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Low-dielectric-constant α-SiCOF film for ULSI interconnection prepared by PECVD with TEOS/C_4F_8/O_2

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Abstract. Amorphous SiCOF films with high carbon concentration are prepared by PECVD (plasma-enhanced CVD) with TEOS/C_4F_8/O_2. The dielectric constant of (α-SiCOF film is reduced to 2.6 and other electric properties are improved remarkably. The moisture resistibility of the film is also improved. Through FTIR and XPS analyses, the chemical construction of α-SiCOF film is investigated. The mechanism of improvements in electrical properties and stability in moisture is further discussed. It is found that the ionic polarization and orientational polarization decrease in α-SiCOF films and contribute a lot to the reduction in dielectric constant. In addition, because of the hydrophobicity of incorporated C−F bonds, the moisture resistibility of α-SiCOF film is improved.

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Low-dielectric-constant interlayer dielectrics are increasingly needed in ULSI technology, because multilevel interconnection induces larger wiring capacitance, which affects the operation speed of ULSI circuits. As promising low-*k* materials, fluorinated silicon oxide films (SiOF) and fluorinated amorphous carbon films were proposed to scale down the RC delay by reducing parasitic capacitance. Many researches are focused on fluorinated silicon oxide films and fluorinated amorphous carbon films in these recent years [1–3]. It was found that SiOF film with high fluorine concentration is liable to absorb moisture, the instability in ambient atmosphere hampers its use in ULSI technology. For fluorinated amorphous carbon film, the moisture resistibility was remarkably improved and the dielectric constant can be reduced to 2.5 [4]. Zhou et al. proposed a method to prepare SiO(F, C) films by implanting CF_4 plasma ions into SiO_2 film. The CF_4 plasma ion implantation reduced the dielectric constant to 2.8 and also improved the bulk resistivity and electrical field breakdown strength. It was concluded in his research that the improvements possibly resulted from incorporated carbon in the films [5]. Recently, CF/SiOF composite films [6] or carbon-doped SiOF films [7] with low dielectric constants and good moisture resistibility were also prepared by doping carbon atoms into SiO_2. It seems that carbon atoms contribute a lot to the reduction in dielectric constant and improvement of moisture resistibility although the incorporated carbon concentration is small. In this paper, we proposed a method to deposit α-SiCOF films with high carbon concentration using PECVD system. The high carbon concentration was obtained by adding C_4F_8 as carbon source into TEOS/O_2 mixture. From $C-V$ measurements, it is found that the relative dielectric constant is reduced to 2.6, much lower than that of conventional SiOF film. At the same time, comparing with SiOF films, we find that the moisture resistibility of obtained film is remarkably improved. In addition, the bulk resistivity and electrical field breakdown strength are also improved. The chemical structure of α-SiCOF film is studied through FTIR and XPS analyses and feasible mechanisms are proposed to explain the improvements in dielectric properties and the moisture resistibility.

1 Experiments

The α-SiCOF films with thickness of 200 nm are deposited using mixture of TEOS, C_4F_8, and O_2 in PECVD system. The scheme of PECVD device is shown in Fig. 1. Through LC loop, RF-power is coupled on the upper electrode with a frequency of 13.56 MHz and power level of 100 W. The bottom electrode is connected to ground. By adjusting the power of the heater, the substrate temperature is fixed at 300 °C. The flow rates of TEOS and O_2 are fixed at 30 sccm, the flow rate of C_4F_8 is varied from 0 to 30 sccm. Argon is used as balance gas. The total flow rate is kept at 90 sccm, and the pressure in the reaction chamber is 80 Pa.

For comparison, conventional SiOF films are prepared using TEOS/SiF_4/O_2 mixture in the same PECVD device. The condition of experiment is the same as that for α-SiCOF film except that C_4F_8 is replaced by SiF_4 and the flow rate of SiF_4 is adjusted for choice.

The film thickness is measured by ellipsometry (632, 8-nm helium–neon laser). The bonding configuration and chemical composition are determined using FTIR and XPS analyses. The dielectric constant is determined through

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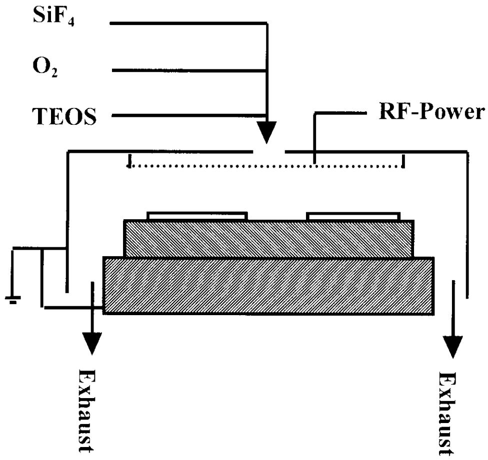

