Effect of F doping on capacitance–voltage characteristics of SiCOH low-k films metal–insulator–semiconductor structure*

Ye Chao(叶 超)† and Ning Zhao-Yuan(宁兆元)

School of Physics Science and Technology, Jiangsu Key Laboratory of Thin Films, Soochow University, Suzhou 215006, *China*

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This paper investigates the capacitance–voltage (C–V) characteristics of F doping SiCOH low dielectric constant films metal–insulator–semiconductor structure. The F doping SiCOH films are deposited by decamethylcyclopentasiloxane (DMCPS) and trifluromethane (CHF_3) electron cyclotron resonance plasmas. With the CHF_3/DMCPS flow rate ratio from 0 to 0.52, the positive excursion of C–V curves and the increase of flat-band voltage V_{FB} from −6.1 V to 32.2 V are obtained. The excursion of C–V curves and the shift of V_{FB} are related to the change of defects density and type at the Si/SiCOH interface due to the decrease of Si and O concentrations, and the increase of F concentration. At the CHF_3/DMCPS flow rate ratio is 0.12, the compensation of F-bonding dangling bond to Si dangling bond leads to a small V_{FB} of 2.0 V.

Keywords: F-SiCOH, low-k dielectrics, capacitance–voltage characteristic
PACC: 7755, 6855

1. Introduction

In order to address the problems caused by the size shrinking continuously in ultralarge-scale integrated chips, such as the RC signal delay, dissipation and cross-link between metal interconnects, porous low dielectric constant (low-k) and ultralow-k materials have been paid great attention.[1−7] The porous SiCOH film prepared by plasma-enhanced chemical vapour deposition (PECVD) becomes a promising candidate for its excellent performance. The dielectric constant (k value) of porous low-k films is mainly reduced by increasing the film porosity. However, the high porosity may lead to the mechanical property deterioration, Cu diffusion and water or contaminant absorption. In order to improve the film properties and still keep a lower k value, the method of preparing low-k materials by combining weak polar bonds with low density pores has attracted much attention,[8−10] such as the F-doping SiCOH film composed of weak Si–F bond and porous Si–O cage.

During depositing F-doping SiCOH films by PECVD, two groups of source gases are usually chosen.[11] One is the separate silicon and fluorine sources, such as SiH_4/CF_4 and $TEOS/C_2F_6$. The other is a single precursor containing both silicon and fluorine, such as SiF_4. With the single precursor, the native Si–F_x bonds can be directly built into the SiO network. But for the separate silicon and fluorine sources, the reaction between silicon and fluorine sources may lead to the deposition of F-doping SiCOH films or the etching of SiCOH films. Therefore, the F doping will affect the structure and properties of films.

In our previous works, we have used decamethylcyclopentasiloxane (DMCPS) and trifluromethane (CHF_3) as the silicon and fluorine sources to deposit F-SiCOH films.[8,12−14] We found that the increase of F doping content led to the structural evolution from SiCOH to Si-doping COF and further to COF films,[12] the decrease of k value from 3.19 to 2.48,[13] the change of film compositions and hydrophobic property,[14] and the n-type dependence of deposition rate on CHF_3/DMCPS flow rate ratio.[12] By analysing the characteristics of CHF_3/DMCPS, we presented that the competition between the deposition of F-doping SiCOH films and the etching of SiCOH films led to the variation of the structure and properties of films.[12]

The capacitance–voltage (C–V) characteristic is an important property for the low-k films application. However, the effect of F doping on C–V characteristic of SiCOH low-k films remains unclear. This paper investigates the C–V characteristic of F doping SiCOH films.

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†Corresponding author. E-mail: cye@suda.edu.cn
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2. Experiment

In the experiment, the films were deposited in an electron cyclotron resonance (ECR) plasma system. The details of ECR system have been described previously.[8,15] The DMCPS (> 98%) and CHF_3 (99.999%) were used as the source gases. The CHF_3/DMCPS flow rate ratio R was chosen as 0, 0.12, 0.24, 0.32 and 0.52. The C–V measurement of Al/F–SiCOH/Si/Al metal–insulator–semiconductor (MIS) structure was carried out by an HP4294A impedance analyser at 1 MHz. The n-Si (100) wafer (5–8 Ω·cm) was used as the substrate. The diameter of top Al electrode was 1.1 mm. The backside electrode was used to obtain a good contact. The thicknesses of films were in the range of 170–600 nm, which were measured by ET350 profiler with the resolution of 10 nm.

