JOURNALOF

Ceramic Processing Research

Effect of CF₄ plasma treatment on fluorinated amorphous carbon films with a low dielectric constant

Ho Jeong Ko^a, Heon Ju Lee^a, Kwang-Man Lee^b and Chi Kyu Choi*

Department of Physics, Cheju National University, Jeju 690-756, Korea ^aDepartment of Energy and Production Engineering, Cheju National University, Jeju 690-756, Korea ^bFaculty of Electronics Engineering, Cheju National University, Jeju 690-756, Korea

The a-C:F films were deposited on a *p*-type Si(100) substrate using an inductively coupled plasma chemical vapor deposition (ICPCVD) system with a mixture of CF₄ and CH₄ gases. A CF₄ plasma treatment with various treatment times was carried out *in situ* for an as-deposited a-C:F film. The CF₄ plasma treatment changed the bonding configuration of the a-C:F film from the fluorine-rich functional groups of C-F_x bonds to the carbon-rich functional groups of -CF-C-CF_x bonds when the plasma treatment time was up to 30 s. However when the plasma treatment time was increased, the bonding structure induced a rearrangement of the chemical bonds forming carbon-rich functional groups in which C-F, C-F₂ and C-F₃ bonds decreased and the peak intensity of the C-C bond increased. The lowest dielectric constant of the a-C:F film was about 2.3 for 30 s plasma treatment time and the electronic susceptibility and the surface charge per electric field were found to be 1.09×10^{-11} C/V·m and 0.99×10^{-18} C·m/V, respectively.

Key words: a-C:F, ICPCVD, CF₄ plasma treatment, dielectric constant.

Introduction

Use of the present silicon dioxide (SiO₂) films as inter-metal dielectric (IMD) layers will result in high parasitic capacitance and crosstalk interference in high density devices [1]. To decrease the resistance of interconnecting metal and capacitance of the IMD layers, many researchers are studying the copper/low-k based interconnect technology. There are a number of requirements for the new low dielectric constant (low-k) materials [2-4], such as low dielectric constant, high thermal stability, good electrical insulation, high mechanical strength and good adhesion to neighboring layers. Among the low dielectric materials, fluorinated amorphous carbon (a-C:F) and parylene polymer films are very promising candidates for an IMD layer, because these materials have low-k, good mechanical properties and cross-linked polytetrafluoroethylene (PTFE)-like structures [4-6]. In general, a-C:F films were deposited from fluorocarbon source gases, such as CF_4 , C_2F_6 or C_3F_8 by PECVD, which consist of the functional groups of $C-CF_x$ bonds. The films have an amorphous C-Ccross-linked structure and have the related C-F_x bonds like those of PTFE, which are different from the homogeneous $(CF_2)_x$ bond structure with a low hydrogen concentration. The bonding structure and the dielectric constant of the a-C:F film are unstable during high thermal processes, which the desorption of unbonded fluorine and the partial removal of hydrogen bonded carbon are the main effects due to thermal annealing in the a-C:F film. This mechanism is promoted by a crosslinked film structure of fluorine bonded to carbon, primarily consisting of CF groups [7]. Therefore, the decrease of the fluorine concentration in the a-C:F film increased the dielectric constant, and the a-C:F film becomes hydrophobic which causes low adhesion to interconnecting electrode materials [8, 9]. Thus a postplasma treatment may be applied in order to activate the a-C:F film surface and the formation of a-C:F film with the homogeneous $(CF_2)_x$ bond structure and enhance adhesion [6, 7, 10]. The composition and the bonding structure of the a-C:F film can be controlled by the plasma treatment with various gases. By low pressure plasma treatment, the reactive species and photons interact with the polymer surface. This interaction depends on the plasma condition and the nature of the polymer, and can result in a crosslinked structure [11].

In this study, a-C:F films were deposited on a p-type Si(100) substrate using an ICPCVD system with a mixture of CF_4 and CH_4 gases. CF_4 plasma treatments with various treatment times was carried out *in situ* on the as-deposited a-C:F film. We investigated the change of characteristics in a-C:F films with CF_4 plasma treatment. The electrical properties of the films were investigated and the refractive index and the dielectric constant were evaluated.

