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Synthesis and Characterization of SiCOF/a-C:F Double-Layer Films with Low Dielectric Constant for Copper Interconnects*

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Abstract: A novel double-layer film of SiCOF/a-C:F with a low dielectric constant is deposited using a PECVD system. The chemical structure of the film is characterized with Fourier transform infrared spectroscopy (FTIR). The measurements of the film refractive index reveal that the optical frequency dielectric constant (n^2) of the film is almost constant as a function of air exposure time, however, with increasing annealing temperature, the value of n^2 for the film decreases. Possible mechanisms are discussed in detail. The analysis of SIMS profiles for the metal-insulator-silicon structures reveal that in the Al/a-C:F/Si structure, the annealing causes a more rapid diffusion of F in Al in comparison with C, but there is no obvious difference in Si. In addition, no recognizable verge exists between SiCOF and a-C:F films, and the SiCOF film acts as a barrier against the diffusion of carbon into the aluminum layer.

Key words: low dielectric constant material; FTIR; SIMS
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1 Introduction

In order to reduce the RC delay of ultra-large scale integrated (ULSI) circuits caused by the parasitic capacitance of multilevel interconnections, it is helpful to introduce low dielectric constant materials as interlayer dielectrics (ILD). Many materials with low dielectric constant have been developed in recent years. According to the International Technology Roadmap for Semiconductors (ITRS), we need materials with dielectric constants below 2.4 for copper interconnects for 65nm technology. Although the dielectric constant of fluorinated amorphous carbon (a-C:F) film may reach as low as 2.1[1,2], the a-C:F film has a low resistance to oxygen plasma and weak mechanical strength, which makes it unusable. We have developed a carbon and fluorine doped SiO_2 film (SiCOF) with a *k* value around 2.7 and good mechanical strength[3~6]. In this work, we deposited a novel double-layer film of SiCOF/a-C:F to try to synthesize the good properties of SiCOF with the low *k* value of a-C:F film. We first characterized this film using Fourier transform infrared (FTIR) spectroscopy, and then investigated the interface and stability of the SiCOF/CF double-layer film by dynamic secondary-ion-mass-spectrum (SIMS) and refractive index measurements.

2 Experiment

All films were deposited with a conventional parallel plate electrode plasma enhanced chemical vapor deposition (PECVD) system, which was described in our previous paper[6]. In the present study, the plasma was enhanced by a radio frequency (RF) of 13.56MHz. The radio frequency power was fixed at about 150W. The first layer film (a-C:F film) was deposited on the Si wafers, which were placed on the bottom electrode plate, rotating at a speed of about 10r/min to improve the temperature distribution on the bottom electrode and the

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uniformity of the deposited film thickness. Subsequently, the second layer film (SiCOF film) was deposited on the as-deposited SiCOF film. The typical deposition conditions are presented in Table 1. C_4F_8, CH_4, and TEOS were used as the feed gases, and were introduced into the reaction chamber through separated mass flow controllers, respectively. Argon was used as the balance gas. In the interest of observing the elemental profiles in metal-insulator-silicon (MIS) structure, a layer of aluminum was deposited on the film by evaporation, forming Al/a-C:F/Si and Al/SiCOF/a-C:F/Al structures. For the sake of investigating the thermal stability, all samples (the double-layer film and the MIS structures) were annealed for 15min at a specific temperature in 99.999% N_2.

Table 1 Typical deposition conditions for the double layer films

Film type	a-C:F film	SiCOF film
Flow rate/sccm	$CH_4=5$; $C_4F_8=21$	$C_4F_8=20$; TEOS = 15
Deposition temperature/℃	200	200
Deposition pressure/Pa	60	80

FTIR spectra of the films were obtained with the spectrometer (Model: AVATAR-360 IR, Nicolet Co.). SIMS profiles of the samples with a MIS structure were done on the SIMS system (Model: IMS-6f, Cameca Co.) with an oxygen gun. The thickness and refractive index of the film were determined with an ellipsometer at 632.8nm. The dielectric constant was determined by capacitance-voltage (*C-V*) measurements of the MIS structure at 1MHz.

3 Results and discussion

The double layer films of SiCOF/a-C:F measured 1μm thick. Figure 1 shows the FTIR spectra of the films. In comparison with a-C:F film, the spectrum of SiCOF film exhibits an evident difference. That is, a new peak at about 927cm^{-1} appears, indicating the existence of Si-F bonds. In the case of a-C:F film, the intense broad absorption peak around 1055cm^{-1} stems from CF_x vibrations[7]. However, as for the double layer film of SiCOF/CF, a shoulder peak at about 1145cm^{-1} should correspond to the out-of-plane oxygen motion of the $Si(O)_4$ configuration in the SiCOF film[8] since the asymmetric stretching of oxygen atoms along the direction parallel to Si-O-Si usually occurs at about 1062cm^{-1}[9]. The shift of the intense peak from 1055 to 1064.5cm^{-1} is due to the superimposition between them.

