A Formation of the Fluorocarbonated-SiO_2 Films on Si(100) Substrate by O_2/FTES-High Density Plasma CVD

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ABSTRACT

Fluorocarbonated-SiO_2 films were deposited on p-type Si(100) substrate using $FSi(OC_2H_5)_3$ (FTES), and O_2 mixture gases by a helicon plasma source. High density O_2/FTES/Ar plasma of $\sim 10^{12}$ cm^{-3} is obtained at low pressure (< 3 mTorr) with RF power above 900 W in the helicon plasma source. Optical emission spectroscopy (OES) is used to study the relation between the relative densities of the radicals and the film properties. The FTES and O_2 gases are greatly dissociated at the helicon mode that is launched at the above threshold plasma density. FTIR and XPS spectra shows that the film has Si-F, and C-F bonds during the formation process of the film which may lower the dielectric constant greatly. The relative dielectric constant, leakage current density, and dielectric breakdown voltage are about 2.8, 8×10^{-9} A/cm^2, and >12 MV/cm, respectively.

INTRODUCTION

Present silicon dioxide(SiO_2) films as an intermetal dielectric(IMD) layers will cause high parasitic capacitance and crosstalk interference in high density devices. Low dielectric materials such as fluorinated silicon oxide(SiOF), fluorinated carbon, and fluorocarbon/SiO_2 IMD layers are needed to solve these problem. SiOF films have been deposited using fluoro-trialkoxy silane group and H_2O mixture by CVD(1-4), TEOS/O_2/C_2F_6(5-6), FTES/O_2(7), SiH_4/N_2O/CF_4(8-9), SiH_4/SiF_4/O_2(10), and TEOS/SF_6(11) mixtures by PECVD, H_2SiF_6/H_2O mixture by liquid phase deposition(LPD)(12). As fluorine concentration increases, the dielectric constant of these films decrease but the films become unstable and water absorptivity increases.(13-17) In these results, N_2O plasma annealing process is added to prevent water absorption and the dielectric constant is obtained above 3.0. SiOF film deposition using SiF_4/O_2 mixture in high density plasma reactor such as electron cyclotron resonance(ECR)(18) or helicon wave plasma(19-20) has been also studied. No water absorption is occurred even when fluorine concentration is high (> 10%). This is explained by the fact that the high ion flux with low energy (< 20eV) makes good crosslinking structure films. Fluorinated amorphous carbon films have been deposited using CH_2/CF_4(C_2F_6) in PECVD(21) and helicon wave plasma CVD(22). The dielectric constant above 2.1 is obtained in these films. Fluorocarbon/SiO_2 composite film has been deposited using hexamethyl disiloxane (HMDSO) and C_6F_6 mixture in the inductively coupled plasma reactor.(23) The dielectric constant above 2.5 is obtained from these films.

Various types of low pressure gas discharges have been used for deposition process. Recent, the concept of a plasma processing apparatus with high density plasma at low pressure has received much attention for film deposition. Films made by low pressure and high density plasma reactors have many advantages such as good film quality and gap filling profile. High ion flux with low ion energy in the high density plasma makes low contamination(24) and good corsslinking films.(25) Moreover, good gap filling profile can be obtained from the process because the processing pressure is very low (< 10 mTorr).(26) Especially, the helicon plasma reactor have attractive features for film deposition because of their high density plasma production characteristics compared with other conventional type plasma sources. Moreover, it is advantageous for dissociating souce gases because high energy electrons exist in the source region. Source gases highly dissociated in the plasma source region can be expanded uniformly over a large diameter substrate by controlling the magnetic field at the position of processing chamber. Thus, helicon plasma sources coupled to a reaction chamber have provided a new method for better high density plasma CVD (HDP-CVD).

In this work, the helicon wave plasma has been utilized for the fluorocarbonated-SiO_2 film deposited using O_2/FTES gas mixture. High density O_2/FTES plasma is characterized with various RF power, gas pressure, and O_2/FTES flow rate ratio. Plasma density and electron temperature are measured using Langmuir probe and relative radical density is measured using OES. Film properties such as chemical bonding structure, F concentration and dielectric constant are investigated. The main goal of this work is to characterize the helicon plasma O_2/FTES deposition method for low dielectric films.

