Vol 10 No 4, April 2001
1009-1963/2001/10(04)/0324-05

Chinese Physics

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ANALYSIS OF THE X-RAY PHOTOELECTRON SPECTRA OF a-SiOCF FILMS PREPARED BY PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION*

DING SHI-JIN(丁士进)[a], WANG PENG-FEI(王鹏飞)[a], ZHANG WEI(张 卫)[a], WANG JI-TAO(王季陶), and WEI WILLIAM LEE[b]

[a] *Department of Electronic Engineering, Fudan University, Shanghai* 200433, *China*

[b] *Taiwan Semiconductor Manufacturing Co. (TSMC), Hsinchu, Taiwan, China*

(Received 8 August 2000; revised manuscript received 19 October 2000)

The preparation of a-SiOCF films from $Si(OC_2H_5)_4$, C_4F_8 and/or Ar using the plasma-enhanced chemical vapour deposition method is reported. The chemical bonding structures of the films are analysed by x-ray photoelectron spectroscopy (XPS). In the case of the films deposited from the mixture with and without Ar, the configurations of F–Si–O–Si, Si–OH, Si–O–Si, C–CF and C–F are contained. However, there is also the C–C configuration in the film prepared from the mixture with Ar. Moreover, it is found that the photoelectron peaks of Si 2p, O 1s and F 1s for the film deposited from the feeding gas with Ar show the same shift of about 1eV toward high binding energy in comparison with those for the film prepared from the feeding gas without Ar. No evidence reveals the presence of an Si–C bond in the films.

Keywords: a-SiOCF film, plasma-enhanced chemical vapour deposition, x-ray photoelectron spectrum

PACC: 6000, 6855, 8140

I. INTRODUCTION

As device dimensions decrease to less than 0.25μm, the smaller metal-interconnect lines and narrower interline space induce an increase in the interconnect delay (i.e. $\tau = RC$), propagation delay, crosstalk noise and power dissipation become significant and limit an improvement in device performance.[1] In order to reduce the RC delay, we may use the low resistivity metal Cu as the metal-interconnect lines instead of the conventional Al alloy, and/or low dielectric constant (k) materials as the interconnect dielectrics. In the case of reducing wiring capacitance, many low k materials have been developed.[2–6] One of these, amorphous carbon- and fluorine-doped silicon oxide (a-SiOCF), has been investigated by several research groups recently.[7–11] This material exhibits a significant improvement in the water resistivity, good thermal stability and adhesion on a silicon substrate, a dielectric constant of about 2.5, about 91% step-coverage in 0.3μm metal pattern and good electricity properties. In this paper, we report the achievement of a-SiOCF films from novel raw materials, and investigate the influence of Ar in the plasma on the chemical bonding structures of the films.

II. EXPERIMENTAL DETAILS

a-SiOCF films were deposited on Si substrates using a conventional parallel plate electrode plasma-enhanced chemical vapour deposition (PECVD) system, described in our previous paper.[10] In our experiments, the plasma was enhanced by a radio frequency (RF) of 13.56 MHz. The radio frequency power was fixed at 50W. The substrate was kept at about 100°C. C_4F_8 and $Si(OC_2H_5)_4$ (TEOS) were used as the feeding gas, which were introduced into the reaction chamber through mass flow controllers, respectively. Ar was used as the balance gas. The TEOS liquid source was stored in a stainless steel container, and no carrier gas was used due to the relative low process pressure. The typical deposition conditions are shown in Table 1. X-ray photoelectron spectroscopy (XPS) spectra of the films were collected by an x-ray photoelectron spectrometer (MicroLab 310-F, VG Scientific, The Surface Analysis Company) using an Mg K_α source with an energy of 1253.6eV. In the interest of fitting the XPS spectra, the spectra were smoothed using the Savitzky–Golay method, and then corrected using a baseline. When fitting the spectra, we adopted the principle of the gradual increase in peaks, and assigned the binding energy (BE) of each peak to a

*Project supported by the National Natural Science Foundation of China (Grant No. 69776026) and Foundation for University Key Teacher by the Ministry of Education of China.

possible BE region. If the fitted curve is in good accordance with the original one, it will be thought that the result is reasonable.

Table 1. The typical deposition conditions of films.