^{*}Corresponding author:

Tel:+82-64-754-3512

Fax: +82-64-756-3506

E-mail: cckyu@cheju.ac.kr

Effect of CF_4 plasma treatment on fluorinated amorphous carbon films with a low dielectric constant

Experiment

The a-C:F thin films were deposited on a silicon substrate using a mixture of CF₄ and CH₄ gases in a radio-frequency ICPCVD system when the rf power was 800 W. CF₄ gas was introduced into the reaction chamber as the source gas for fluorine and CH₄ gas was used as a carbon source gas, and the flow rate ratio $R(\%) = [CF_4/(CH_4+CF_4)] \times 100$ was 75% and the total flow rate was kept at 60 sccm. The samples were annealed at 400 °C for 30 minutes in a vacuum. The CF₄ and CH₄ gases were introduced into the reaction chamber, and the discharge pressure was controlled with a Baratron gauge and kept at about ~200 mTorr. To investigate the surface treatment effect of a-C:F films by the CF₄ plasma, we carried out in-situ CF₄ plasma treatments with various plasma treatment times (from 10 to 50 s) after deposition. During the plasma treatment, 40 sccm of CF₄ gas was introduced into the reaction chamber, in which the discharge pressure was kept at about 170 mTorr. Fourier transform infrared (FTIR) spectroscopy, performed in the absorbance mode with a spectrometer (Bruker IFS-66/S), was used to determine the bonding configurations for the related C-F and C-C bonds in the films. The chemical bonding structure was characterized by using X-ray photoelectron spectroscopy (XPS, VG ESCALAB 210). The thickness and the refractive index of the a-C:F films were measured using an ellipsometer (Gaertner L116C). Electrical properties, such as the dielectric constant (at 1 MHz) and the breakdown voltage were also investigated using MIS (Al/a-C:F/p-Si) structures, in which evaporated aluminum was used as the top electrode, and were immediately measured in a vacuum to eliminate the influence of moisture.

Results and Discussion

Figure 1 shows the FTIR spectra of the a-C:F films with various plasma treatment times, when the asdeposited sample was formed with a flow rate ratio R(%) of 75% and were annealed at 400 °C for 30 minutes in a vacuum. The spectra are generally broad and overlapped due to the complex stoichiometry and the amorphous nature of the films. The intense peak at about 1200 cm⁻¹ is attributed to the stretching mode related to $C-F_x$ bonds. The spectra in the range of 900 to 1500 cm⁻¹ were from overlapped C-F, C-F₂ and C-F₃ bonds. The five fitted peaks in the C-F_x bond were assigned to the C-F₃ stretching mode at 990 cm⁻¹, the C-F stretching mode at 1070 cm⁻¹ and 1330 cm⁻¹, the C-F₂ symmetric and asymmetric stretching mode at 1150 cm⁻¹ and 1240 cm⁻¹, respectively. The bonding structure remains the same in all samples (see the dotted lines in Fig. 1). The peak position of the $C-F_2$ symmetric and asymmetric stretching mode shifted to higher wavenumbers (blue shift) and the peak position



Fig. 1. FTIR spectra of the a-C:F films as a function of CF_4 plasma treatment time, when the as-deposited sample is formed with $R(\%)=[CF_4/(CH_4+CF_4)]\times100$ flow rate ratio of 75%.



Fig. 2. C 1s electron orbital XPS narrow spectra of the a-C:F films with various CF_4 plasma treatment times of as-deposited, 30 and 50 s.

of C-F and C-F₃ remained unchanged with plasma treatment time. The broad peaks in the range from 1600 to 1800 cm⁻¹ are associated with C=C, F₂C=C and F₂C=CF unsaturated double bonds. The C=C (olefinic) stretching mode is normally observed at 1600 cm⁻¹ in organic compounds when C atoms are back bonded to H atoms, but the peak is typically shifted to higher frequencies when the H atoms are replaced by F atoms [12]. The bonding structure of the plasma treated samples was similar to untreated samples. The peak intensity of the C-F₂ symmetric stretching and the C-F₃ stretching mode at 1150 and 980 cm⁻¹ increased slightly with plasma treatment time. The peak position of C- F_2 symmetric stretching mode shifted to higher wavenumbers (blue shift) as the plasma treatment time increased, while the peak position of the C- F_2 symmetric stretching mode with a plasma treatment of 50 s was shifted by 6 cm⁻¹ compared to that of the asdeposited sample.

The XPS narrow scans of the C1s peaks were deconvoluted by fitting the data with a number of Gaussian peaks. The deconvoluted XPS C1s spectra of the asdeposited sample and samples with CF₄ plasma treatment times of 30 and 50 s are shown in Fig. 2. It is observed that four different chemical components of carbon produce peaks such as C-C, C-F, C-F₂ and C-F₃ peaks. The binding energy of the C-C bond at 285.0 eV was unchanged as a function of plasma treatment time,



Fig. 3. The relative contents areas of $(CF_2+CF_3)/CF_x$ (x=1, 2 and 3), CF_2/CF_x and $(C-C)/CF_x$ for a-C:F films as a function of CF_4 plasma treatment times for the results fitted from Fig. 2.

but the binding energy of the C-F₂ and C-F₃ bonds shifted to a high binding energy (blue shift) up to 30 s CF₄ plasma treatment time and the the C-F₂ and C-F₃ bonds shifted about 0.8 and 1.1 eV to a lower binding energy, respectively. From the above results, we can infer that a greater incorporation of fluorine with carbon is associated with a higher binding energy, due to the high electronegativity of fluorine [13].