From the C–V curve, the flat-band voltage $V_{\rm FB}$ was obtained according to the flat-band capacitance $C_{\rm FB}$ given by[16]

$$C_{\rm FB} = \frac{\varepsilon_{\rm ox}}{t_{\rm ox} + \left(\frac{\varepsilon_{\rm ox}}{\varepsilon_{\rm s}}\right)\sqrt{\left(\frac{kT}{q}\right)\left(\frac{\varepsilon_{\rm s}}{qN_{\rm A}}\right)}}, \quad (1)$$

where $t_{\rm ox}$ was the thickness of films, $\varepsilon_{\rm ox}$ was the relative dielectric constant of films, $\varepsilon_{\rm s}$ was the relative permittivity of Si wafer, k was Boltamann's constant, T was the temperature, and $N_{\rm A}$ was the doping density given by[17]

$$\frac{\partial(1/C^2)}{\partial V} = \frac{2}{q\varepsilon_0\varepsilon_{\rm s}N_{\rm A}A^2}, \quad (2)$$

where C was the capacitance in the depletion region, V was the gate bias, and A was the area of top electrode.

To understand the effect of F doping on C–V characteristic, the compositions and bonding configurations of the F-doping SiCOH films were analysed. The compositions of films were measured by a Kratos XSAM-800 x-ray photoelectron spectroscopy (XPS) with Al Kα irradiation (1486.6 eV) at the resolution of 0.9 eV. The surface cleaning was applied on the films in the XPS chamber with 3 keV Ar^+ ions (10 μA/cm^2, 5 min). The bonding configurations of films were characterized by a JASCO 600 Plus Fourier transform infrared (FTIR) spectroscopy in the wavenumber range of 600–4000 cm^{-1} with the resolution of 3 cm^{-1}. The FTIR data were analysed by using the JASCO Spectra Analysis program. To analyse the reaction in the plasma, the species were measured by an optical emission spectroscopy (OES) (Ocean Optics, S2000 miniature fibre optic spectrometer) in the wavelength range of 200–800 nm with the resolution of 0.35 nm.

3. Results and discussion

The normalized C–V curves of the films deposited at different CHF_3/DMCPS flow rate ratio are shown in Fig. 1. Without the F doping ($R = 0$), the C–V curve shows a negative excursion. With the F doping, the positive shift of C–V curves is seen. At $R = 0.12$, a steep C–V curve without smear is obtained. With the R increase, however, the smeary C–V curves appear. From the C–V curves, the flat-band voltages $V_{\rm FB}$ are obtained, as shown in Fig. 2. Without the F doping ($R = 0$), the $V_{\rm FB}$ has a negative value (−6.1 V). With the F doping and at $R = 0.12$, a small positive $V_{\rm FB}$ (2.0 V) is obtained. With the further increase of R to 0.52, the $V_{\rm FB}$ increases continuously to 32.2 V. The results show that the F doping in the SiCOH films leads to the positive excursion of C–V curves and the positive flat-band voltage $V_{\rm FB}$.

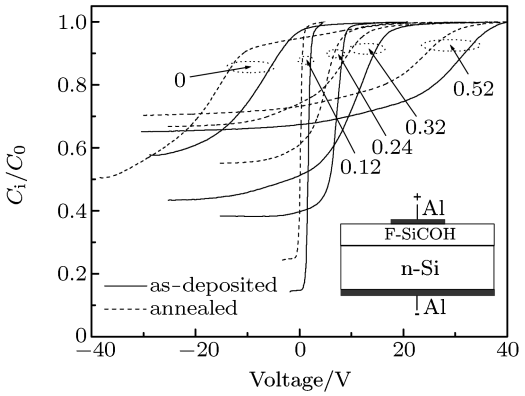


Fig. 1. C–V curves of the as-deposited films and the annealed films deposited at the CHF_3/DMCPS flow rate ratio of 0 to 0.52.

