200°C range, and then varies slightly in the 200-400°C range. From these results, the optimal annealing temperature of sample A for obtaining thermal stability at high temperature is 200°C.

Figure 1b is the variation of the atomic ratio of sample B (deposited at 10:1 $\text{CF}_4:\text{CH}_4$) with increasing annealing temperature. Its result is similar to that of the Fig. 1a. The atomic ratios of the elements of the film vary widely in the 25-200°C range and then change slightly in the 200-400°C range. The atomic ratio of carbon increases from 68 to 81% with increasing annealing temperature. The atomic ratio of hydrogen decreases from 6 to 4% after annealing at 100°C. Similar to the earlier results, the atomic ratio of fluorine decreases from 26 to 17% in the 25-200°C range, and then decreases slightly to 15% in the 200-400°C range. One difference from the result of Fig. 1a is a higher atomic ratio of fluorine, about 15% even after annealing at 400°C. This might be induced from the higher fluorine content of as-deposited sample B. However, although the annealing temperature increases continuously, the atomic ratio of fluorine in sample B saturates at a higher value than for sample A. This is due to the differences in the structures of samples A and sample B, discussed in detail later.

Refractive index and dielectric constant.—As shown in Fig. 2a, the refractive indexes of the films in the 632.8 nm wavelength increase from 1.4 to 1.8 with increasing annealing temperature. It is due to the reduction of fluorine content with high electronegativity in the films. The difference between the refractive indexes of the two films is reduced with increasing annealing temperature, since the difference between the F contents of the two samples decreases. This implies that the difference between the electronic polarization decreases with increasing annealing temperature.¹⁴ Sample A has a larger refractive index than sample B since it has a lower F content.

To obtain the dielectric constant of an a-C:F film, the C-V characteristic is measured at 1 MHz in a metal insulator semiconductor (MIS) structure (Al/a-C:F/Si). From the C-V curve, the dielectric constant of the film is obtained by Eq. 1

$$k = \frac{dC}{\epsilon_0 A} \quad [1]$$

where k is the relative dielectric constant, C is the capacitance of the film, ϵ_0 is the dielectric permittivity of vacuum, and A is the area of the MIS diode.

Figure 2b shows the variation of the dielectric constant of the a-C:F thin films with increasing annealing temperature. The dielectric constant of sample A increases from 3.2 to 3.65 with increasing annealing temperature, because the fluorine content decreases. Similar to sample A, it is observed that the dielectric constant of sample B increases rapidly from 2.35 to 2.8 in the 25-200°C range and then increases slowly in the 200-400°C range, again due to abrupt decrease of fluorine content in the 25-200°C range.

However, the dielectric constant of sample B does not become closer to the value of sample A, different from the variation of the refractive index. Although the electronic polarizations of the two samples are close at high annealing temperature, since the refractive indexes of the two samples are close, as shown in Fig. 2a, the difference between the dielectric constants does not change significantly. This implies that the ionic and dipole polarizations do not decrease with increasing annealing temperature. To investigate the reasons for this result, characterization of the variations of the structure and the bonding configuration during annealing are dealt with later.

Thermal evolution of bonding configuration.—To investigate the variation of bonding configuration with increasing annealing tem-