Feeding gas	$TEOS/C_4F_8/Ar$	$TEOS/C_4F_8$
Flow rate	TEOS=15sccm; C_4F_8=18.5sccm	TEOS=15sccm; C_4F_8=18.5sccm
Working pressure	70Pa	40Pa

Ⅲ. RESULTS AND DISCUSSION

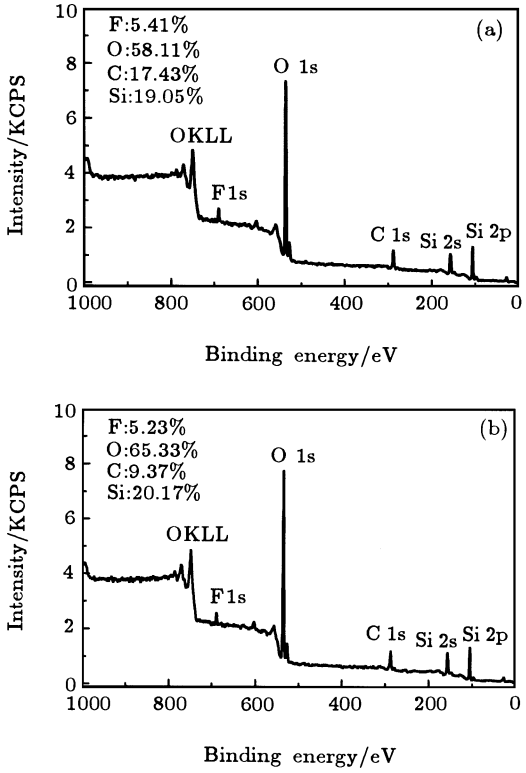


Fig.1. XPS survey spectra of the films deposited from the feeding gas (a) with Ar and (b) without Ar.

The XPS survey spectra of the films deposited from the mixtures with or without Ar indicate that the films are composed of silicon, carbon, oxygen and fluorine, as shown in Fig.1. According to the elemental sensitivity factor method, the relative concentrations of elements can be obtained from formula (1), and the relative contents of the same elemental atoms located at different chemical states can be calculated according to formula (2).

$$X_A = \frac{I_A/S_A}{\sum_i I_i/S_i} \tag{1}$$

$$N_k = \frac{I_k}{\sum_i I_i} \tag{2}$$

where S is the relative sensitivity factor by taking F 1s as a criterion, I is the area of the photoelectron peak. The relative concentrations of Si, C, O and F in the films are presented in Fig.1. From the results it can be found that the addition of Ar causes a decrease in oxygen concentration and an increase in carbon concentration in the film, and the concentrations of silicon and fluorine do not vary significantly. Notably, since the plasma polymeric film contains free radicals, therefore, when it is exposed to the atmosphere, these free radicals easily combine with oxygen and water, which will lead to an increase in oxygen concentration on the surface of the film.[12]

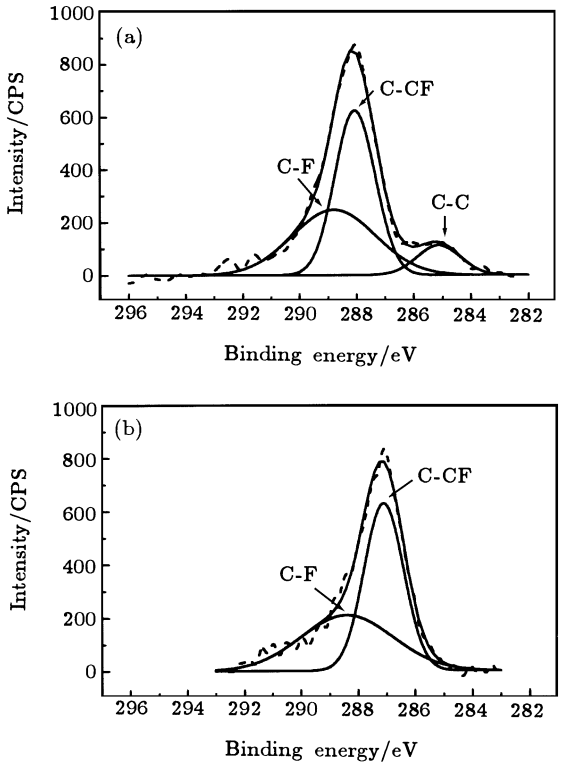


Fig.2. High-resolution C 1s spectra with Gaussian components of the films deposited from the feeding gas (a) with Ar and (b) without Ar.