EXPERIMENTS

A schematic diagram of the helicon plasma reactor is shown in Fig. 1. This system consists of the discharge and the reaction region. Helicon wave plasma is generated by means of a Nagoya type III antenna for a m = ±1 mode which is set around a quartz tube. The discharge tube is 10 cm in diameter and 60 cm in length. The reaction chamber is 30 cm in diameter and 40 cm in length. The four magnetic field coils have the relative dimension as shown in Fig. 1. The resulting magnetic field (B_0) is uniform within 0.1% inside a volume of 30cm in diameter and 70 cm in length and can be raised up to 1.5 kG. The RF power of

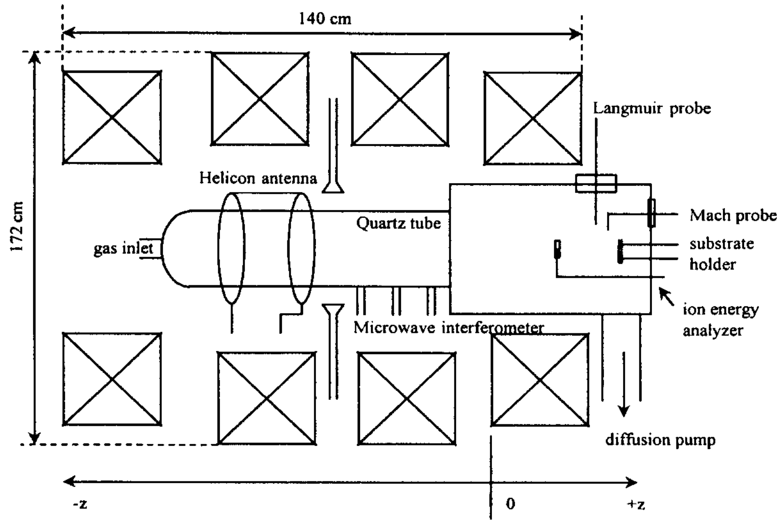

Fig. 1 A schematic diagram of the helicon plasma reactor.

3 ~ 18MHz is supplied continuously from an oscillator-amplifier system and is varied up to 1.2 kW. A base pressure of ~10^{-6} Torr is reached before each deposition by the rotary and diffusion pump system. The O_2 and Ar gases are introduced through a mass flow controller system into the source chamber. The FTES liquid source is stored in a stainless steel container and vapor flow rate is controlled by a mass flow controller. No carrier gas is used due to low process pressure (<5 mTorr). The discharge pressure is measured by a baratron gauge.

The electron density and electron temperature are measured by a fast injection Langmuir probe and calibrated by a microwave interferometer. The OES is set up using a high gain diode array attached to a triple-grating monochromator which detects the emission of the excited species in the plasma. The OES is used to study the relationship between the relative concentrations of the radicals (F, Si, O, and C) and the film properties. The fluorocarbonated -SiO_2 film is deposited on 5 inch p-type Si(100) wafers in the flow rate ratio of the O_2/FTES mixture gas as 0.17 with addition of Ar gas at 700 Gauss, 1 mTorr and 1 kW rf power, which is 30% of the Ar in the mixture gas. We are reported that the helicon mode is launched, and the film is deposited at this deposition conditions(27). Film properties such as chemical bonding structure and dielectric constant are investigated. Chemical bonding structure is characterized using Fourier transformed (FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS). Dielectric constant is measured using a metal insulator semiconductor (MIS) (Al/fluorocarbonated-SiO_2 film/p-Si) structure.

RESULTS AND DISCUSSION

To estimate the dissociation rate of the FTES gas, the relative amount of radicals are investigated by OES. The emission intensity (I_x) by a neutral X can be expressed as follows.

$$I_x = k'^{x}_{e} n_e [X] \qquad [1]$$

where k_e^x is the rate coefficient of the excitation process, n_e is the electron density, and $[X]$ is the density of the X species (X=F, Si, O, C, and H). k_e^x is a function of the electron temperature which is nearly constant as RF power increases in the helicon plasma source. Hence, the emission intensities normalized by the electron density are representative of the relative densities of each species.

