Vol 16 No 2, February 2007
1009-1963/2007/16(02)/0524-05

Chinese Physics

© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Improvement of electrical properties of Cu/SiCOH low-k film integrated system by O_2 plasma treatment*

Qian Xiao-Mei(钱晓梅)[a], Wei Yong-Xia(卫永霞)[a], Yu Xiao-Zhu(俞笑竹)[a], Ye Chao(叶 超)[a], Ning Zhao-Yuan(宁兆元)[a], and Liang Rong-Qing(梁荣庆)[b]

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

[b] *Institute of Modern Physics, Fudan University, Shanghai* 200433, *China*

(Received 17 July 2006; revised manuscript received 16 August 2006)

This paper investigates the effect of O_2 plasma treatment on the electric property of Cu/SiCOH low dielectric constant (low-k) film integrated structure. The results show that the leakage current of Cu/SiCOH low-k integrated structure can be reduced obviously at the expense of a slight increase in dielectric constant k of SiCOH films. By the Fourier transform infrared (FTIR) analysis on the bonding configurations of SiCOH films treated by O_2 plasma, it is found that the decrease of leakage current is related to the increase of Si-O cages originating from the linkage of Si dangling bonds through O, which makes the open pores sealed and reduces the diffusion of Cu to pores.

Keywords: porous SiCOH film, O_2 plasma treatment, electrical property
PACC: 7280S, 8140R, 5275R

1. Introduction

As the device dimensions continuously shrink in ultralarge-scale integrated circuits (ULSI), the resistance–capacitance (RC) delay of interconnects becomes a major problem, which leads to signal propagation delay, dissipation and cross-link between metal interconnects. In order to deal with these problems, the SiO_2/Al structure must be replaced by low dielectric constant materials and low resistivity metal interconnects. As a substitute for SiO_2, the porous low dielectric constant (low-k) and ultra-low dielectric constant (ultralow-k, $k < 2$) materials have attracted much attention recently.[1−5] Among the porous low-k and ultralow-k materials under study, the SiCOH low-k film prepared by plasma-enhanced chemical vapour deposition (PECVD) becomes a promising candidate for its excellent performance and the capacity of extending to ultralow-k.[6−10] Meanwhile, copper has been adopted as a substitute for Al interconnects in ULSI due to its lower resistivity.

However, the integration of Cu/SiCOH porous low-k dielectrics remains challenging. Owing to the existence of open pores at the surface of SiCOH low-k films, the diffusion of Cu into porous SiCOH low-k films can take place under the action of bias or thermal treatment, which will lead to the increase of leakage current and the deterioration of electrical property. To reduce the Cu diffusion, a thin barrier is usually deposited on the surface of porous SiCOH films by the atom layer deposition. So, the new transition layer must be introduced to Cu/SiCOH system and the new process must be used.[11−13]

Due to the existence of Si dangling bonds at the surface of porous SiCOH films,[14−15] if we increase the linkage of Si dangling bonds by O_2 plasma treatment, most open pores may be sealed. In this paper, the effect of O_2 plasma treatment on the leakage current of Cu/SiCOH integrated structure and the dielectric constant of SiCOH low-k films is investigated. The results show that the leakage current of Cu/SiCOH structure can be reduced greatly by O_2 plasma surface treatment at the expense of a slight increase of dielectric constant k. By the Fourier transform infrared (FTIR) analysis, the decrease of leakage current is proved to be related to the increase of closed pores.

2. Experiment

The SiCOH films were deposited by electron cyclotron resonance (ECR) plasma chemical vapour

*Project supported by the National Natural Science Foundation of China (Grant No 10575074), the Specialized Research Fund for the Doctoral Program of Higher Education of China and the Foundation of Key Laboratory of Thin Films, Jiangsu Province, China.

deposition (CVD). The experimental procedures have been introduced elsewhere.[16−17] Decamethylcyclopentasiloxane (DMCPS) ($[Si(CH_3)_2O]_5$, > 98%) was used as the precursor to deposit SiCOH films. The precursor was vaporized from a thermostatic evaporator maintained at 90 °C and carried by argon gas to the processing chamber. To prevent re-condensation of DMCPS, the delivery lines were heated and kept at a temperature of 90 °C also. The input microwave power was controlled by a microprocessor and kept at 300 W, and the reflected power was less than 3 percent of the input power. The base pressure of 10^{-3} Pa was reached before deposition and discharge pressure was kept at 1×10^{-1} Pa. The DMCPS and Ar flow rates were kept at 6 sccm and 4.6 sccm, respectively. The deposition time was 30 min. After the deposition, the as-deposited SiCOH films were treated by O_2 ECR plasma. The O_2 flow rate was kept at 5 sccm. The input microwave power varied in the range of 300–800 W. The plasma treatment time was 5 min.