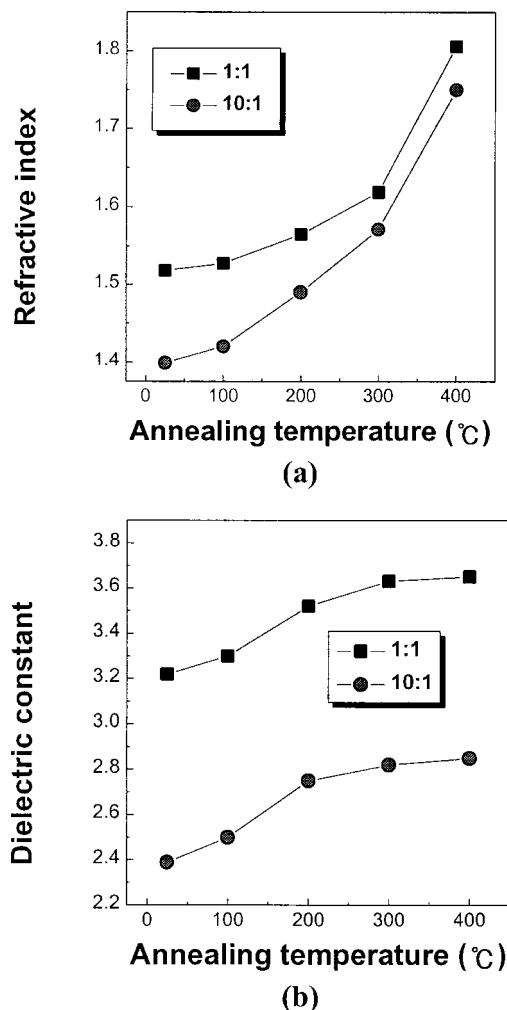


Figure 2. Variations of (a) refractive index and (b) dielectric constant of a-C:F thin films with annealing temperature.

perature, the hot-stage XPS was carried out. Figure 3 shows the variation of C 1s binding energy XPS spectra of the a-C:F sample A deposited at 25°C, 400 W, and $\text{CF}_4:\text{CH}_4 = 1:1$ with increasing annealing temperature (100, 200, 300, and 400°C). (Sample A has the higher dielectric constant.) The positions of the C 1s binding energy peaks in the XPS spectra shift to lower binding energy due to the charging effect, so only the relative positions of the peaks are relevant.

In order to analyze quantitatively the content of each bonding configuration, the C-F bonding peaks in the XPS spectra were deconvoluted to four Lorentz-Gaussian peaks as shown in Fig. 4. First, the background of each spectrum is set and the peaks are deconvoluted. Second, each deconvoluted peak is integrated and this integrated area represents the concentration of each bonding configuration. Figure 5 shows the evolution of bonding configuration with increasing annealing temperature. It is observed that the concentration of C-C or C-H bonds grows markedly, while the C-F bonding content is significantly reduced, and the C-F₂ and the C-F₃ bonding contents are almost constant with increasing annealing temperature. Thus, it is assumed that C-C bonds are thermally more stable than C-F_x bonds. In particular, it is observed that the C-F₂ and C-F₃ bonds are more stable than the C-F bond in C-F_x bonding configurations.

Figure 6 shows the variation of C 1s binding energy XPS spectra of the a-C:F sample 2 deposited at 25°C, 400 W, and $\text{CF}_4:\text{CH}_4 = 10:1$ with increasing annealing temperature (100, 200, 300, and

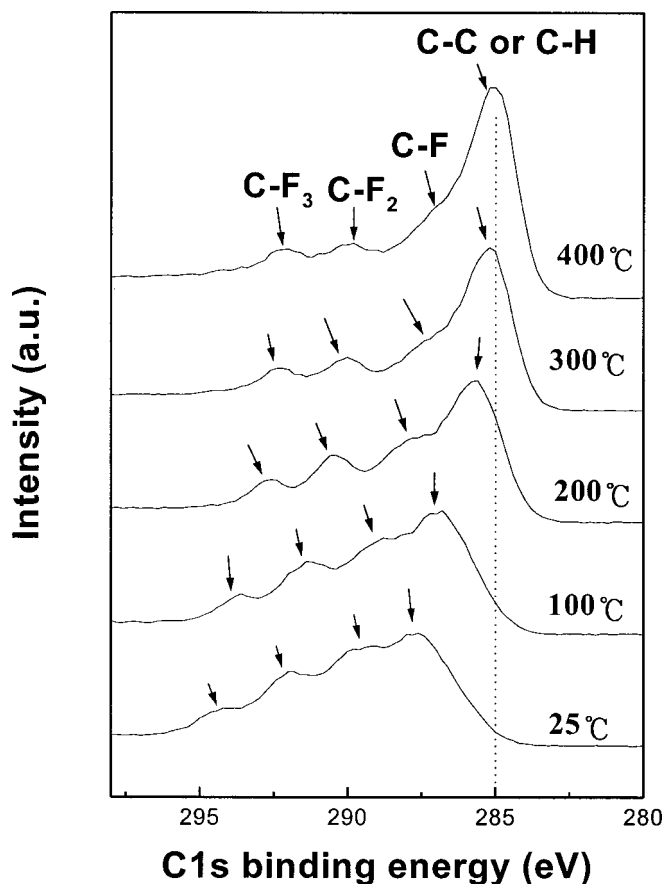


Figure 3. C 1s binding energy (XPS) spectra of a-C:F thin films deposited at 25°C and 400 W, and $\text{CF}_4:\text{CH}_4 = 1:1$ with increasing annealing temperature.