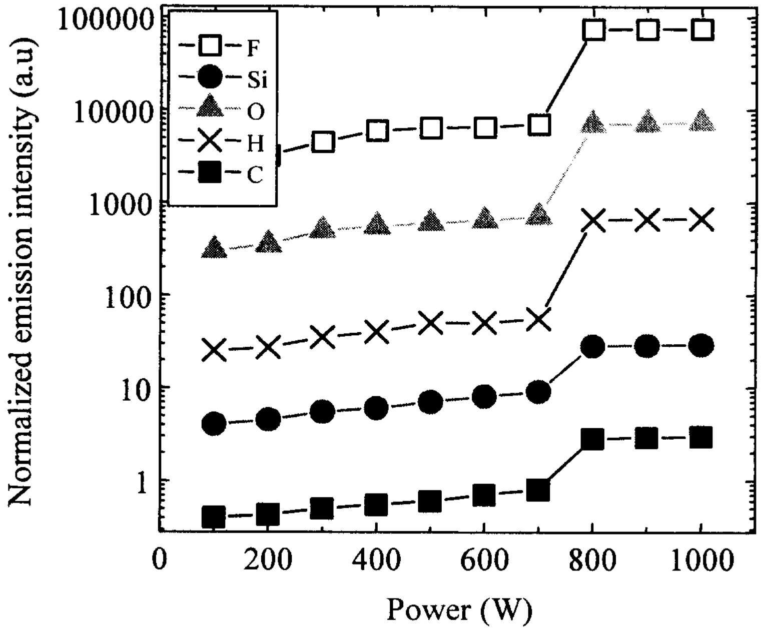

Fig. 2. The normalized emission intensity vs. RF power. The discharge condition is 1 mTorr in flow rate ratio of O_2/FTES=0.17 with addition of Ar gas as 30%, 7 MHz of RF power and 700 Gauss of magnetic field.

Figure 2 shows the normalized emission intensities of F (703.7 nm), Si (288.2 nm), O (777 nm), C (247.9nm), and H (656.2 nm) with various RF power. The normalized intensities are greatly increase at 700 W and this implies that the FTES gas is greatly dissociated as the helicon mode is launched. The helicon mode is not launched when the plasma is generated with O_2/FTES mixture without Ar, and at below 700 W of the RF power. The important point to launch helicon mode is efficient production and preservation of energetic electrons. The energetic electrons are lost to the walls before they have deposited most their energy in the plasma at low rf power. Most energetic electrons are not reflected although the sheaths on the walls reflect electrons. It is known that the helicon mode is launched above threshold electron density.(28) However, it is difficult to make enough electron density to launch the helicon mode in the case of FTES plasma because FTES absorbs electrons during its dissociation process. Thus, additional electrons are needed to launch helicon mode and this is possible by means of Ar gas addition. We find that 30% of Ar addition makes suitable processing condition for deposition in these experiments.

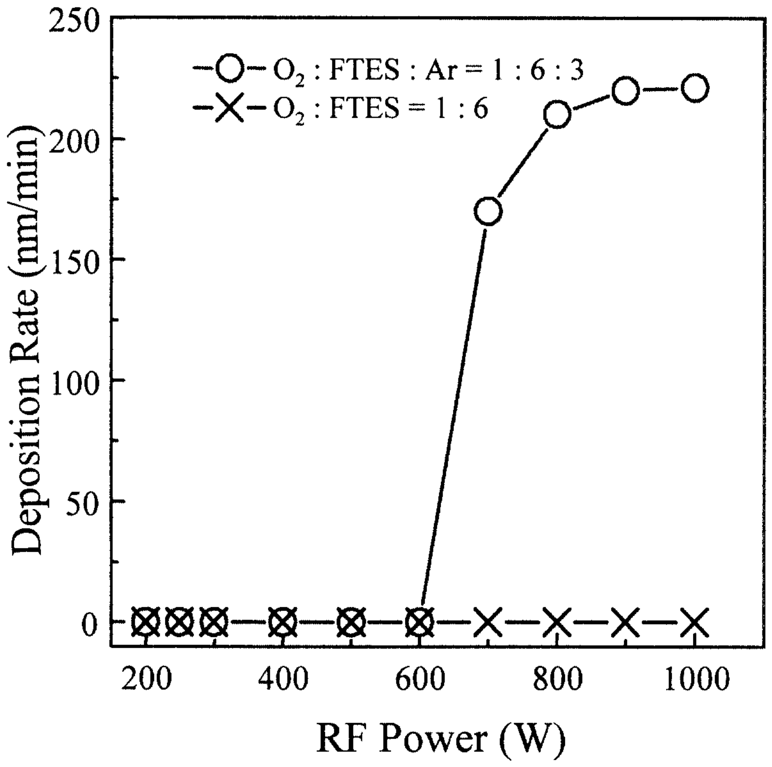

Fig. 3. Deposition rate vs. RF power. The discharge conditions are 1 mTorr of pressure, 7 MHz RF power, and 700 Gauss of magnetic field.