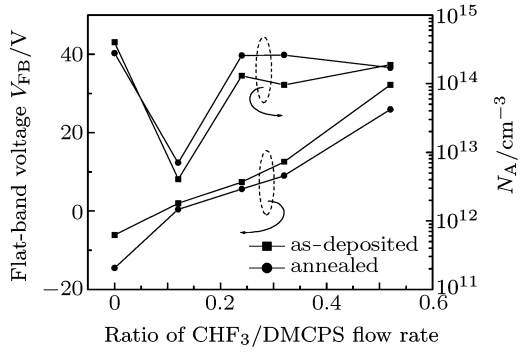


Fig. 2. Dependence of flat-band voltage $V_{\rm FB}$ and doping density $N_{\rm A}$ on CHF_3/DMCPS flow rate ratio.

The excursion of C–V curves is related to the interface states, which may be from the Si dangling bond or the charged ions at the Si/SiO interface.[18] The flat-band voltage V_{FB} depends on the type of charged ion at the interface. The negative V_{FB} is due to the existence of positive charged ion at the interface.[19] For the SiCOH low-k films, the interface states are attributed to the defects associated with excess silicon or excess oxygen at or near the Si/SiCOH interface.[20] But for the F-doping SiCOH films, the interface states may also include the dangling bond defect located near the F-bonding site[21] except for the defects from excess silicon or excess oxygen. Therefore, the effect of F doping on C–V characteristic of SiCOH films is more complex.

To identify the possible factors affecting the C–V characteristic of F-doping SiCOH films, the compositions and bonding configurations of the F-doping SiCOH films are analysed. The XPS spectra of the films deposited at the CHF_3/DMCPS flow rate ratio of 0, 0.24, 0.32 and 0.52 are shown in Fig. 3.

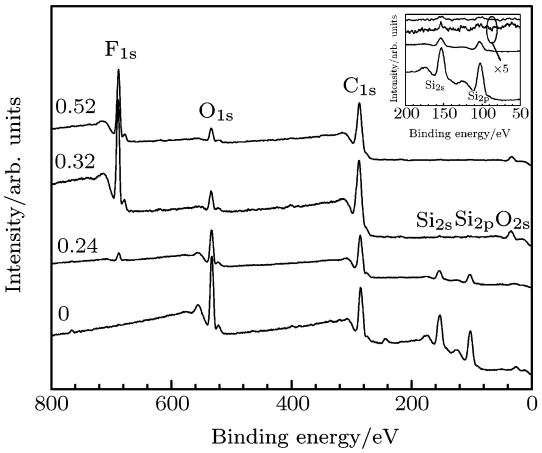


Fig. 3. The XPS spectra of the films deposited at the CHF_3/DMCPS flow rate ratio of 0, 0.24, 0.32 and 0.52.

The relative concentrations of Si, O, C and F elements at different CHF_3/DMCPS flow rate ratio are shown in Fig. 4, which are calculated from the intensities of Si_{2p} (102.25 eV), C_{1s} (284.95 eV), O_{1s} (532.75 eV) and F_{1s} (688.50 eV) peaks. With the increase of CHF_3/DMCPS flow rate ratio, the Si and O concentrations decrease, the F concentration increases, while the C concentration has a small variation. Therefore, the Si, O and F are mainly factors affecting the C–V characteristics. The FTIR spectra of the films deposited at the CHF_3/DMCPS flow rate ratio of 0, 0.12, 0.24, 0.32 and 0.52 are shown in Fig. 5. At $R = 0$, the bonding configurations of SiCOH film include the Si–H (2179 cm^{-1}), Si–CH_3(1264 cm^{-1}), Si–O–Si (1013 cm^{-1}), H–Si–O (869 cm^{-1}) and Si–O (821 cm^{-1}). With the F addition ($R = 0.12 - 0.32$), the bonding configurations include the Si–O–Si (from 1090 cm^{-1} to 1097 cm^{-1}), C–F_2 (1153 cm^{-1}), Si–F (from 916 cm^{-1} to 934 cm^{-1}), Si–O (814 cm^{-1}), $(CH_2)_n$ (724 cm^{-1}) and C=C (1659 cm^{-1}). The absorption peaks of Si–H and Si–CH_3 disappear. With the further increase of F ($R = 0.52$), the bonding configurations include the C—F_2 (1153 cm^{-1}, 1274 cm^{-1} and 1343 cm^{-1}), C=C (1659 cm^{-1}), C=O (1840 cm^{-1}) and $(CH_2)_n$ (723 cm^{-1}). The absorption of Si–O–Si peak decreases.