400°C). As the annealing temperature increases, the peaks sharpen and the background of the spectra is reduced. It is assumed that the peaks sharpen because F atoms loosely bonded with carbon atoms are released while tightly bonded fluorine atoms remain during the annealing process. Thus, the decrease of the background is due to the peak sharpening (loss of loosely bonded F atoms) and the reduction of the intensity of the C-F bonding configuration (decrease of the F content).

Following the deconvolution and integration procedure as for sample A, the evolution of the bonding configuration with increasing annealing temperature is shown in Fig. 7. In accordance with the case of sample A, it is observed that the concentration of C-C bonds grows, while the C-F bond concentration decreases, and the C-F₂ and C-F₃ bonding contents vary slightly as annealing temperature increases from 25 to 400°C. As observed before, it is found out that the C-F₂ and C-F₃ bonds are thermally more stable than the C-F bond in C-F bonding configurations.

According to the mechanism for reduction of dielectric constant discussed in an earlier study,¹⁴ C-F₂ and C-F₃ bonding configurations are more effective than the C-F configuration for reducing the dielectric constant of the film since they induce smaller electronic and ionic polarizations. The observation that the dielectric constants of the two samples do not converge after annealing, unlike the case of the refractive index (Fig. 2a and b) can be explained as follows. As the annealing temperature increases, the F content decreases in both samples and becomes more similar. The difference of electronic polarization decreases, as does the refractive index since they are related by the following equation, $k_e = n^2$, where k_e is the electronic polarization and n is the refractive index.