Fig. 1. The scheme of PECVD device

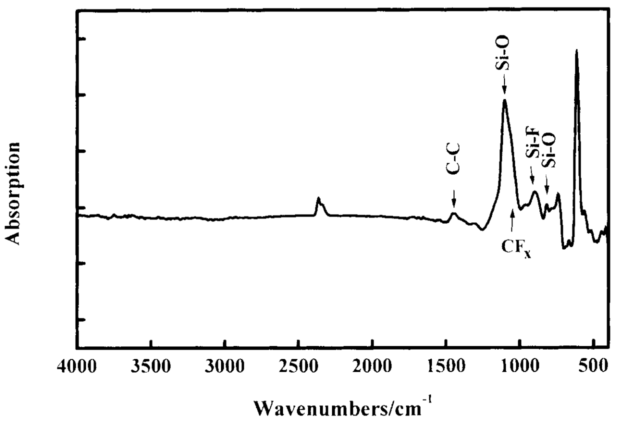

Fig. 3. FTIR transmission spectrum of α-SiCOF film in the region of 400–4000 cm^{-1} (the sharp absorption at 617 cm^{-1} is for silicon lattice vibration)

capacitance–voltage $(C-V)$ measurements of Al/thin film/silicon (MIS) structure at 1 MHz.

2 Results and discussion

2.1 Chemical composition and bonding configuration

By adding C_4F_8 as source of carbon and fluorine to the mixture of TEOS/O_2, α-SiCOF films with high C content were obtained. The XPS spectrum for one α-SiCOF film deposited with C_4F_8 flow rate of 30 sccm is shown in Fig. 2. From the XPS analysis, it is found that the carbon atom concentration is as high as 25 at. %, even higher than that of Si atom. The carbon atoms incorporated in film result in the structural changes of the film, which can be determined in the FTIR spectra of α-SiCOF film. Figure 3 is the FTIR spectrum for the α-SiCOF film deposited with C_4F_8 flow rate of 30 sccm. The peak centered at 1430 cm^{-1} corresponds to C—C stretching mode absorption and another peak centered at 740 cm^{-1} indicates the amorphous and cross-link nature of the film [8]. Since the vibration frequency of C—F bonds in $=CF_2$ and $\equiv$ CF structures is in the region of 980–1400 cm^{-1}, therefore, some of the absorption peaks corresponding to C—F stretching mode are overlapped by the peak due to Si—O stretching mode at the band near 1080 cm^{-1}. Absorption for Si—F stretching vibration is found at 940 cm^{-1}, indicating some F atoms exist in the film as Si—F bonds. Especially, there are no stretching mode absorption peaks for C—H stretching vibration which should be found in the band near 2900 cm^{-1}. Because C—H bonds are easily detachable by ion bombardment during the film formation process, most of them are eliminated out of the film. The reduction of H incorporation will enhance the thermal stability [9] and the adherence ability of the film [10].

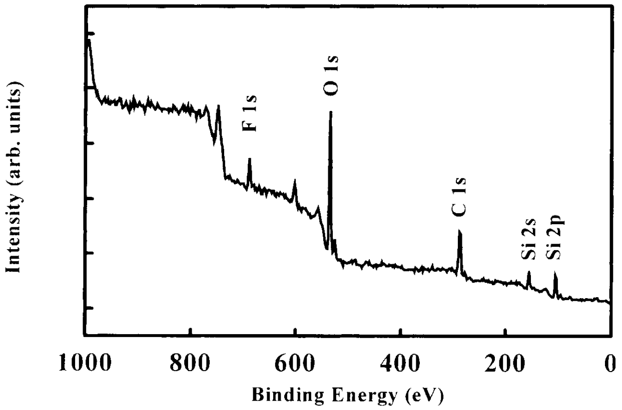

Fig. 2. XPS spectrum for α-SiCOF film deposited with C_4F_8 flow rate of 30 sccm

The chemical configuration of α-SiCOF films changes with the C_4F_8 flow rate during the deposition. Figure 4 shows a serial of FTIR spectra in the region of 980–1250 cm^{-1} for α-SiCOF films deposited with different C_4F_8 flow rates. It shows that with the flow rate of C_4F_8 increasing, the peak area due to $\equiv$ C—F structures centered at 1070 cm^{-1} is enlarged. The peak around 1050 cm^{-1} is for C—F bonds, the stability of the film will be improved when more $\equiv$ C—F structures exist in the film, because high content of $\equiv$ C—F structures will strengthen the cross-link nature of the amorphous film by cross-link in three dimensions. At the same time, Fig. 5 shows a series of FTIR spectra in the region of 3560–3740 cm^{-1} for α-SiCOF films deposited with different C_4F_8 flow rate. The absorption peak for the highly polarized Si—OH components at 3660 cm^{-1} is reduced with C_4F_8 flow rate increasing. In consideration of the contribution of Si—OH components to the orientation polarization, the reduction of Si—OH components will decrease the dielectric constant of the film. Therefore, varying C_4F_8 flow rate can modify the properties of films. Whereas, the increase of C_4F_8 flow rate will suppress the deposition rate because the increase in concentration of free radicals F· will enhance the etching process by the reaction with the film already formed.

