Effect of Annealing on the Bonding Structure and Dielectric Properties of a-C: F Thin Films

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Received 5 October 2004; Accepted 31 December 2004

Fluorinated amorphous carbon thin film (a-C:F) considered as a potential candidate for intermetal dielectric material was deposited on a *p*-type Si(100) substrate by using an inductively coupled plasma chemical vapor deposition (ICPCVD) system with carbon tetra fluoride (CF_4) and methane (CH_4) gases. Fourier transform infrared spectra showed that the annealed film had C-F, C-F_2, C-F_3, C=CF_2 bonds. Annealing of a-C:F films induced a re-arrangement of the chemical bonds in the film, in which the fluorine-rich functional groups such as -CF_2, CF_2-CF- and -CF_2 -CF_2- bonds are changed to carbon attached functional groups of -C-CF-, CF-C-CF_3, -CF-C-CF and -CF-C-CF_2 chain structure. The annealed films showed a decrease in the fluorine to carbon ratio and increase in C=C bonds in the films. A reduction of the dielectric constant is obtained by varying the C-F_x bonding configuration, as well as by incorporating fluorine atoms. The lowest dielectric constant of as-deposited film is 1.96 and the annealed film is 2.02 for the [CF_4 / (CF_4+CH_4)] flow rate ratio of 66%.

INTRODUCTION

The shrinkage in the integrated circuits with an increased complexity and with multilevel metal layers demands low dielectric constant material to improve the parasitic capacitance and signal delay. The problem of using silicon dioxide (SiO_2) films as intermetal dielectric (IMD) layers will be high parasitic capacitance and crosstalk interference in high density devices [1]. Low–k materials need low dielectric constant, good thermal stability, higher mechanical strength and good adhesion to neighboring layers. These stringent requirements makes the fluorinated amorphous (a–C:F) films as a promising candidate for the new low–k material. The dielectric constant of a–C:F films deposited using plasma enhanced chemical vapor deposition (PECVD) [2] and helicon wave plasma CVD [3] can be changed from 2.1 to 2.8 by controlling the fluorine concentration. Recently, a–C:F thin films deposited using high–density plasma chemical vapor deposition (HDPCVD) have been investigated as a new IMD material [4,5]. These films have an amorphous C-C cross-linked structure and have the related C-F_x bonds like those of PTFE. The strong C-F_x bonds in the a-C:F film decreases its dielectric constant while cross-linked structure maintains the film's stability. The growth of a-C:F films with low dangling bond concentrations by thermal CVD has been reported [6], and since plasma CVD using only carbon tetrafluoride (CF_4) brings about no deposition of films, methane (CH_4) and CF_4 gases are used. However, the origin of the low dielectric constant, the atomic structure, and the role of fluorine and carbon atoms in these films are still uncertain. In this study, we investigate the a–C:F thin films deposited on a Si(100) substrate by using inductively coupled plasma chemical vapor deposition (ICPCVD) with gas mixtures of CF_4 and CH_4 for different flow rate ratios. Also the detailed bonding structure of a–C:F films using XPS and the relation between the dielectric constant and the concentration of C–F_x bond in a–C:F thin films were studied. The dielectric properties of the films were also studied.

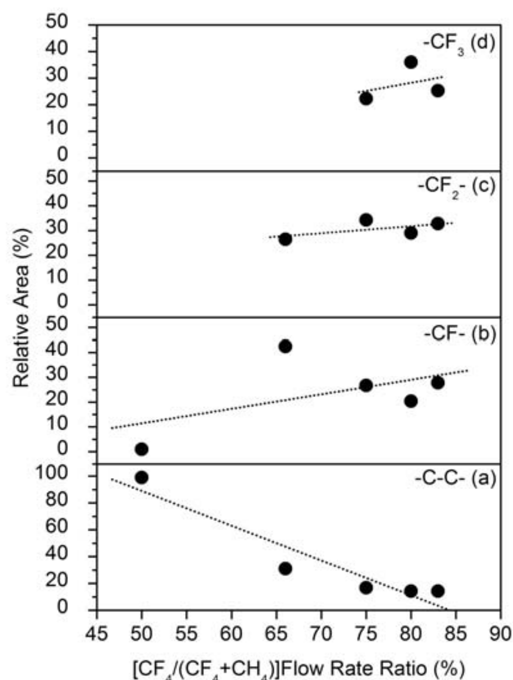

Fig. 1 The results of Gaussian peak fitting from XPS spectra (a) –C–C–, (b) –CF–, (c) $–CF_2–$ and (d) $–CF_3$