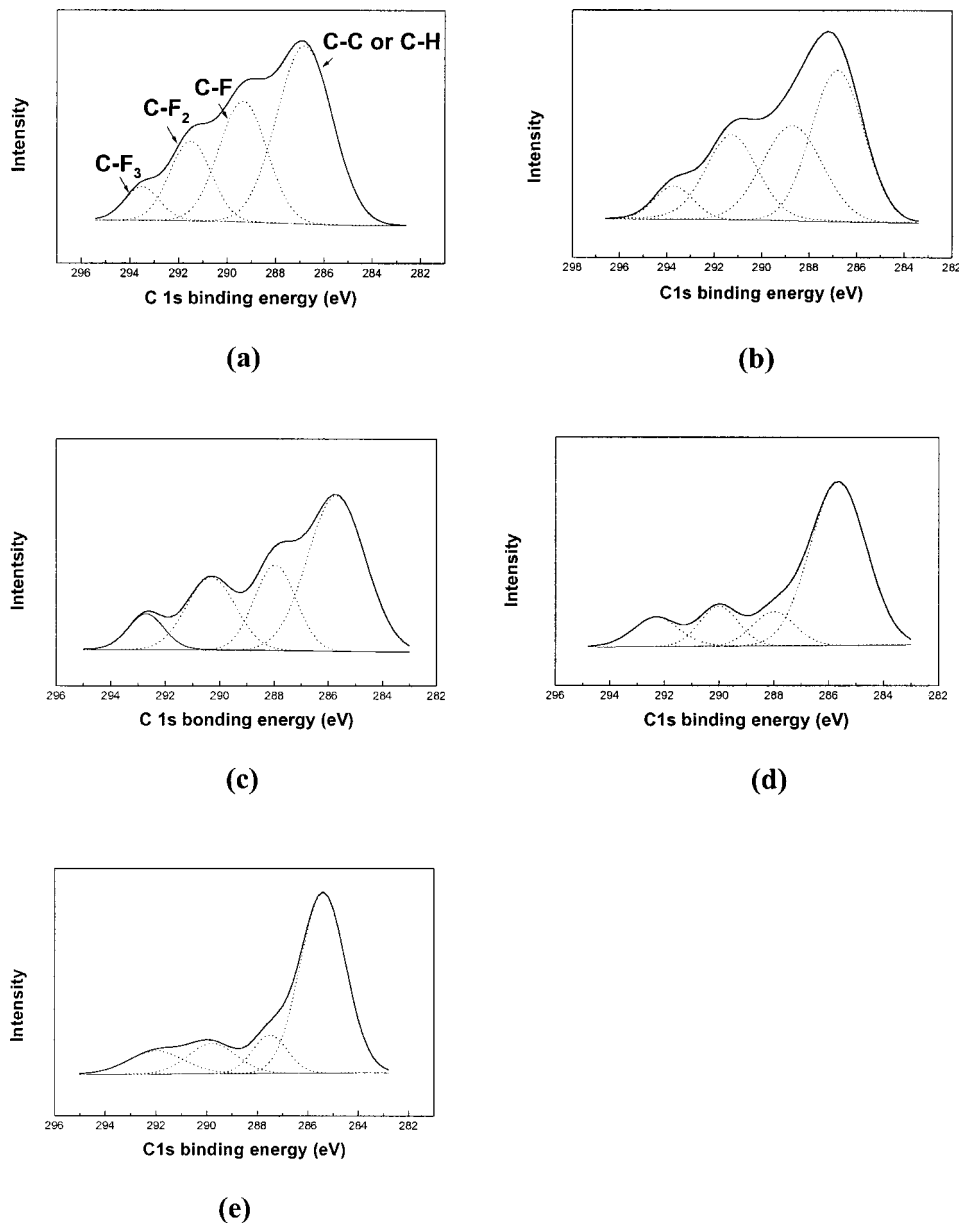


Figure 4. Deconvolution of C 1s binding energy peaks of a-C:F sample 1 annealed at various temperature. (a) 25, (b) 100, (c) 200, (d) 300, (e) 400°C.

However, in sample A, the content of the thermally stable bonding, C-F₂ and C-F₃, is small and that of the unstable bonding, C-F is large. As shown in the Fig. 2 and 5, the dielectric constant increases due to the decrease of the C-F bonding during the annealing process. In sample B, with low dielectric constant as-deposited, the dielectric constant is about 2.85 even at 400°C. The dielectric constant does not increase further since the content of the unstable C-F bonding configuration is smaller than in sample B, and the thermally stable C-F₂ and C-F₃ bonding configurations are virtually constant. Thus, the dielectric constant of sample B does not increase above 2.85. Finally, the increase in dielectric constant of a-C:F films with annealing is due largely to evolution of the thermally unstable C-F bonding.

From the above results, we obtain a few conclusions for the thermal stability of the bonding configuration. First, the loss of C-C bonds are lower than that of C-F_x bond species during annealing process, because the F atom is unstably bonded with the C atom. Second, the C-F₂ and C-F₃ bonds are more stable than C-F bonds in C-F_x bonding configurations.

Thermal structure evolution model.—The structure of the film can be inferred from the variations of bonding configuration and area density with the annealing temperature. As the annealing temperature increases, the C-C bond content abruptly increases while the C-F bond content abruptly decreases. On the other hand, the C-F₂ and C-F₃ bond contents are virtually constant, as shown in Fig. 5 and 7. The increase in the C-C bond content during annealing implies that the film becomes more crosslinked, and the decrease in the C-F bond content implies that the C-F bonds supply the site required for crosslinking the structure. Thus, the C-F bond is broken by thermal release of F, and the broken bonds allow the neighboring carbon atoms to crosslink. The C-F₂ bond concentration is almost constant with increasing annealing temperature, while the C-F₃ bond concentration decreases slightly in the 25-200°C range and then increases slightly in the 200-400°C range. The slight decrease in the 25-200°C range is due to the decrease of the edging group through crosslinking, the C-F₃ bonding concentration slightly increases in the 200-400°C range since the relative content in the film increases due to the decrease of the C-F bonding concentration. Figure 8