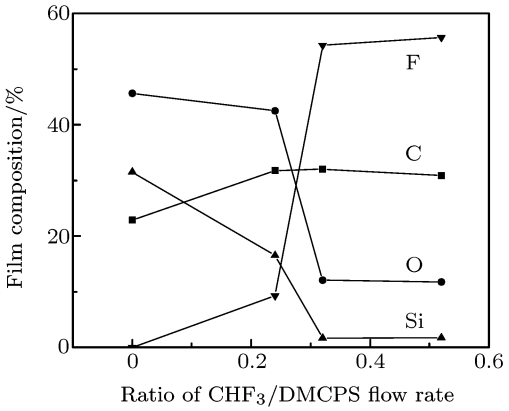


Fig. 4. Dependence of relative concentrations of Si, O, C and F elements on CHF_3/DMCPS flow rate ratio.

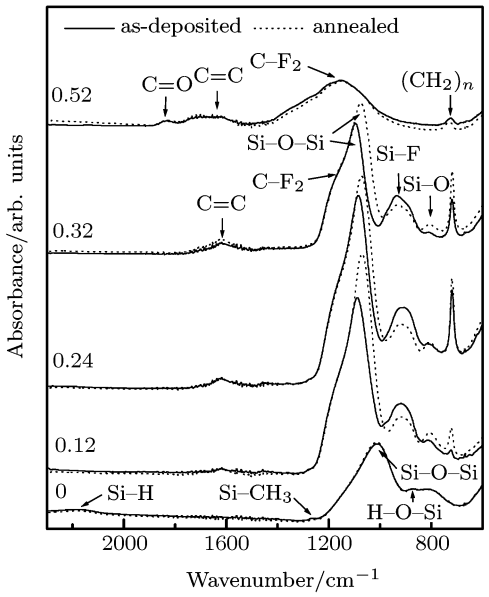


Fig. 5. The FTIR spectra of the as-deposited films and the annealed films deposited at the CHF_3/DMCPS flow rate ratio of 0 to 0.52.

According to above results, the effect of F doping on C–V characteristic can be discussed as follows.

Without the F doping ($R = 0$), the high Si and O concentrations lead to more defects associated with the Si and O dangling bonds. As a result, a high doping density N_A (4.02×10^{14} cm^{-3}) is obtained, as shown in Fig. 2. The high density of interface states leads to the negative excursion of C–V curve and the negative V_{FB}.[22] With the F doping ($R = 0.12$), the Si and O concentrations decrease and the F concentration increases. The H atoms in weak Si–H bonds are replaced by F atoms,[23] and the Si dangling bonds are saturated by forming Si–F bonds. Therefore, the F doping leads to the decrease of Si dangling bonds and Si–H bonds. As a result, the doping density N_A decreases greatly (4.06×10^{12} cm^{-3}). The compensation of negative F ion to positive Si ion leads to a small positive V_{FB} (2.0 V). With the increase of F doping ($R = 0.24 - 0.32$), the etching reaction between F and Si to form SiF_x ($x = 1$ and 2), which can be seen at 380.00 nm and 440.05 nm[12] in the OES of CHF_3/DMCPS plasmas (Fig. 6), leads to the decrease of Si concentration in the films. The residual Si dangling bonds in the films are almost compensated by F. Meanwhile, the reaction between O and C to form CO, which can also be seen at 561.0 nm[24] in the OES of CHF_3/DMCPS plasmas (Fig. 6), makes the decrease of O concentration. The excess F is absorbed into the films in C–F bonds, which leads to a high doping density N_A (1.31×10^{14} cm^{-3}) and the positive shift of V_{FB} to 12.6 V. With the increase of R to 0.52, the increase of F concentration leads to the further increase of doping density N_A (1.90×10^{14} cm^{-3}) and the further positive shift of V_{FB} to 32.2 V.

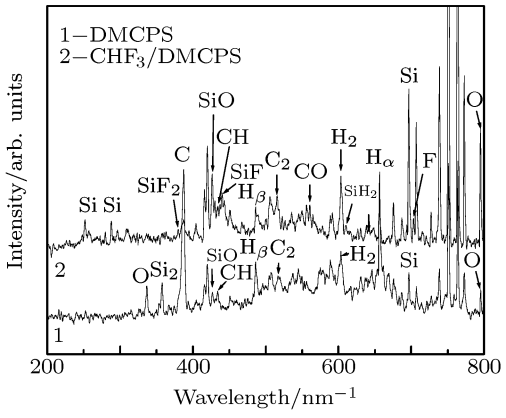


Fig. 6. Optical emission spectra of the DMCPS and the CHF_3/DMCPS ($R = 0.24$) ECR plasmas.

