Low-k Fluorinated Amorphous Carbon Films Prepared by Inductively Coupled Plasma Chemical Vapor Deposition using CF₄/CH₄ mixture gases

Chi Kyu Choi, Doo Chul Kim

Department of Physics, Cheju National University, Cheju 690-756, Korea

Abstract

Fluorinated amorphous carbon thin films were deposited on a p-type Si(100) substrate using carbon tetrafluoride (CF_4) and methane (CH_4) mixture gases by an inductively coupled plasma chemical vapor deposition. Fourier transform infrared and X-ray photoelectron spectroscopy spectra show that the film has C-F, $C-F_2$, $C-F_3$, $C-CF_x$ and C-C bonds. The dielectric constant may be decreased greatly due to the C-F bond in the film. It is found that the $C-F_x$ bonding configuration changes from a C-F bond to $C-CF_x$ and $C-F_3$ bonds as a function of the CF_4/CH_4 flow rate ratio. Therefore, the reduction of the dielectric constant can be obtained by the variation of $C-CF_x$ bonding configuration as well as the incorporation of fluorine. The relative dielectric constant, leakage current density, and dielectric breakdown field of as-deposited film with the flow rate ratio of CF_4/CH_4 as 7 at 200 mTorr working pressure and 800 W rf power are about 2.4, 7×10^{-12} A/cm^2 and above 15 MV/cm, respectively.

INTRODUCTION

Miniaturization of electronic circuits with an increased complexity and multilevel metal layers demand intermetal dielectric (IMD) materials with low dielectric constant. Present silicon dioxide (SiO_2) films as IMD layers will result in high parasitic capacitance and crosstalk interference in high density devices [1]. Low dielectric materials such as fluorinated silicon oxide (SiOF) and fluoropolymer IMD layers have been tried to solve this problem. In the case of SiOF film, as the fluorine concentration is increased, the dielectric constant of the film decreases but the film becomes unstable and water absorbability increases [2-4]. A dielectric constant above 3.0 is obtained in these films. Fluoropolymers such as polytetrafluoroethylene (PTFE) are known as low dielectric constant (~2.0) materials; however, their poor thermal stability and low adhesive force have hindered their use as IMD materials [5].

Fluorocarbon/SiO$_2$ composite film has been deposited using hexamethyl disiloxane (HMDSO) and C$_6$F$_6$ mixture in the inductively coupled plasma(ICP) reactor [6, 7], and a dielectric constant above 2.5 has been obtained from these films. Fluorinated amorphous carbon(a-C:F) films have been deposited using plasma enhanced chemical vapor deposition (PECVD) [8] and helicon wave plasma CVD [9]. It has been reported that the dielectric constant of a-C:F films can be changed from 2.1 to 2.8 by controlling the fluorine concentration [8-10].

Recently, a-C:F thin films deposited using high density plasma chemical vapor deposition (HDPCVD) have been investigated as a new IMD material. However, the origin of a low dielectric constant, atomic structure, and the role of fluorine in the films are yet uncertain.

In this study, we prepared a-C:F thin films which have cross-linking structures and good thermal stability as low dielectric constant IMDs for ultralarge scale integration (ULSI) multilevel interconnections. The a-C:F were deposited on a Silicon substrate by inductively coupled plasma chemical vapor deposition (ICPCVD) using gas mixtures of CF$_4$ and CH$_4$ with various deposition conditions. We investigated the effects of fluorine content, a bonding configuration, the dielectric constants, and the characteristics of thin films required for devices processes.

EXPERIMENTS

The a-C:F thin films were deposited using the ICPCVD system. ICP is generated by the four turn coil which is set around a quartz tube. A 13.56 MHz-rf power is supplied continuously from an oscillator-amplifier system and is varied up to 1 kW. The base pressure of ~ 10^{-6} Torr is reached before each deposition. CF$_4$ gas is introduced into the reaction chamber as the source gas for fluorine, and CH$_4$ gas is used as a carbon source gas. The CH$_4$ gas flow rate is constant at 5 sccm and the CF$_4$ flow rate is varied from 25 to 35 sccm. The discharge pressure is measured by a Baratron gauge.