2.2 Electric properties

Table 1 is the comparison of the electrical properties between SiOF film and α-SiCOF film deposited in this experiment. SiOF film with F concentration of 8.7 at.% is prepared using TEOS/SiF_4/O_2 mixture in the same PECVD system. α-SiCOF film with the fluorine content of 8.7 at.% and C content of 25.0 at.% is also formed. It can be seen from this table that the dielectric constant of the α-SiCOF film is much lower

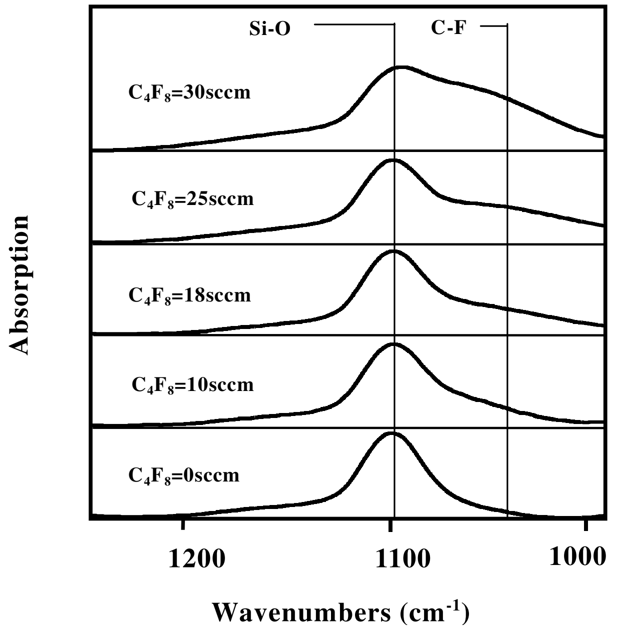

Fig. 4. A serial of FTIR spectra in the region of 980–1250 cm^{-1} for α-SiCOF films deposited with different C_4F_8 flow rates

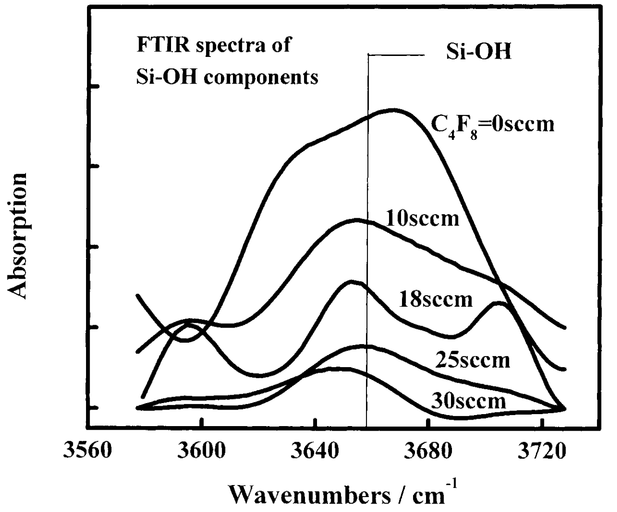

Fig. 5. FTIR spectra for Si–OH groups in the region of 3560–3740 cm^{-1}

than that of conventional SiOF film. At the same time, the leakage current density of the α-SiCOF film is reduced. The breakdown strength of the α-SiCOF film is also improved.

In the conventional SiOF films, fluorine plays an important role in reduction of dielectric constant. As reported in [11], the F incorporation will decrease the polarizabilty of Si–O bond and relax the structure of SiOF film, resulting in the reduction in dielectric constant. For a different mechanism, the reduction of dielectric constant of α-SiCOF film is due to the contribution of both C and F atoms incorporated in the film. As seen in Table 1, the two films have the same F content, whereas the difference of relative constant between two film is 0.91, indicating that C atoms contribute a lot to the decrease of dielectric constant of C-doped SiCOF film.