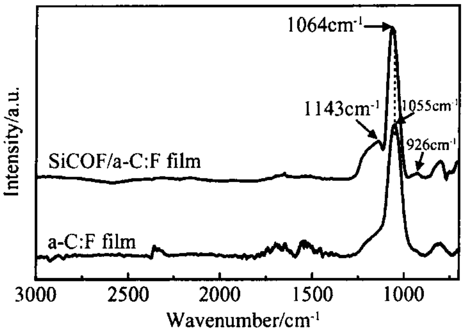

Fig. 1 FTIR spectra of the films in the region of 3000～700cm^{-1}

Owing to the fact that the refractive index (n) of film is related to certain film qualities, such as the amount of polarizable species, film composition, and film density, the dependence of n on the air exposure time and the annealing temperature is measured. Figure 2 shows the dependence of the optical frequency dielectric constant (n^2) on air exposure time and the annealing temperature. When the film is exposed to air for less than three days, n^2 is not stable and manifests a slight increase. After its exposure to air for four days, n^2 almost remains constant. This indicates that the double layer film has a strong resistance to water. For instance, the value of n^2 increases by about 0.46% when exposed to air for 10 days. If the film absorbs moisture from the air, it is possible that the hydrolysis of Si-F bonds in the film will take place, leading to the formation of Si-OH, and even to the presence of physically absorbed water in the film. These highly polarizable species can increase the refractive index of the film. On the other hand, n^2 decreases with increasing annealing temperature. This may be due to the loss of Si-OH and H_2O in the film. However, the thickness of the film increases with the annealing temperature, as indicated in Fig. 3. This suggests that the refractive index of the film is related to the thickness. Yoo et al.[10] reported that the stress of the SiOF film increases as the refractive index decreases. Accordingly, in some degree the decrease of the refractive index of the film with annealing temperature results from the increase in the film stress, which is accompanied by the increase of the film thickness due to thermal expansion. Of course, the increase in the film thickness also causes a decrease in the film density, which helps decrease the film's refractive index.

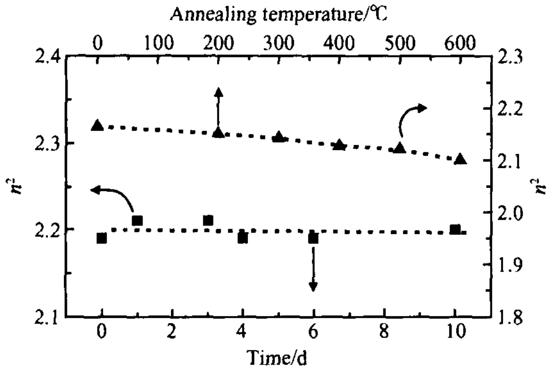

Fig. 2 Dependence of n^2 on air exposure time and annealing temperature

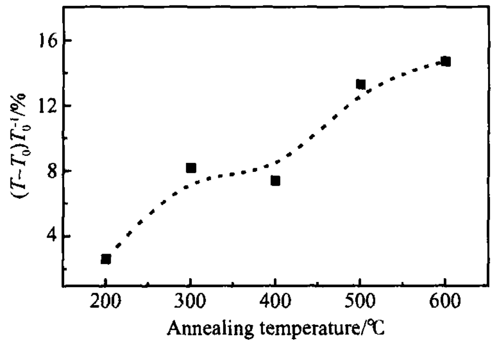

Fig. 3 Dependence of $(T-T_0)/T_0$ on annealing temperature T_0 and T represent the initial and subsequent thickness of the film, respectively.

Figure 4 shows the SIMS profiles of Al/ a-C :F/ Si before and after annealing, respectively. It can be seen that the annealing leads to diffusion of F and C into the Al film, and the diffusion of F is faster than that of C. However, the diffusion rates of F and C in silicon are almost equal with or without annealing. SIMS profiles of Al/ SiCOF/ a-C :F/ Si before and after annealing are shown in Fig. 5. In the case of the non-annealed sample, the SIMS profiles of C and F are almost symmetrical, as seen in Fig. 5(a). This indicates that the SiCOF film has a good adhesion to the a-C :F film. At the interface between Al and SiCOF, profile terraces of F and Si appear. This means that during the evaporation deposition of Al, some compounds with certain stoichiometric ratios are formed —possibly aluminum fluoride and silicide. After annealing at 350 ℃ for 10min the terrace of the F profile disappears, and its shape becomes distorted. This reveals that aluminum fluoride is not stable against annealing, and F atoms diffuse further into the aluminum layer. In addition, the terrace of the Si profile persists, suggesting that aluminum silicide is stable against annealing. From the profile of the Si between the Al layer and Si substrate, it can be seen that the intensity of Si increases monotonically without any step. This also demonstrates that no recognizable verge exists between SiCOF and CF films. Compa-