The high-resolution C 1s XPS spectra of the films are indicated in Fig.2. In the case of the C 1s spectrum of the film deposited from the mixture with Ar, as seen in Fig.2(a), it can be found that the interesting region is 283–293eV. The interesting region of the

C 1s spectrum in Refs.[9, 13] for a-SiCOF film is in the region of 283–296eV, which is deconvoluted into four components. Accordingly, it is reasonable to use three components to fit the C 1s spectrum in the 283–293eV region. In fact, the attempts to reduce and increase the number of peaks are unsuccessful due to the obvious deviation between the fitted curve and the original and the existence of a very small BE difference. The three peaks obtained by Gaussian distribution fitting locate at about 285eV, 288eV and 288.8eV, respectively. The two peaks at around 285eV and 289eV should be attributed to C–C and C–F, respectively.[9,13] The peak around 288eV is assigned to C–CF.[14] From peak areas it can be concluded that C–C, C–CF and C–F configurations account for about 10%, 50% and 41%, respectively. Regarding the C 1s spectrum of the film deposited from the mixture without Ar, the 285–293eV region is of interest. Therefore, two Gaussian components are used to fit the spectrum, the obtained peaks appear at about 287eV and 288.4eV, which should be assigned to C–CF[9,13] and C–F[15], respectively. The percentages of C–CF and C–F configurations are equal

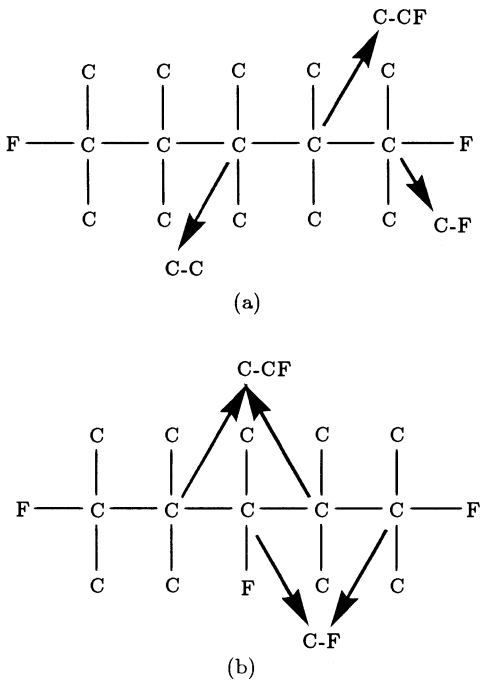


Fig.3. The structures of the fluorocarbons in the films deposited from the feeding gas (a) with Ar and (b) without Ar.

to about 56% and 44%, respectively. Evidently, the peak corresponding to C–C disappears. The structures of the fluorocarbons in the films may be described in Fig.3. Moreover, the absence of the peak at about 283.4eV, which is characteristic of C 1s electrons in Si–C bond, reveals that there is no Si–C bond in the films.[16,17] This indicates that the fluorocarbon is embedded in the SiOF matrix.

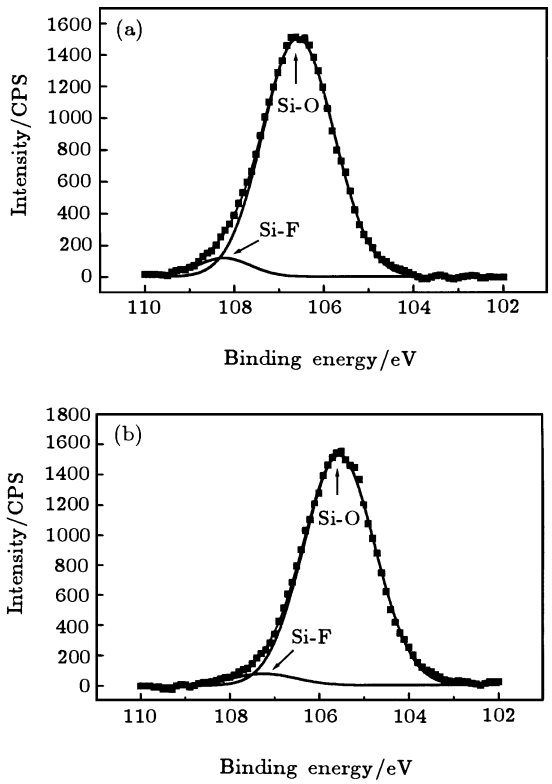


Fig.4. High-resolution Si 2p spectra with Gaussian components of the films deposited from the feeding gas (a) with Ar and (b) without Ar.