The films were deposited on the six inch Si substrate. The wafers were in a floating potential and were not intentionally heated. The deposition parameters were the flow rate of CF$_4$ and CH$_4$, the rf power, and the working pressure. Film properties such as the refractive index and chemical bonding structure were investigated. Fourier transform infrared(FTIR) spectroscopy, performed in absorbance mode with a model DA8 Bomem spectrometer, was used to determine bonding configurations with the related C-F and C-C bonds in the films. The thickness and refractive index of the deposited a-C:F films were measured by using an ellipsometer. Electrical properties such as the dielectric constant, leakage current, and breakdown voltage (at 1 MHz) were also investigated using MIS(Al/a-C:F film/p-Si) structures. Chemical bonding structure was characterized using X-ray photoelectron spectroscopy(XPS).

RESULTS AND DISCUSSION

Figure 1 shows the FTIR absorption spectra for four a-C:F samples prepared with different CF$_4$/CH$_4$ flow rate ratios at 200 mTorr working pressure and 800 W rf power. The curves are displayed with different scales for comparison and the height has no real meaning. The spectra are

generally broad and overlapped due to the complex stoichiometry and the amorphous nature of the film. The intense peak at 1,108 cm-1, called the transverse optical (TO) mode, is attributed to the asymmetric stretching of the fluorine atoms along the parallel direction to C-F [1]. The position of the C-F asymmetric stretching mode at about 1,108 cm^{-1} is almost unchanged. The band at 970 cm-1 is due to the symmetric C-F₃ stretching. The band at 1399 cm^{-1} is due to the C-CF$_x$ bond and the band at 1,450cm^{-1} is due to the C-C bond [12-13]. From these results, we know that C-C, C-F, C-F₃, and C-CF$_x$ bonds exist in the deposited a-C:F film. This FTIR spectra was taken a month after the

films were deposited. We obtained the same spectra right after the films are prepared as shown in Fig. 1. The FTIR spectra of samples annealed at 500 ℃ 20 min are unchanged in the bonding structures. This means that the films do not absorb any moisture in the air and the Si-OH (3650 cm^{-1}) and H-O-H(3230 cm^{-1}, 3440 cm^{-1}) bonds are formed during the deposition process because the H radicals exist in the plasma. However, only small amount of H atoms remains in the film because the H atoms are detachable easily from the surface by ion bombardment which occurs very frequently in the high density plasma [15].
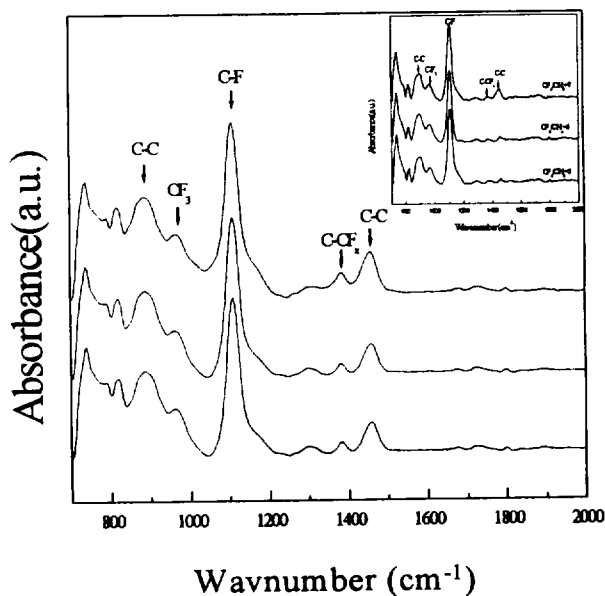

Figure 1. FTIR spectra of the a-C:F films prepared with different CF₄/CH₄ flow rate ratio. The discharge conditions are 200 mTorr working pressure and 800 W rf power.

Atomic concentrations of an a-C:F film deposited at CF₄/CH₄= 7 are investigated by XPS depth profile. The film is uniform in composition and has a smooth interface. There is no oxygen

atom pileup at the a-C:F/Si interface because the carbon and fluorine atoms react directly with the silicon on the surface of the Si substate. The atomic concentrations of the carbon and fluorine

atom are nearly the same. The chemical stoichiometric formula of the film is $C_{0.52}F_{0.48}$ but the film annealed at 500 ℃ for 20 min is $C_{0.54}$ $F_{0.46}$. Many authors have reported that the strength of the $C-F_3$ and $C-F_2$ bonding configurations against thermal annealing are weaker than that of the C-F configuration in the film [16, 17]. Therefore, the decrease of the fluorine concentration due to thermal annealing leads to the increase of C-C crosslinking. The chemical stoichiometric change from $C_{0.52}$ $F_{0.48}$ to $C_{0.54}$ $F_{0.46}$ after annealing signifies that a few fluorine atoms in the $C-F_3$ and $C-F_2$ bonding configurations are diffused out from the bulk to the outside by thermal annealing.