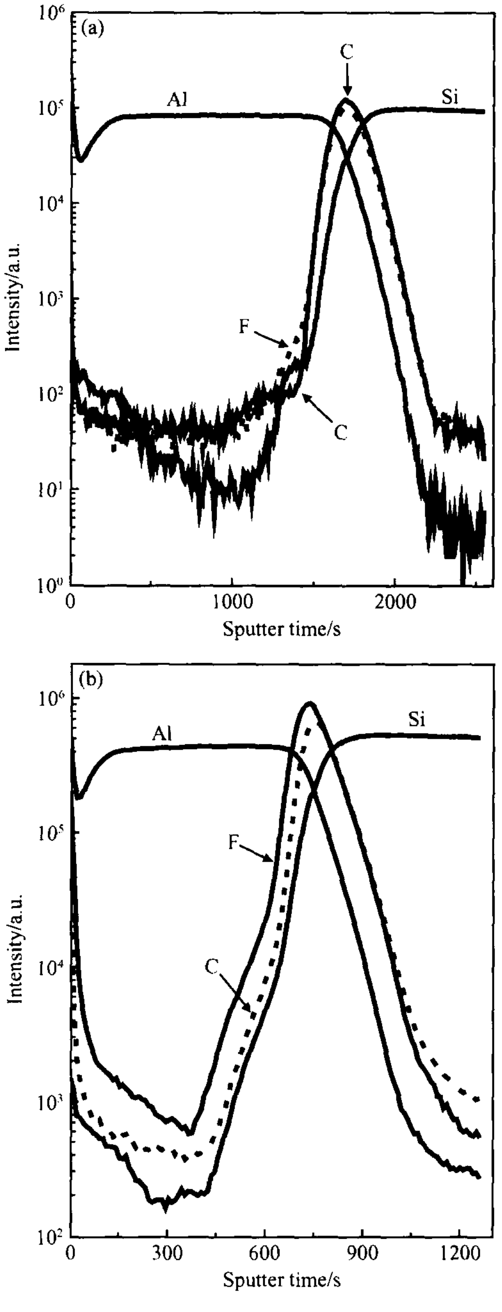

Fig. 4 SIMS profiles of the Al/ a-C :F/ Si structure without annealing (a) and with annealing at 350 ℃ for 10min in N_2 (b)

ring Fig. 5 (b) with Fig. 4(b), we find that the SiCOF film acts as a diffusion barrier of carbon into the aluminum layer according to the relative locations of the C and Si curves, which is mainly due to the formation of aluminum silicide.

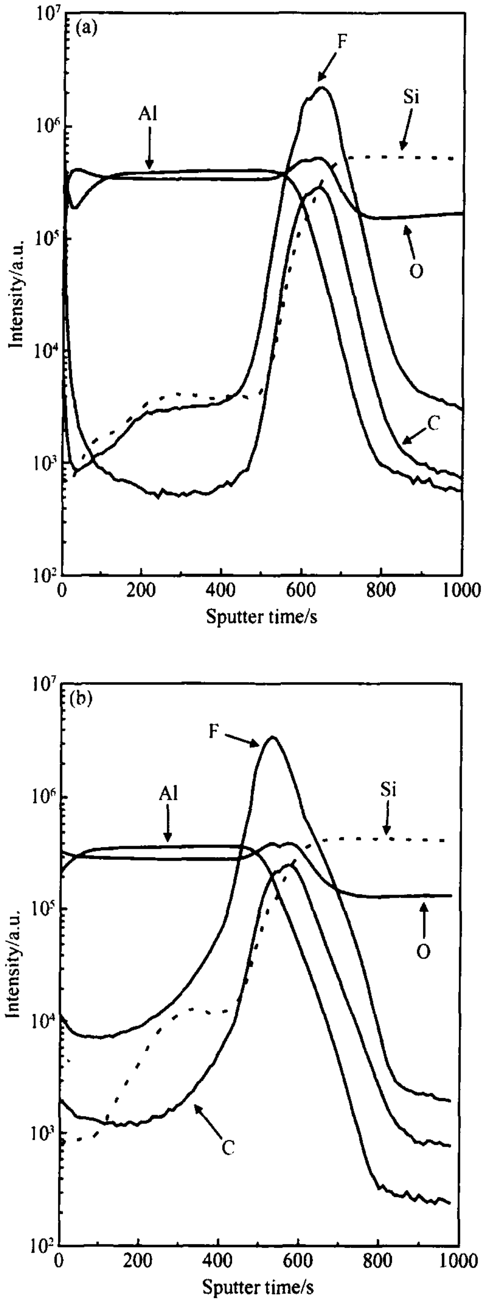

Fig. 5 SIMS profiles of the Al/SiCOF/a-C : F/Si structure without annealing (a) and with annealing at 350 ℃ for 10min in N_2 (b)