Figure 3 shows the relative content area of each bonding mode quantitatively from the deconvolution of the C 1s narrow scan XPS spectra. The ratio of the $(CF_2+CF_3)/CF_x$ bonding mode increased by about 73.2 % by plasma treatment for 10 s and then it shows a slight increase of about 85.1% to 30 s. The ratio of CF_2/CF_x increased 59.3% by a 30 s treatment and then it decreased by about 32.7% after 50 s. The ratio of the CF/CF_x and $(C-C)/CF_x$ bonding modes decreased by about 25.4% and 41.2% up to 30 s and then it increased about 19.3% and 62.6% after 50 s treatment time. These results mean that the fluorine-rich functional groups such as CF₂ and CF₃ increased up to 30 s as a function of CF_4 plasma treatment time, but the CF_2 mode of the a-C:F film decreases after 30 s treatment time. From these results, when the plasma treatment time is up to 30 s, the a-C:F film consists of fluorine rich $-C-F_x$ functional groups such as $-CF_2$, CF_2 -CF- and -CF₂-CF₂- bonds. But when the plasma treatment time is increased, C-F, C-F₂ and C-F₃ bonds decreased and the C-C bond peak increased. These results indicate that the number of C-F2 bonds increase gradually more than that of C-F and C-F₃ bonds as the plasma treatment time increases. This means that the bonding structure of the a-C:F film is changed to a homogeneous (C- F_2 _x due to the surface fluorination by the plasma treatment and is likely to form a cross linked structure



Fig. 4. Cross-sectional FESEM micrographs of the a-C:F films with various CF₄ plasma treatment times.

[9, 14]. Therefore, we can infer that the cross linked structure in the film was enhanced and the bonding structure changed from C-F bonds to fluorine-rich C-F_x bonds attached to skeleton chains, and the film surface became hydrophobic by the C-F_x bonds from the result

of Wei et al. [15]. Figure 4 are a cross-sectional FESEM micrographs of a-C:F films with various CF_4 plasma treatment times. The thickness of the as-deposited sample is about 153.7 nm, and the thickness of the CF_4 plasma treatment at 10, 20, 30, 40 and 50 s are observed to be about 144.4, 135.0, 110.6, 103.1 and 96.6 nm, respectively. The thickness of the a-C:F films with the CF_4 plasma treatment time decreased. From Fig. 1, 3 and 4 results, we can infer that the a-C:F film is etched due to CF_4 radicals and the bonding structure of the a-C:F film induced a rearrangement of the chemical bonds forming carbon-rich functional groups when the CF_4 plasma treatment time is greater than 30 s.

Figure 5 shows the atomic concentration of carbon and fluorine atoms in a-C:F film as a function of



Fig. 5. The atomic concentration (%) of carbon and fluorine, which was calculated by XPS survey scan spectra.



Fig. 6. The refractive index and dielectric constant of a-C:F films as a function of CF_4 plasma treatment times.

plasma treatment time. The F concentration increased abruptly from 42% to 67% for a treatment time of 20 s and then it decreased slightly. The C concentration decreased from 57% to 35% for a 20 s treatment time and then it increased slightly. This result matches that of the results in Fig. 3 and 4. In our experiment, the thickness of the a-C:F film decreased above 30 s treatment time.