Figure 4 is high-resolution Si 2p XPS spectra. Two peaks are obtained for each spectrum by Gaussian distribution fitting. The attempt to fit the spectrum with one Gaussian component is not successful because of disagreement between the original and the fitted curve. Furthermore, the attempt to increase the Gaussian components also fails as a result of the occurrence of peak overlap or blurry BE difference. In consideration of the existence of Si–F and Si–O bonds in the SiO_2:C, F films, confirmed by FTIR spectrum,[9,10] the two peaks should result from Si–F and Si–O. The BE shift can be qualitatively understood using the spherical potential model for an atom;[18] that is, the BE of core electrons represents a balance between the attractive force of the positive nucleus and the repulsive force of valence electrons which are assumed to lie on the surface of a sphere. If the effective positive charge on an atom is larger, photoelectrons from the core level of the atom will then appear at higher BE. Since the Pauling electronegativity value for F (4.0) is larger than that for O (3.65), the effective positive charge on the Si atom of the Si–

F bond is larger than that of the Si–O bond. As a consequence, the photoelectrons from the Si 2p core level of Si–F should appear at higher BE in comparison with Si–O. For the Si 2p spectrum of the film deposited from the feeding gas with Ar, the two peaks at 106.6eV and 108.2eV correspond to Si–O and Si–F, respectively. According to the peak areas, it can be found that the relative concentrations of Si–O and Si–F configurations are about 94% and 6%, respectively. This indicates that Si–O bonds dominate in the film in comparison with Si–F bonds, which is also in accord with the relative concentrations of elements calculated by XPS measurements. As for the Si 2p spectrum of the film deposited from the feeding gas without Ar, the two peaks corresponding to Si–O and Si–F locate at 105.5eV and 107.2eV, and account for 95.5% and 4.5%, respectively. Obviously, the two peaks exhibit a shift of about 1eV in the direction of lower binding energy. We believe that this shift has a large contribution to the outside relaxation effect induced by the atoms or molecules around Si atoms, because the

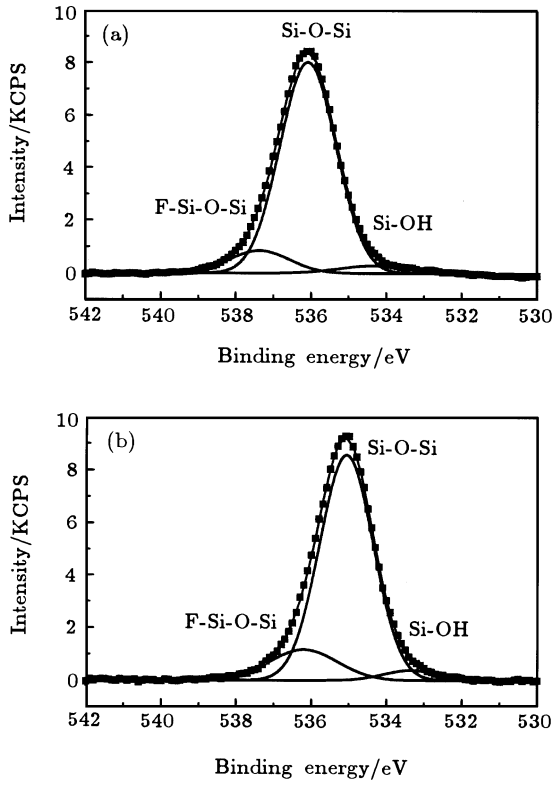


Fig.5. High-resolution O 1s spectra with Gaussian components of the films deposited from the feeding gas (a) with Ar and (b) without Ar.

fluorocarbon incorporated into the film deposited from the mixture with Ar is different from that of the mixture without Ar.