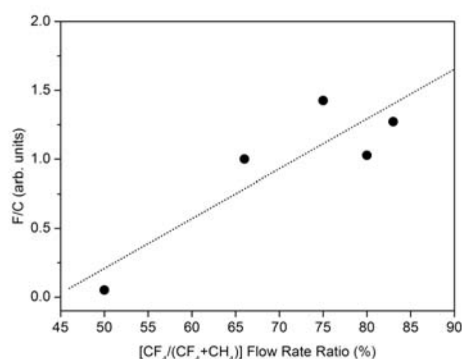

Fig. 2 The ratio of fluorine to carbon from XPS spectra as function of $[CF_4/(CF_4+CH_4)]$ flow rate ratios.

EXPERIMENT

a–C:F thin films were deposited on a p–type Si(100) substrate by using mixtures of CF_4 and CH_4 gases in a radio–frequency (13.56 MHz) planar type ICPCVD system. The wafers were kept in a floating potential and were not intentionally heated. The wafers were cleaned by using a standard cleaning procedure before loading them into the reaction chamber. Inductively coupled plasma was generated by means of a spiral coil, which was set around a quartz tube. A base pressure of about 10^{-6} Torr was reached before each deposition. CF_4 gas was introduced into the reaction chamber as the source gas for fluorine, and CH_4 gas was used for the carbon source. The flow rate ratio of R (%) = $[CF_4 / (CF_4+CH_4) \times 100]$ are varied as 50, 66, 75, 80 and 83% and the total flow rate has been maintained as 60 sccm. The CF_4 and CH_4 gases were introduced through a mass flow controller (MFC) into the reaction chamber, and the discharge pressure was measured with a Baratron gauge and kept at 400 mTorr. The rf power was kept at 800 W for each deposition. The substrate temperature is maintained at room temperature. To investigate the influence of carbon and fluorine contents of a–C:F thin films by thermal treatment, we carried out post–annealing at 500°C for 1 hour in Ar ambient at 1 Torr. The chemical bonding structure of a–C:F thin films were analyzed by using X–ray photoelectron spectroscopy (XPS, VG Esca 200R) and Fourier transform infrared spectroscopy (FTIR). The thickness and refractive indices of the as–deposited and annealed a–C:F films were measured by using an ellipsometer. The dielectric constant was investigated using metal insulator semiconductor (MIS: (Al/a–C:F/p–Si)) structures.

RESULTS AND DISCUSSION

Figure 1 shows the results of the Gaussian peak fitting of XPS narrow scan spectrum. The peaks are deconvoluted into four components such as –C–C– at 286 eV, –CHF– or –CF– at 288 eV, $–CF_2–$ at 290 and $–CF_3$ at 292 eV, in which the major peak is assigned to –CF– bonding mode. The C 1s spectra with R(%) flow rate ratio of 75, 80 and 83% consist of four peaks, which are assigned to the –CF–, $–CF_2–$,$–CF_3$ and –C–C– bonding modes. The chemical shift of the C–CF– bond is due to the higher content of fluorine atoms and a–C:F film consists of carbon attached functional groups such as –C–CF–, $–CF–CF_3$, –CF–CF– and $–CF–CF_2–$ chain structure [7]. The relative area of the C–CF bond increased with the increase in the flow rate ratio. For the films with R (%) flow rate