The deposition rate with various power is shown in Fig. 3. Referring to the deposition rate with O_2/FTES/Ar mixture, we can see that deposition rate increases greatly 175 nm/mim to 700 W where the helicon mode is launched. No deposition is observed when the plasma is generated without Ar because the helicon mode is not launched.(29) When the helicon mode is launched, it is known that there are a lot of high energy electrons in source region. Thus, the FTES gas is dissociated greatly in the plasma source region when the helicon mode is launched.(29)

The FTIR spectrum of the film made with the discharge conditions of 1 kW, 7 MHz RF power, 1 mTorr of flow rate ratio as 0.17 is shown in Fig. 4. The spectrum is generally broad and overlapped due to the complex stoichiometry and the amorphous nature of the film. The intense band at 1,070 cm ^{1}, called TO (transverse optical) mode, is attributed to the asymmetric stretching of the oxygen atoms along the direction parallel to Si-O-Si and the band at 800 cm ^{1} is

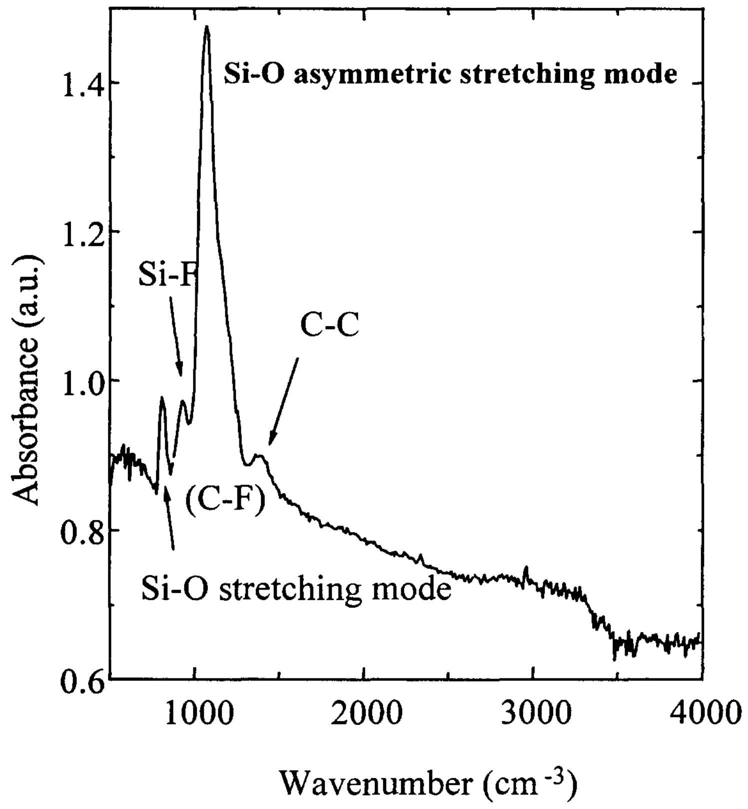

Fig. 4. FTIR spectrum of the SiOF film. The discharge condition is 1 mTorr in flor rate ratio of O_2/FTES=0.17 with addition of Ar gas as 30%, 1kW of 7MHz RF power and 700Gauss of magnetic field.

due to the symmetric Si-O-Si stretching.(30) The band at 930cm^{-1} is for Si-F bonds and the band at 1410 cm^{-1} is for C-C bonds. Small broad bands at 3,500 cm^{-1} are due to Si-OH (3,650 cm^{-1}), H-O-H (3,230, 3440 cm^{-1}) bond.(31) C-F bonds may exist in the film but the band for C-F bond (near 1,100 cm^{-1}) is overlapped by the Si-O bands, so it is not shown in the FTIR data.(23) From these results, we suggest the "bond-termination" effect of F atom in the SiO_2 films. As the films are being grown, F atoms are bounded to Si atom with breaking of Si-O-Si chains and the arms of F-bonded Si on the surface are terminated. The arm is relatively free and rarely interact with the neighoring atoms. Therefore, the residual Si-O bondings are positioned in equilibrium angles and the bond angles are less dispersed. The after-grown films are to be "relatively" regular and the films grown finally are similar to thermal oxide.