4 Conclusion

Using PECVD, we have first deposited a-C : F film from a mixture of C_4F_8/CH_4/Ar on silicon wafer and subsequently deposited another layer of SiCOF film on the a-C : F film from C_4F_8/TEOS/Ar. The measurements of the film's refractive index show that the optical frequency dielectric constant (n^2) of the film almost remains constant as air exposure time varies, suggesting that the double-layer films have excellent resistance to moisture. However, with the increase of annealing temperature, the value of n^2 for the film decreases. There are three possible reasons for this: (1) a loss of highly polarizable Si - OH and H_2O in the film; (2) an increase in the film stress; and (3) a decrease in the film density. The SIMS profiles of the Al/a-C : F/Si structure reveal that annealing causes a more rapid diffusion of F in Al in comparison with C, but there is no obvious difference in Si. The SIMS profiles of the Al/SiCOF/a-C : F/Si structure show that no recognizable verge exists between SiCOF and CF films, and during the evaporation deposition of Al some compounds with certain stoichiometric ratios are formed ——possibly aluminum fluoride and silicide. On the other hand, the SiCOF film acts as a barrier against the diffusion of carbon into the aluminum layer.

References

[1] Endo K, Tatsumi T. Fluorinated amorphous carbon thin films grown by plasma enhanced chemical vapor deposition for low dielectric constant interlayer dielectrics. J Appl Phys, 1995, 78 (2): 1370

[2] Endo K, Tatsumi T, Matsubara Y. Deposition of silicon dioxide films on amorphous carbon films by plasma enhanced chemical vapor deposition for low dielectric constant interlayer dielectrics. Appl Phys Lett, 1997, 70(9): 1078

[3] Wang P F, Ding S J, Zhang D W, et al. An amorphous SiCOF film with low dielectric constant prepared by plasma-enhanced chemical vapor deposition. Thin Solid Films, 2001, 385 (1/2): 115

[4] Ding S J, Zhang Q Q, Zhang D W, et al. Copper metallization of low-dielectric-constant a-SiCOF films for ULSI interconnects. J Phys: Conden Mater, 2001, 13 (31): 6595

[5] Ding S J, Zhang D W, Wang J T, et al. Chemical bonding of magnetron-sputtered copper on PECVD amorphous SiCOF film. Appl Surf Sci, 2003, 206 (1~4): 321

[6] Wang P F, Ding S J, Zhang J Y, et al. Low-dielectric-constant a-SiCOF film for ULSI interconnection by PECVD with TEOS/C_4F_8/O_2. Appl Phys A, 2001, 72(6): 721

[7] Limb S J, Gleason K K, Edell D J, et al. Flexible fluorocarbon wire coatings by pulsed plasma enhanced chemical vapor deposition. J Vac Sci Technol A, 1997, 15(4): 1814

[8] Lucovsky G, Wong C K, Pollard W B. Vibrational properties of glasses-intermediate range. J Non-Cryst Solids, 1983, 59/

60:839

[9] Ding S J, Wang P F, Zhang D W, et al. The influence of Ar addition on the structure of a-SiOCF film prepared by plasma-enhanced chemical vapor deposition. J Phys D: Appl Phys, 2001, 34(2): 155

[10] Yoo W S, Swope R, Mordo D. Plasma enhanced chemical vapor deposition and characterization of fluorine doped silicon dioxide films. Jpn J Appl Phys, 1997, 36(1A): 267

铜互连中 SiCOF/a-C∶F 双层低介电常数薄膜的制备和表征*

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摘要：用等离子体化学气相淀积系统制备了一种新颖的 SiCOF/a-C∶F 双层低介电常数介质薄膜，并用红外光谱表征了该薄膜的化学结构. 通过测量介质的折射率发现该薄膜长时间暴露在空气中，其光频介电常数几乎不变. 然而，随退火温度的增加，其光频介电常数则会减小. 基于实验结果讨论了几种可能的机理. 二次离子质谱分析表明在 Al/a-C∶F/Si 结构中 F 和 C 很容易扩散到 Al 中，但在 Al/SiCOF/a-C∶F/Si 结构中，则没有发现 C 的扩散，说明 SiCOF 充当了 C 扩散的阻挡层. 分析还发现在 SiCOF 和 a-C∶F 之间没有明显的界面层.

关键词：低介电常数介质；FTIR；SIMS

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