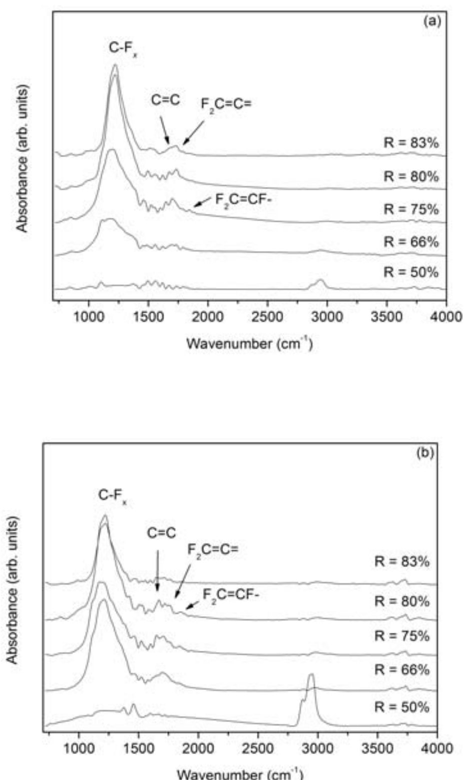

Fig. 3 The FTIR spectra was a function of flow rate ratios in (a) as deposited and (b) 500°C annealed a-C:F thin film.

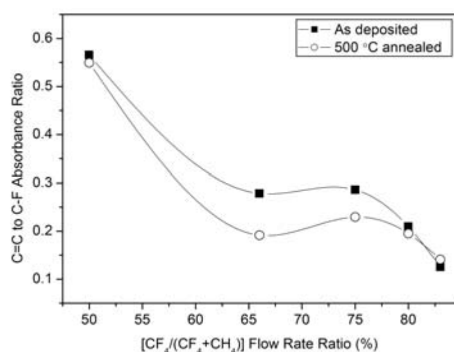

Fig. 4 The C=C to C-F stretching absorbance ratio, $A_{C=C}$ /A_{C-F} for as–deposited and 500°C annealed a–C:F films for [CF_4/(CF_4+CH_4)] flow rate ratios of 50, 66, 75, 80, 83 and 90%.

ratios of 50 to 75%, $-CF_2-$ and $-CF_3$ bonds from the –CF– group are formed. The relative area of –C-C bond is decreased and the C-F$_x$ (x=1,2,3) bond increased with R(%) flow rate ratio. From the above results, we can infer that the higher binding energy peak in the XPS spectra can be assigned to more fluorine–incorporated bonding configurations [8]. Figure 2 shows the ratio of fluorine to carbon integrated intensities calculated from XPS survey scan spectra of a–C:F thin films as a function of flow rate ratio. The F/C ratio increased as the R (%) flow rate ratio increases from 50 to 83%. From the results of Fig. 1 and 2 we can infer that an increase in the concentrations of the C–F$_2$ and the C–F$_3$ contents at a higher R (%) flow rate ratios of 80 and 83% respectively is observed.

Figure 3 shows the FTIR spectra of as–deposited and 500°C annealed a–C:F films for R (%) flow rate ratios of 50, 66, 75, 80, 83 and 90%. Two characteristic peaks of the a-C:F films are observed at around 1200 and 1700 cm^{-1} for R(%) flow rate ratio of 66% with and without annealing. The CH group peak (around 2900 cm^{-1}) appeared only at the R (%) flow rate ratio of 50%, and then increased after annealing at 500°C. Therefore, this shows no possible incorporation of fluorine in the a-C:F film at the R(%) flow rate ratio of 50%. The strong peak at approximately 1200 cm^{-1} is assigned to CF$_x$, where $1 \le x \le 3$ and the peak at approximately 1700 cm^{-1} indicates the presence of unsaturated carbon double bonds associated with F$_2$C=CF (at 1850 cm^{-1}), F$_2$C=C (at 1730 cm^{-1}), and C=C (at 1620 cm^{-1}) above the R(%) flow rate ratio of 66%[4]. The C=C stretching mode is normally observed at approximately 1600 cm^{-1} in organic compounds where C atoms are bonded to H atoms. However, the absorption peak is typically shifted to higher frequencies when the H atoms are replaced by F atom [9]. Figure 4 shows the variation in the ratio of C=C to C-F stretching absorbance ($A_{C=C}/A_{C-F}$) in the a-C:F films for as deposited and 500°C annealed a–C:F films with R (%) flow rate ratios of 50, 66, 75, 80 and 83%. The ratio was estimated by measuring the area of the corresponding bonds in the FTIR spectra of Fig. 4. The $A_{C=C}$ and A_{C-F} are the area of C=C peaks between 1500 and 1900 cm^{-1}, and the area of C-F$_x$ peaks between 950 and 1500 cm^{-1}, respectively. The ratio of $A_{C=C}$ to A_{C-F} is shown to decrease with increase in R(%) flow rate ratio and by annealing. For the R(%) flow rate ratios of 66 and 75%, the difference of the ratio of $A_{C=C}$ to A_{C-F} for as deposited