To confirm the existence of C-F bonds in the film, the XPS narrow scan spectrum of the C 1s peak is deconvoluted by fitting the data with a number of Gaussian peaks. The C 1s spectrum is interpreted based on the chemical shift assignments made by using previous results[18].

The deconvoluted XPS C 1s electron orbital spectrum of as-deposited and annealed films with the flow rate ratio of CF_4/CH_4 as 5 and 7 at 200 mTorr working pressure and 800 W rf power are shown in Fig. 2. It is observed that six different components of carbon produce peaks such as C-C(282.5 eV), $C-CF_x$(284.6eV, $x \leq$ 3), C-F(286.7 eV), $C-F_2$(288.6 eV), C-H(280 eV), and $C-F_3$(290.5 eV) bonds[9, 13, 1]). As shown in the figure, the bonding structures changed with the CF_4/CH_4 gas flow rate ratio. The relative peak area of the C-C component decreased from 34.2% to 24.2% and that of the C-H component decreased from 9.8% to 6.2% with the increase of the CF_4/CH_4 gas flow rate ratio. On the other hand, the relative peak areas of the $C-CF_x$, C-F, $C-F_2$, and $C-F_3$ components increased. In the annealed samples, C-C, $C-CF_x$, C-F, $C-F_2$, and $C-F_3$ bonds of the film decreased slightly. This means that many $C-CF_x$ bond branchs attached at skeleton chains are broken and the CF_x at the end of main chain is reformed to CF_2 or CF_3.
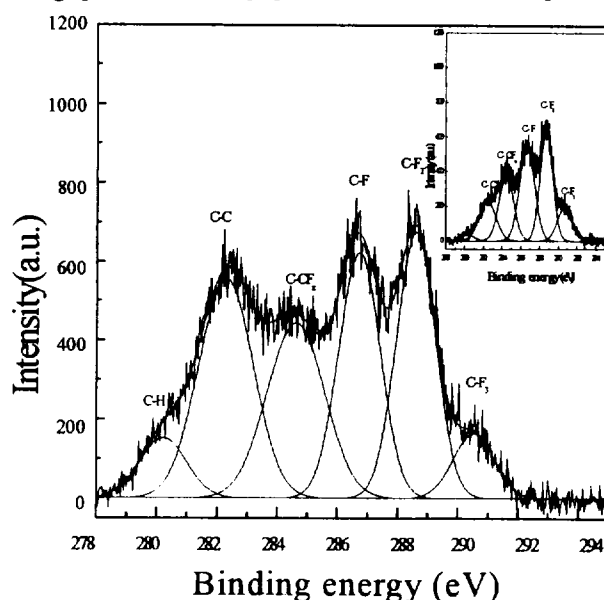

Figure 2. C 1s electron orbital spectrum of the same sample with CF_4/CH_4 = 7 flow rate ratio at 200 mTorr working pressure and 800 W rf power.

From the above results, we suggest that the greater incorporation of fluorine with carbon is associated with higher binding energy, since more energy is required to take out the electron of the core level due to high electronegativity of fluorine[R14]. Therefore, the higher binding energy peak in the XPS spectrum can be assigned to more fluorine-incorporated bonding configurations