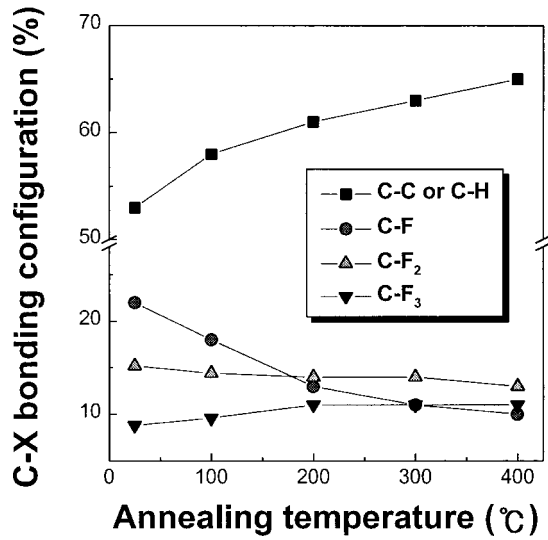


Figure 5. Evolution of bonding configuration in a-C:F thin films deposited at 25°C and 400 W, and CF₄:CH₄ = 1:1 with increasing annealing temperature.

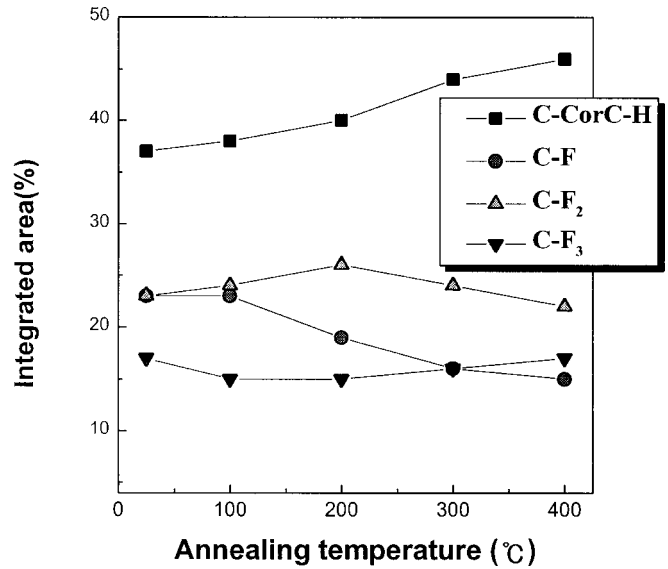


Figure 7. Evolution of bonding configuration in a-C:F thin films deposited at 25°C and 400 W, CF₄:CH₄ = 10:1, with increasing annealing temperature.

shows the variation of the area densities of sample 1 and sample 2 with increasing annealing temperature. The area density is obtained from ERD-TOF and film thickness. As discussed before, the area density increases with increasing annealing temperature since the structure is crosslinked, in accordance with the result of the evolu-

tion of the bonding configuration. Figure 9 is a schematic model for the structure evolution of a-C:F thin films during the annealing process based on the above discussion.

The optimal condition of a-C:F thin films to satisfy the low dielectric constant and thermal stability.—According to the theory of the dielectric constant reduction mechanism in our previous study,¹⁴ the conditions to obtain low dielectric constant in a-C:F films are (i) high content of F; (ii) the C-F_x bonding configuration has to exist in a form of C-F₂ and C-F₃ instead of C-F; (iii) the structure should not be crosslinked.

The results of this study on thermal stability are as follows; (i) F atoms are less stable than C atoms during annealing, so the film has to have a low F content; (ii) in the C-F_x bonding configurations, the C-F₂ and C-F₃ bondings are more stable than C-F bonding during annealing; (iii) the crosslinked structure is stable during annealing.