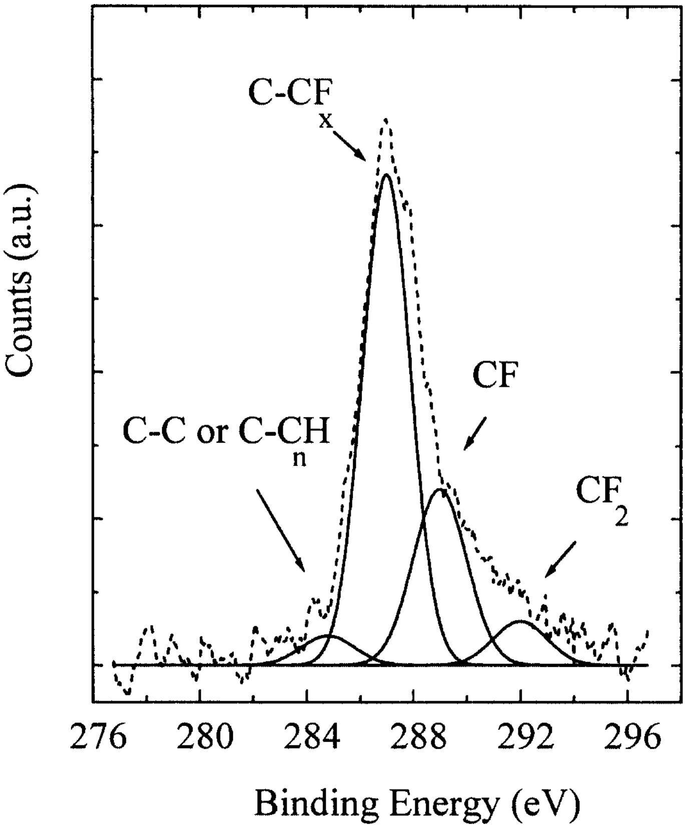

Fig. 5. C 1s XPS spectrum of the SiOF film deposited at the same condition with Fig. 4.

This FTIR spectrum is taken after a month later from the film deposition. We get the same spectra right after the film deposition. This means that the film does not absorb any moisture in the air and the Si-OH and H-O-H bonds are formed during the deposition process because the O and H radicals exist in the plasma. However, only small amount of H atoms remains in the film because the H atoms are detachable easily form the surface by ion bombardment which occurs very frequently in the helicon wave plasma.(25)

To confirm the existence of C-F bonds, we use XPS measurements, whose C 1s is signal is shown in Fig. 5. The peaks are deconvoluted into four components. The main peak is C-CF_x at 287 eV and small peaks are C-F at 289 eV, and C-F_2 at 292 eV.(22) C-C or C-CH_n at 285 eV is very small. In the XPS depth profile, we known that the fluorocarbonated-SiO_2 film is uniform in composition and has a smooth interface. Referring to the above results, we can summarize the deposition process as follows. First, the source gases are greatly dissociated into Si, C, F, H, and O radicals. There are also some species which are not dissociated and we can see that these species contain F-Si, Si-O, O-C, C-C, and C-H bonds considering the chemical structure of F-Si(OC_2H_5)$_3$. Si-F, Si-O, C-F, and C-O bonds can be made during the deposition process because F and O radicals are easily react with Si and C. Also, Si-H, O-H, C-H, and H-F bonds can be made. However, because CO and H species on the film are volatile and detachable easily by ion bombardment that occurs very frequently during the film formation process, we can infer that the main remaining bonds in the film are Si-F, Si-O, C-F (or C-CF). In the case of O_2/FTES CVD methods, there are no C-F bonds because the FTES precursors such as F-Si-$(OC_2H_5)_{n-1}(OH)_{5-n}$ chemically react with O_2 on the substrate and $(OC_2H_5)_{n-1}(OH)_{5-n}$ is alternated with O.(7) Thus, the film composition is different between CVD where no C-F bonds exist and helicon plasma CVD where C-F bonds exist.

Figure 6 shows a C-V plot of MIS capacitor formed at flow rate of O_2, FTES and Ar gas, 1 sccm, 6sccm, and 3sccm, respectively, and the thickness of the fluorocarbonated-SiO_2 film and the area of Al electrode is 1100Å and $2.5\times10^{-3}cm^2$, respectively. The calculated dielectric constant of the film is about 2.8. This value is lower than that other SiOF films(> 3.0) but higher than that of fluorocarbon/SiO_2 composite film using HMDSO/C_2F_6 (> 2.5) or fluorinated amorphous carbon film (> 2.1). The dielectric constant of the films formed in this study are increased as the fraction of O_2/FTES flow rate ratio increases. It is suggested that the F concentration contained much by means of C-F bond in the film. Figure 7 shows leakage current density as a function of the applied voltage. The applied voltage to the Al electrode is from 0 to 100V. The current density was stable, where the breakdown was not observed within 100V and the leakage current density increased slightly at around 10 volt. The leakage current density was $8\times10^{-9}A/cm^2$ at applied voltage 3V. This value was less than $3.0\times10^{-7}A/cm^2$ of the SiOF films formed by PECVD. These results indicate that the fluorocarbonated-SiOF films are more stable in leakage current characteristics than conventional intermetal dielectric films.