The dielectric constant comprises three components due to electronic, ionic, and orientational polarization and its value is frequency dependent. In the visible region, the dielectric constant results from only electronic polarization and is equal to the square of the refractive index. As Zhou et al. reported, carbon doping had almost no effect on the refractive index of SiO_2 film [5]. Thus, the contribution due to electronic polarization is not the major reason for dielectric constant decrease in the α-SiCOF film corresponding to carbon doping. The ionic polarization results from the displacement of atoms or ions in the electric field. For instance, in the film composed by $A^{\delta+}$–$B^{\delta-}$–$A^{\delta+}$–$B^{\delta-}$ network, the ions $A^{\delta+}$ and $B^{\delta-}$ move in the opposite direction when they are put in the electric field. The displacement of $A^{\delta+}$ and $B^{\delta-}$ will result in the ionic polarization. The ion polarization can be predicted using the formula [12]:

$$\alpha_i = \delta^2/(d^2u/dx^2) = \delta^2/k\,, \tag{1}$$

where δ is the partial charge on atom, x is the distance between A and B atoms, u is the potential energy of atom, and k is force constant of the bond. In the amorphous SiCOF film, the cross-link between carbon atoms results in a very small partial charge (δ) on C atom. In consideration of formula (1), the ionic polarization contribution to dielectric constant is also small when δ is small.

There should be no orientational polarization in pure SiO_2 film. However, in the process of depositing SiO_2 film with TEOS, Si–OH components were formed. The Si–OH components contribute a lot to the orientational polarization of SiO_2 films. It is reported that the orientational polarization of the SiOF film is reduced by the elimination of highly polarized Si–OH components. That is because F doped into the film will decrease the Si–OH components in SiOF film by replacing –OH group with F. For the same reason, the Si–OH components are reduced in α-SiCOF films. Furthermore, because the Si content is smaller than that in SiOF film, the Si–OH components are much fewer in α-SiCOF films. As has already been discussed,the Si–OH components are remarkably reduced with C_4F_8 flow rate increasing. Then, the major part of the difference of dielectric constant may stem from the reduction in ionic polarization and orientational polarization in α-SiCOF film.

In Table 1, comparing to SiOF film, the leakage current density of α-SiCOF film is reduced and its breakdown strength is increased. The improvements of these electric properties may result from the etching process accompanying the film deposition. The etching of F· radical will improve the planarity of film [5], at the same time, highly polarized components such as Si–OH and H–O–H will be removed

Table 1. Comparison of the electrical properties between SiOF film and α-SiCOF film

	Dielectric constant	Leakage current density (pA/cm^2 at 5 V/μm)	Breakdown strength (MV/cm)
SiOF film	3.51	155	8.4
α-SiCOF film	2.60	139	10.4

from the film. Therefore, the breakdown strength increases and leakage current density of the film decreases.

2.3 Moisture resistibility

We use the MAS (moisture absorption stress) test to measure the moisture resistibility of α-SiCOF film. In the MAS test, films were humidified in 80% r.h. at 80 °C for 3 h. FTIR spectra were taken before and after the MAS test. The FTIR spectra for α-SiCOF film deposited with C_4F_8 flow rate of 30 sccm almost have no change after the MAS test. Indicating α-SiCOF films are stable in moisture. As Yang et al. reported, Si−F reacts with H_2O and forms a strong polarized Si−OH groups [13]. The leakage current density and dielectric constant will increase after moisture absorption because the formation of Si−OH groups. In the FTIR spectrum of α-SiCOF film, the Si−OH peak area is small and it did not increase after the MAS test, which will result in the improvements in stability of leakage current density and dielectric constant of α-SiCOF film. The stability in moisture for SiCOF film may result from the hydrophobicity of C−F bonds. In [13], the reaction between C−F bonds and H−O−H was researched. Using, ab initio configuration interaction theory, the reaction energy of the reaction of $H_2O + 2C{-}F \longrightarrow 2HF + C{-}O{-}C$ was calculated and this reaction was found to be endothermic, therefore, less moisture was absorbed by reacting with C−F bonds in α-SiCOF film. On the contrary, the reaction between Si−F bond and H−O−H is exothermic. Since there are fewer Si atoms and Si−F bonds in α-SiCOF film and a great part of F atoms are combined with C, therefore, the incorporation of C−F bonds will result in the good moisture resistibility of the α-SiCOF films.

3 Conclusion

α-SiCOF films with improved electric properties and moisture resistibility are prepared by PECVD. Through FTIR and XPS analyses, the chemical composition and bonding construction are investigated. It is found that the ($\equiv$C−F structure concentration is increased and Si−OH components are reduced with C_4F_8 flow rate increasing. The incorporated hydrophobe C−F bonds will enhance the moisture resistibility of film. At the same time, since highly polarized Si−OH components are reduced, the contribution of orientational polarization will be decreased accordingly. The ionic polarization is also decreased because of the amorphous and cross-link nature of the film. In addition, the deposition of α-SiCOF films is accompanied by corrosion of F· free radicals, the planeness of films is improved and the micro-defects in the films are reduced. The breakdown strength and the bulk resistance of the film are also improved.

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