For the low-k films, the change of porosity can also affect the V_{FB}.[25] Because the F doping can lead to the decrease of pore density,[8] the effect of pore density and F-related bonds on V_{FB} are further analysed. By deconvolving the FTIR peaks between 700 cm^{-1} and 1300 cm^{-1} in Gaussian profile, the peaks area of Si–O–Si cage, C–F and Si–F are obtained. The dependence of V_{FB} on the peaks area is shown in Fig. 7. With the increase of C–F and Si–F areas, the V_{FB} shifts to a positive voltage. With the increase Si–O–Si cage area, however, the V_{FB} shifts to a negative voltage. Due to the positive shift of V_{FB} with the increase of porosity, which is related to the transformation of the closed network of individual pores into the open one,[21] the increase of closed Si–O–Si cage leads to the negative shift of V_{FB}.

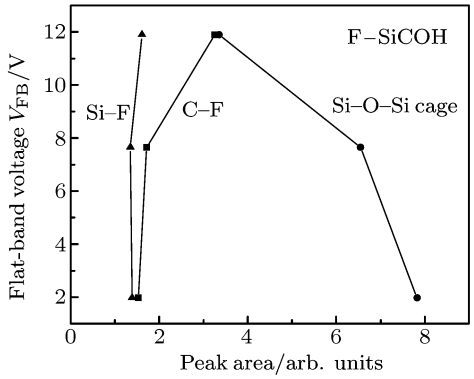


Fig. 7. Dependence of flat-band voltage V_{FB} on peaks area of Si–F, C–F and Si–O–Si cage for the as-deposited F–SiCOH films.

During the back-end processing of the line (BEL) in integrated circuits, the highest processing temperature for the BEL structure is around 400–450 °C.[26] The thermal impact may also make influence on the C–V characteristic of SiCOH low-k films. Therefore, the C–V characteristics of annealed F-doping SiCOH films (at 400 °C for 4 h in vacuum) are obtained, as shown in Fig. 1. After the annealing, the C–V curves all shift to negative voltage again, and the V_{FB} is in the range of −14.5 to 25.9 V. Without the F doping ($R = 0$), the negativeV_{FB} shift is related to the slight decrease of Si–H and Si–CH_3, and the slight increase of Si–O–Si cage. With the F doping ($R = 0.12-0.32$), the thermal treatment leads to a red-shift of Si–O–Si peaks and an increase of peak intensity, a decrease of Si–F peak intensity, and an increase of Si–O and $(CH_2)_n$ peaks. The red-shift of Si–O–Si peaks indicates the formation of more closed Si–O networks in the films. The decrease of Si–F peak intensity means the decrease of dangling bond defect located near the F-bonding site. The decrease of F negative ion at the interface and the increase of closed Si–O networks make the V_{FB} shift to a negative voltage. With the

further increase of F doping content ($R = 0.52$), the negative$V_{\rm FB}$ shift is related to the slight decrease of C–F_2 and $(CH_2)_n$.

4. Conclusions

In conclusions, the C–V characteristics of F-doping SiCOH low-k films MIS structure are investigated. The F-doping SiCOH low-k films are deposited by CHF_3/DMCPS ECR plasmas. With the increase of CHF_3/DMCPS flow rate ratio from 0 to 0.52, the positive excursion of C–V curves and the increase of flat-band voltage $V_{\rm FB}$ from −6.1 V to 32.2 V are obtained. The excursion of C–V curves and the shift of $V_{\rm FB}$ are related to the change of defects at the Si/SiCOH interface due to the decrease of Si and O concentrations, and the increase of F concentration. At the CHF_3/DMCPS flow rate ratio of 0.12, the compensation of F-bonding dangling bond to Si dangling bond leads to a small $V_{\rm FB}$ of 2.0 V. For the annealed films, the decrease of Si–F and the increase of Si–O–Si network lead to the negative$V_{\rm FB}$ shift.

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