Figure 6 shows the refractive indices and the dielectric constants of the a-C:F films with various plasma treatment times for the sample formed with a flow rate ratio R (%) of 75%. The dielectric constant of the asdeposited film is 3.2. However, when a plasma treatment is carried out, the dielectric constant of the film decreases to 2.3 for a plasma treatment of 40 s and then it increases slightly to 2.6 for a treatment time of 50 s. The refractive index (n) of the as-deposited sample decreased from 2.4 to 2.2 as the plasma treatment time increased to 40 s and then it increased to 2.3 for a 50 s treatment time. From these results, we know that the dielectric constant of the a-C:F films decreases with increasing $C-F_2$ bonds. It is, thus, concluded that the bonding configuration between carbon and fluorine atoms, as opposed to the total fluorine concentration, is the important factor which determines the value of the dielectric constant. The susceptibility from the contribution of electrons of the a-C:F films is calculated using the relation, $\varepsilon_e = n^2$, from the refractive index of Fig. 6. In the as-deposited film, the electronic susceptibility is calculated to be 1.27×10^{-11} C/V·m. The electronic susceptibility of the film treated by a CF4 plasma for 40 s decreases to 1.09×10^{-11} C/V m. However, when the a-C:F film is treated for 50 s, the electronic susceptibility increased to 1.11×10⁻¹¹ C/V·m. In the asdeposited film, the surface charge per electric field is calculated as 1.39×10^{-18} C·m/V. The Q/E of the film treated by a CF₄ plasma for 40 s decreases to about 0.99×10^{-18} C·m/V. But when the a-C:F film is treated for 50 s, the Q/E increased to 1.1×10^{-18} CPm/V. From these results, we know that a-C:F films treated by a CF_4 plasma have a dielectric constant lower than that of the as-deposited film because the susceptibility is related to the dielectric constant by $\chi_e = \varepsilon_e - 1$. The results mean that the bonding configuration of the plasmatreated film is rearranged on the surface layer due to the fluorine-rich functional groups of CF_x bonds.

Conclusions

The bonding structure and the electrical properties of a-C:F films with CF_4 plasma treatments as well as its influence on the dielectric constant were studied. These results indicate that a-C:F films with CF_4 plasma treatments changed the bonding configuration such as C-F₂, C-F₃, CF₃-CF₂, C=CF₂ and CF=CF₂ until the plasma treatment time is 30 s in which the cross-linked structure of a-C:F film are broken due to the highly ordered

fluorine bond group. When the plasma treatment time is 50 s, the bonding structure of a-C:F films had the carbon-rich functional groups of C-C bond such as -C-CF-, CF-C-CF₃, -CF-C-CF and -CF-C-CF₂ bonds. The lowest dielectric constant was about 2.3 for a 30 s plasma treatment time. The surface modification of a-C:F film with the CF₄ plasma treatment plays an important role in decreasing the dielectric constant and the surface charge of the film.

Acknowledgements

This work was supported by research grant from the Chuong-bong Academic Research Fund of the Cheju National University.

References

- 1. Y. Ma, H. Yang, J. Guo, C. Sathe, A. Agui, and J. Nordgren, Appl. Phys. Lett. 72 (1998) 3353-3355.
- S.Y. Jing, H.J. Lee, and C.K. Choi, J. Korean Phys. Soc. 41 (2002) 769-773.
- K. Endo and T. Tatsumi, Appl. Phys. Lett. 68 (1996) 2864-2866.
- 4. Y.H. Kim, H.J. Kim, J.Y. Kim, and Y. Lee, J. Korean Phys.

Soc. 40 (2002) 94-98.

- S. Takeishi, H. Kudoh, R. Shinohara, A. Tsukune, Y. Sato, H. Miyazawa, H. Harada, and M. Yamada, J. Electrochem. Soc. 143 (1996) 381-385.
- 6. S.H. Yang, S.H. Lee, J.W. Park, S.S. Sohn, J.W. Park, and J.Y. Kim, J. Korean Phys. Soc. 35 (1999) s361-s364.
- L. Valentini, E. Braca, J. M. Kenny, G. Fedosenko, J. Engemann, L. Lozzi, and S. Santucci, Diamond and Related Materials 11 (2002) 1100.
- S.A. Visser, C.E. Hewitt, J. Fomalik, G. Braunstein, C. Srividya, and S.V. Babu, Surf. Coat. Technol. 96 (1996) 210-222.
- 9. S.H. Yang and J.W. Park, Jpn. J. Appl. Phys. 40 (2001) 694-697.
- N. Ariel, M. Eizenberg, Y. Wang, and S.P. Murarka, Materials Science in Semiconductor Processing 4 (2001) 383.
- S. Vallon, A. Hofrichter, B. Dr'villon, J.E. Klemberg-Sapieha, L. Martinu, and F. Poncin-Epaillard, Thin Solid films 290-291 (1996).
- C.B. Labell and K.K. Gleason, J. Electrochem. Soc. 147 (2000) 678-681.
- 13. S.S. Han H.R. Kim, and B.S. Bae, J. Electrochem. Soc. 416 (1999) 3383.
- Y. Izumi, M. Katoh, T. Ohte, S. Ohtani, and A. Kojima, Appl. Surf. Sci. 100-101 (1996) 179-183.
- T.C. Wei, C.H. Liu, J.M. Shieh, S.C. Suenm and B.T. Dai, Jpn. J. Appl. Phys. 39 (2000) 7015-7018.