as seen in Fig. 2. We know that C-F and $C-F_2$ bonding contents become more dominant with the increased CF_4 flow rate, and these bonds can be formed during the deposition process. It can be explained by the existence of the $C-CF_x$, $C-F_2$, C-H, and $C-F_3$ bonds which implies that the film has a less crosslinked structure [18].
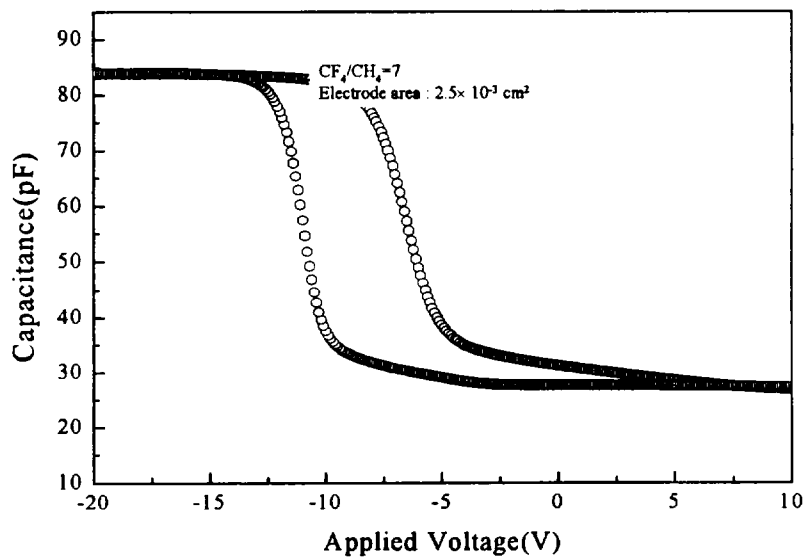

Figure 3. C-V characteristics of the a-C:F films. CF_4/CH_4 flow rate ratio is 7 and the discharge conditions are 200 mTorr working pressure and 800 W rf power.

Figure 3 shows the C-V plot of MIS capacitor formed at flow rate ratio of CF_4/CH_4 =7 and the thickness of the a-C:F film and the area of Al electrode are 650 Å and 2.5×10^{-3} cm², respectively. The calculated dielectric constant of

the film deposited at room temperature (RT) is about 2.4. This value is smaller than those of other SiOF films(~3.1) [4] but larger than that of fluorinated amorphous carbon film (~2.3) deposited by helicon wave plasma CVD [9].
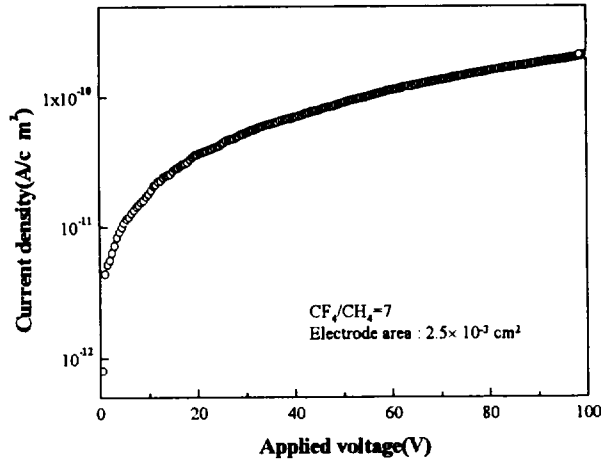
Figure 4. I-V characteristics of the same sample as in Fig. 3.

Figure 4 shows the current density as a function of the applied voltage for the same sample in Fig. 3. The applied voltage to the Al electrode is varied from 0 to 100V. The breakdown is not observed under 100 V and the current density is increased slightly as the applied voltage increased. The current density is saturated with the increase of applied voltage. The dielectric breakdown field is 15 MV/m. The leakage current density is 7×10^{-12} A/cm^2 at an applied voltage of 3 V. These values are less than the SiOF films formed by PECVD and fluorocarbonated-SiOF films formed by O$_2$ and fluorotriethoxysilane(FTES, FSi[OC$_2$H$_5$]$_3$)-helicon plasma CVD [6]. From these results, we assume that the a-C:F film is more stable and more dense than those of our previous results [4, 6, 11].
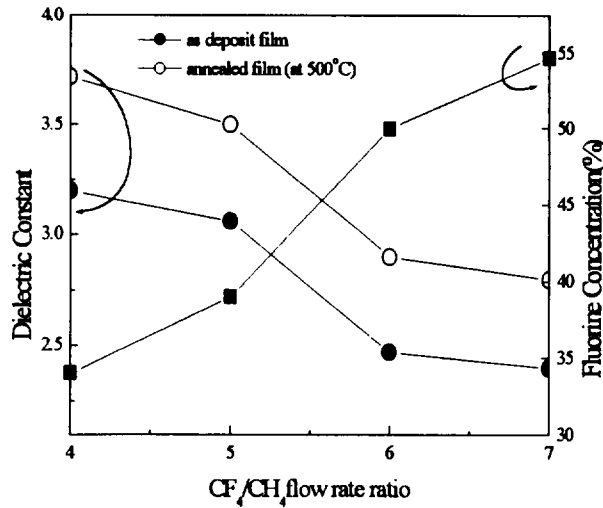