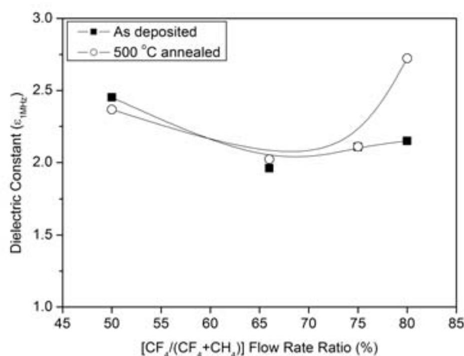

Fig. 5 The dielectric constant of as deposited and 500°C annealed a-C:F thin film as function of R (%) flow rate ratios.

to annealed a-C:F film is more greater than in the other flow rate ratios. This result indicates that the decrease of the ratio of $A_{C=C}$ to A_{C-F} is due to increase in the fluorine concentration and the formation of cross-link structure by reduction of carbon double bonds in the film. The C=C bond forms cross linked chain of -C-CF at annealing. Hence the a-C:F film structure has more cross-linked structure [10]. But, at the case of 80 and 83%, there is no rearrangement of the structure by the excess of fluorine in the film, because the excess fluorine and carbon react to from fluorocarbon gas and it vapors out.

The dielectric constant of a–C:F films as a function of R (%) flow rate ratio is shown in Fig. 5. For as–deposited films, the dielectric constants are 2.45, 1.96, 2.11, 2.15 and for the annealed films are 2.02, 2.11 and 2.72 for R (%) flow rate ratios of 50, 66, 75 and 80%, respectively. But when the flow rate ratio is 50%, the dielectric constant of annealed film is decreased to 2.36 when compared with as–deposited film. This may be due to the decreased fluorine content in the film due to annealing. It is, thus, concluded that the dielectric constant of the a-C:F films decreases with increasing C-F_2 and C-F_3 bonds. Therefore, the reduced dielectric constant can be attributed to the enhanced fluorination of the films due to the higher R (%) flow rate ratio. This coincides with the results of XPS and FTIR studies. The more cross-linked structure in a-C:F film helps in decreasing the dielectric constant. From these results, we assume that the bonding configuration between the carbon and fluorine atoms, as opposed to the total fluorine concentration, is the important factor that determines the dielectric constant.

CONCLUSIONS

Fluorinated amorphous carbon thin films were deposited on a p–type Si(100) substrate by using mixtures of CF_4 and CH_4 gases for various [CF_4/(CF_4+CH_4)] flow rate ratios. XPS studies showed the increase in the concentrations of C–F_2 and C–F_3 contents at higher R (%) flow rate ratios. The chain structure of the a-C:F film consists of the fluorine-rich functional groups of C-C bonds such as -C-CF-, CF-C-CF_3, -CF-C-CF and -CF-C-CF_2 bonds. The degree of crosslinking in the film increases at high temperature annealing for the flow rate ratios of 66 and 75% respectively, and the dielectric constant is found to be less for high crosslinked a-C:F film. The lowest dielectric constant of 1.96 and 2.02 is observed at [CF_4 / (CF_4+CH_4)] flow rate ratio of 66% for as-deposited and annealed films, respectively.

ACKNOWLEDGEMENT

This work was supported by grant No. R01–1999–000–00092–0 from Korea Science and Engineering Foundation.

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