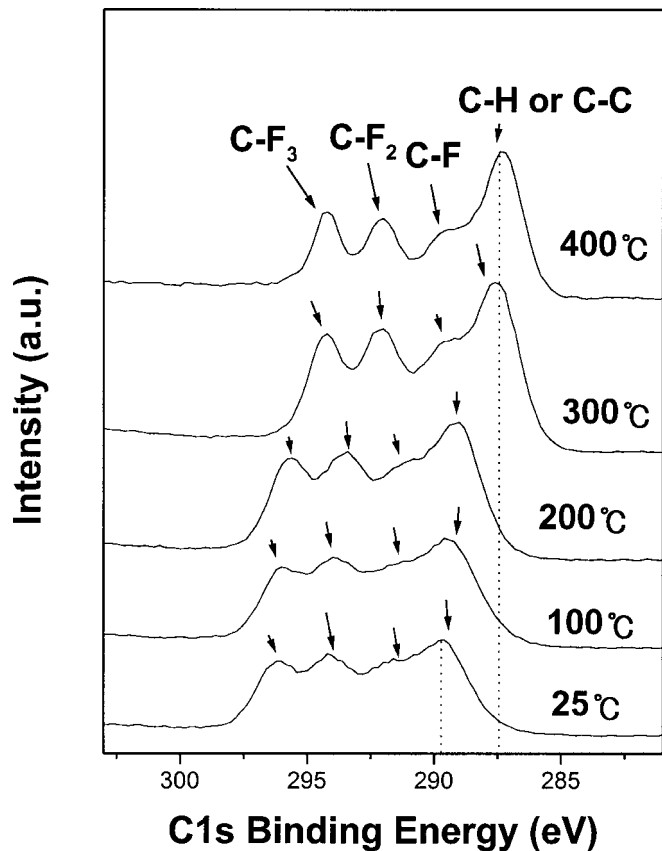


Figure 6. C 1s binding energy XPS spectra of a-C:F thin films deposited at 25°C and 400 W, and CF₄:CH₄ = 10:1 with increasing annealing temperature.

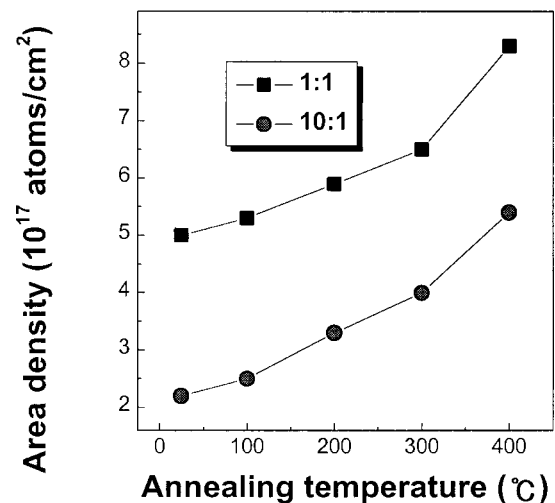


Figure 8. Variation of the area densities of (a) sample 1 (CF₄:CH₄ = 1:1) and (b) sample 2 (CF₄:CH₄ = 10:1) with increasing annealing temperature.

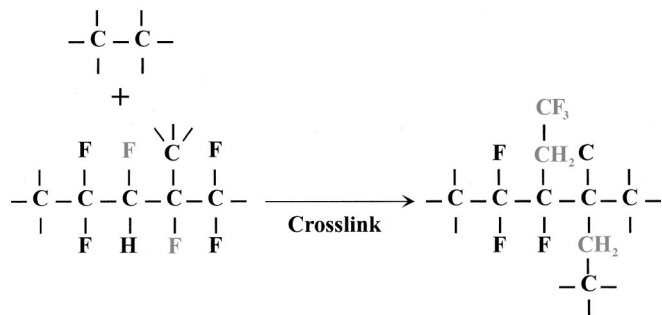


Figure 9. Model for the structure evolution of a-C:F thin films with increasing annealing temperature.

From the above results, we present the optimal conditions to obtain a-C:F films with the low dielectric constant and good thermal stability. (i) The film has to have a compatible F content to make a compromise between low dielectric constant and good thermal stability. (ii) The C-F_x bonding configurations have to exist in the form of C-F₂ and C-F₃ instead of C-F. (iii) The film should have a somewhat crosslinked structure.

Conclusion

Fluorinated amorphous carbon (a-C:F) thin films deposited by ICP-CVD were annealed with increasing temperature (100, 200, 300, and 400°C). As the annealing temperature increases, the refractive indexes and the dielectric constants of the films increase due to reduction of the F content. In the C-F_x bonding configurations, the C-F bondings decrease and the C-F₂ and C-F₃ bondings are virtually

constant with increasing annealing temperature. Thus, the C-F₂ and C-F₃ bondings are thermally more stable than the C-F bonding. This means that the dielectric constant decreases mainly due to reduction of electronic polarization since the ionic and dipole polarizations are not varied significantly. The structure of the film is crosslinked with increasing annealing temperature, with sacrifice of the C-F bonding providing sites for crosslinking.

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