Figure 5. F concentration and the dielectric constant of the a-C:F films as a function of the CF$_4$/CH$_4$ flow rate ratio and after in situ annealing at 500℃ for 20 min.

Figure 5 shows the fluorine concentration and dielectric constant of the film as a function of the CF_4/CH_4 flow rate ratio. The fluorine concentration is increased and the dielectric constant is decreased with the increase of CF_4/CH_4 flow rate ratio. The dielectric constant and the fluorine concentration are obtained at about 2.4 and 55% at the flow rate ratio of $CF_4/CH_4=7$, respectively. This could be attributed to fluorination in the films. This observation corresponds well with previous results which also showed a dependence of the dielectric constant on the fluorine content[10]. The permanent dipole moments of the C-H, C-F and C-F_2 bonds are 15, 0.6, and 0.5, respectively[20]. Both the XPS and FTIR analyses indicate that an increase is observed in the concentrations of the C-F_2 and the C-F_3 components at a higher CF_4/CH_4 gas flow ratio. It is thus concluded that the dielectric constant of the a-C:F films decreases with an increase in C-F_2 and C-F_3 bonding. Therefore, the reduced dielectric constant can be attributed to the enhanced fluorination of the films due to the higher CF_4/CH_4 gas flow ratio.
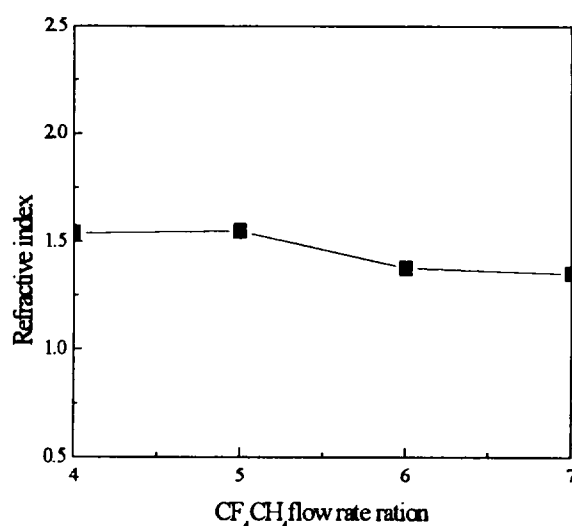

Figure 6. Refractive index of the films as a function of the CF_4/CH_4 flow rate ratio.

The dielectric constant of the annealed films with various CF_4/CH_4 flow rate ratio at 500°C for 20 min in Ar ambient are shown in Fig. 5. The dielectric constant of the film with $CF_4/CH_4=7$ flow rate ratio is 2.8. This value is larger than that of as-deposited film. It is an indication that F atoms in the film diffuse out by thermal annealing. From these results, we assume that the bonding configuration between carbon and fluorine atoms, as opposed to the total fluorine concentration, is an important factor that determines the value of the dielectric constant.

The evolution of the refractive index is shown as a function of the CCF_4/CH_4 flow rate ratio in Fig. 6. In this figure, when the flow rate ratio of the CF_4/CH_4 mixture gas increased, the refractive index of the films decreased. The refractive index of the a-C:F film is deposited at the flow rate ratio of CF_4/CH_4 as 7 is about 1.32. This value is

lower than that of the SiO$_2$ film ($\sim$ 1.45) [21]. This result suggests that the refractive index depends upon the F concentration in the film. A film of low refractive index has low dielectric constant. We know that the dielectric constant(k) can be represented by the square of the refractive index(n), k\propto n^2.