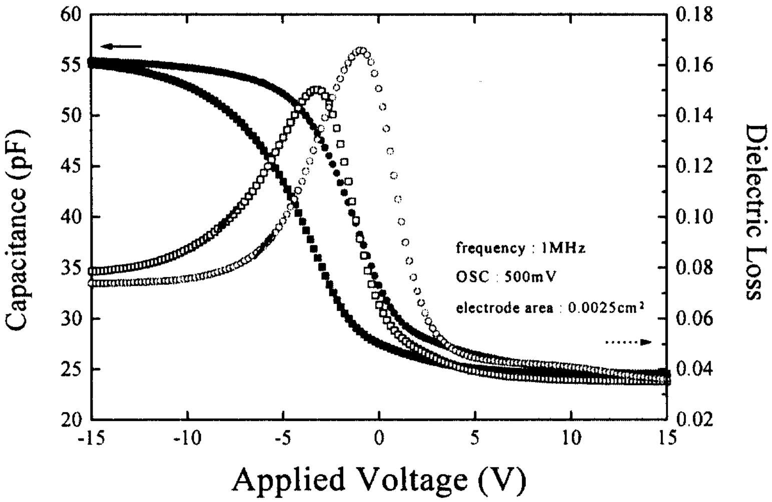

Fig. 6 Characteristics of C-V plot of MIS capacitor.

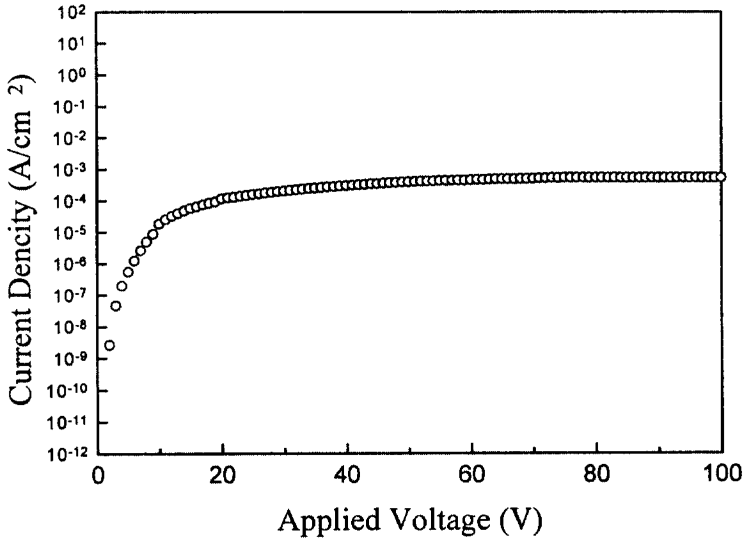

Fig. 7. The leakage current density as a function of the applied voltage.

CONCLUSIONS

High quality Fluorocarbonated-SiO_2 films with low dielectric constant was formed on the Si(100) substrate using O_2/FTES-helicon plasma CVD. The helicon mode for high density plasma in the O_2/FTES mixure gas with addition Ar gas as 30% is launched above 700 Gauss of magnetic field, 1 kW of the RF power, and 1 mTorr of the working pressure. The Fluorocarbonated-SiO_2 film is deposited only in the helicon mode where the source gases are highly dissociated by the energetic electrons. The source gases are greatly dissociated into Si, C, F, H, and O radicals. There are also some species which are not dissociated and we can see that these species contain F-Si, Si-O, O-C, C-C, and C-H bonds considering the chemical structure of $F-Si(OC_2H_5)_3$. Si-F, Si-O, C-F, and C-O bonds can be made during the deposition process because F and O radicals are easily react with Si and C. The dielectric constant of the formed film is obtained 2.8, and the breakdown was not observed within 100V. The leakage current density was stable and measured 8×10^{-9}A/cm^2. From these results, we known that the fluorocarbonated-SiOF films formed by O_2/FTES-helicon plasma CVD have attractive advantages on the application for intermetal dielectric layer of the high density devices.

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