Similarly, the high-resolution O 1s spectra of the two films are separated into three Gaussian components, as shown in Fig.5. This reveals that oxygen atoms have three chemical states in the two films. It can be believed that they are due to F–Si–O–Si, Si–O–Si and Si–OH configurations. In the case of the O 1s spectrum of the film deposited from the mixture with Ar, the three peaks locate at 537.4eV, 536.1eV and 534.3eV, respectively. It is well known that the binding energy of atom core electrons depends on the effective charge distribution on the atom. When the effective negative charge on an atom increases, the BE of the atom core electrons will decrease.[18] According to the elemental electronegativity, it can be inferred that the effective negative charge distribution on an oxygen atom of F–Si–O–Si, Si–O–Si and Si–OH is in the sequence of F–Si–O–Si<Si–O–Si<Si–OH, so the peaks at 537.4eV, 536.1eV and 534.3eV should be assigned to F–Si–O–Si, Si–O–Si and Si–OH, respectively. They account for 10%, 86% and 4% respectively on the basis of peak areas. As for the O 1s spectrum of the film deposited from the mixture without Ar, the peaks corresponding to F–Si–O–Si, Si–O–Si and Si–OH configurations locate at 536.2eV, 535.1eV and 533.4eV, which account for 14%, 82% and 4%, respectively. Similarly, the decrease of about 1eV in the binding energy can be observed.

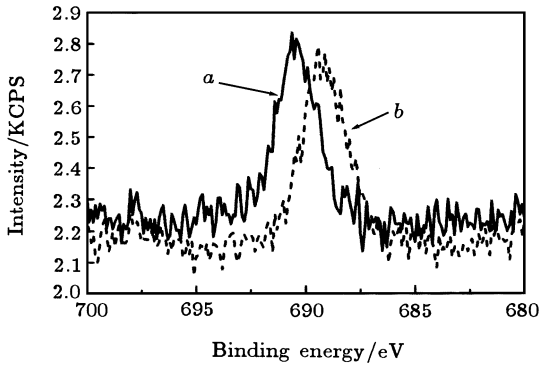


Fig.6. High-resolution F 1s spectra of the films deposited from the feeding gas (a) with Ar and (b) without Ar.

Owing to a small amount of fluorine atoms in the films, the intensity of the F 1s signal is very weak, and the signal-to-noise ratio is not perfect, as described in Fig.6. Therefore, it is difficult to obtain accurate information about fluorine chemical states by Gaussian distribution fitting. In addition, the shift of about 1eV in the direction of low binding energy is also observed in comparison with the F 1s spectrum of the film deposited from the mixture without Ar.

In a word, the influence of Ar addition on the bonding configurations of silicon, oxygen and fluo-

rine is not evident. However, the bonding configuration of carbon is affected seriously by the addition of Ar. As mentioned above, the presence of Ar in the plasma leads to the formation of fluorocarbon with a higher degree of cross-linked structure. It is reported that one of the origins of the poor thermal stability for the fluorocarbon is the reduction of a cross-linked structure,[19] so it can be expected that the film deposited from TEOS/C_4F_8/Ar has an excellent thermal stability. In view of the different structures of the fluorocarbons in the films deposited from the feeding gas with and without Ar, we think Ar addition shifts the electron energy distribution function towards higher energy in the plasma,[20] high energetic electrons cause the sufficient dissociation of TEOS and C_4F_8. Accordingly, a large amount of carbon free radicals are produced in addition to Si and F free radicals. When one carbon free radical combines with four other carbon free radicals, the configuration of the carbon atom surrounded by four C–C bonds is formed. Of course, there are also some species containing Si–O, C–F, C–O and C–H etc. However, CO and H species on the film are volatile and easily detachable by ion bombardment, so the main bonds in the film are Si–F, Si–O, C–F and C–C.

IV. CONCLUSION

We have prepared a-SiOCF films from TEOS, C_4F_8 and/or Ar by PECVD method. Under our experimental conditions, the deposited films contain F–Si–O–Si, Si–OH, Si–O–Si, C–CF and C–F configurations. However, in the presence of Ar in the plasma, the deposited film contains a C–C configuration in addition to the above-mentioned configurations. That is to say, the addition of Ar to the feeding gas causes the formation of the fluorocarbon with a higher degree of cross-linked structure. Moreover, no sign manifests the existence of the Si–C bond, indicating that the fluorocarbons are embedded in the matrix of SiOF. In the case of the film deposited from the feeding gas with Ar, the photoelectron peaks of Si 2p, O 1s and F 1s show the same shift of about 1eV towards a high binding energy in comparison with the film deposited from the mixture without Ar. This might be due to the outside relaxation effect induced by the atoms or molecules around the core atom.

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