CONCLUSIONS

The a-C:F composite film is deposited without intentional heating or biasing, using CF$_4$/CH$_4$ gas mixture in the ICPCVD system. The film has C-F bonds in addition to C-CF$_x$, C-F$_2$, C-H, C-F$_3$, and C-C bonds because the F and C radicals dissociated from the CF$_4$ gas can easily react and attend the film formation. The dielectric constant of the film deposited at flow rate ratio of CF$_4$/CH$_4$ =7 was 2.4, but that of the sample annealed at 500°C was 2.8. As the CF$_4$/CH$_4$ flow rate ratio increased, the dielectric constant decreased. The concentration of fluorine atoms may be the limiting factor in determining the dielectric constant. The leakage current density is 7 $\times$ 10^{-12} A/cm^2 and the dielectric breakdown voltage was not observed below 100 V. By the analysis with FTIR spectroscopy, no moisture is absorbed in the films. These facts imply that the film has good crosslinked structure due to high ion flux with low ion energy in the ICP.

From these results, we know that the a-C:F films formed by CF$_4$/CH$_4$ ICP-CVD have attractive advantages for the application of an intermetal dielectric layer on the high density devices.

REFERENCES

1. T. Homma, Y. Kutsuzawa, K. Kunimune, and Y. Murao, Thin Solid Films 235, 80 (1993).

2. S. Mizuno, A. Verma, H. Tran, P. Lee, and B. Nguyen, Thin Solid Films 283, 30 (1996).

3. S. Takeishi, H. Kudoh, R. Shinohara, A. Tsukune, Y. Satoh, H. Miyazawa, H. Harada, and M. Yamada, J. Electrochem. Soc. 143, 381 (1996).

4. J. H. Kim, S. H. Seo, S. M. Yun, H. Y. Chang, K. M. Lee, and C. K. Choi, Appl. Phys. Lett. 68, 1507 (1996)

5. M. Horie, J. Vac. Sci. Technol. A13, 2490 (1995).

6. K. S. Oh, M. S. Kang, K. M. Lee, D. S. Kim, C. K. Choi, S. M. Yun, H. Y. Chang, and K. H. Kim, Thin Solid Films 345, 45 (1999).

7. D. Kim, Y. Lee, and N. Park, Appl. Phys. Lett. 69, 2776 (1996).

8. H. Yang, D. J. Tweet, Y. Ma, and T. Nguyen, Appl. Phys. Lett. 73, 1514 (1998).

9. Endo and T. Tatsumi, Appl. Phys. Lett. 68, 2864 (1996).

10. K. Endo and T. Tatsumi, Appl. Phys. Lett. 68, 2864 (1996).

11. S. M. Yun, H. Y. Chang, K. M. Lee, D. C. Kim, and C. K. Choi, J. Electrochem. Soc. 145, 2578 (1998).

12. L. J. Bellamy, The Infra-Red Spectra of ComplexMolecules, (Chapman and Hall Ltd., third edition, 1975), p.9 and p.372.

13. I. Banerjee, M. Harker, L. Wong, P. A. Coon, and K. K. Gleason, J. Electrochem. Soc. 146(6),

2219(1999).

14. S. S. Han, H. R. Kim, and B. S. Bae, J. Electrochem. Soc. **416**, 3383(1999).

15. K. Seaward, J. Turner, K. Nauka, and A. Nel, J. Vac. Sci. Technol. **13**, 118(1995).

16. H. Yokomichi, T. Hayashi, and A. Masuda, Appl. Phys. Lett. **72**, 2704(1998).

17. H. Yokomichi, T. Okina, and T. Hayashi, *Surface Modification Technologies X*, edited by T. S. Sudarshan, K. A. Khor, and W. Reitz(The Institute of Materials, London, 1997), p.946.

18. S. Takeishi, H. Kudo, R. Shinohara, M. Hashino, S. Fukuyama, J. Yamakuchi, and M. Yamada, J. Electrochem. Soc. **143**, 1797(1997).

19. H. H. Park, K. H. Kwon, J. L. Lee, K. S. Suh, O. J. Kwon, K. I. Cho, and S. C. Park, J. Appl. Phys. **76(8)**, 4595 (1994).

20. D. R. Lide ed., CRC Handbook of Chemistry and Physics 77th Ed.(CRC Press, Boca Raton), 9-5(1996).

21. G. Lucousky, M. J. Manitini, J. K. Srivatava, and E. A. Irene, J. Vac. Technol. **135**, 530(1987).