The leakage currents of Al/SiCOH/Si and Cu/SiCOH/Si metal-insulator-semiconductor (MIS) structures were measured using Keithley 6517 A electrometer. The diameter of Al or Cu dot as a top electrode was 1.1 mm. The capacitance–voltage measurements of Al/SiCOH/Si MIS structures were carried out using HP4294A impedance analyser at 1MHz. Dielectric constant was calculated from the accumulative capacitance. The thicknesses of films were in the range of 200–800 nm measured by ET350 profiler. The bonding configurations of SiCOH films were characterized by FTIR spectroscopy using JASCO 600 Plus system in the wavenumber range of 600–4000 cm^{-1}. The spectra were normalized to the films thickness according to Beer's law. Then the FTIR data were analysed using the JASCO Spectra Analysis program.

3. Results and discussion

3.1. Leakage current

The dependences of leakage current density (J) on applied electric field (E) for Al/SiCOH and Cu/SiCOH integrated structures are shown in Fig.1, where the SiCOH films have been treated by O_2 plasma in the power range of 300–800 W. It can be seen that for the as-deposited films, the leakage current densities are different for different top electrodes. For the Al electrode, the leakage current density J at 1 MV/cm is about 2×10^{-8} A/cm^2, which is close to that of O-doped SiCOH films.[18] But for Cu electrode, J increases obviously and is close to 1×10^{-2} A/cm^2. The result indicates that the Cu/SiCOH integrated structure can lead to the remarkable increase of leakage current.

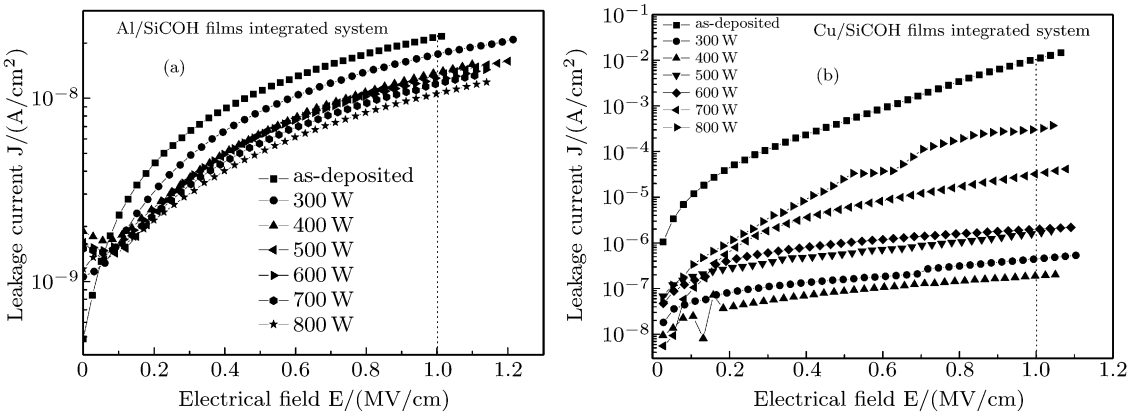


Fig.1. Dependence of J on E for (a) Al/SiCOH and (b) Cu/SiCOH integrated system.

For the SiCOH films treated by O_2 plasma, the leakage current densities for both Al/SiCOH and Cu/SiCOH integrated structures decrease, especially for Cu/SiCOH integrated structures as shown in Table 1. For the porous SiCOH film treated at 400 W, the J of Cu/SiCOH structure is slightly higher than that of Al/SiCOH structure. The result means that the electric property of Cu/SiCOH system can be obviously improved by O_2 plasma treatment of porous SiCOH films.

Table 1. The leakage currents for Al/SiCOH and Cu/SiCOH integrated structures at different treatment powers.

Power/W	Leakage current (A/cm^2)	
	Al/SiCOH	Cu/SiCOH
0	2.15×10^{-8}	1.05×10^{-2}
300	1.75×10^{-8}	4.51×10^{-7}
400	1.39×10^{-8}	1.91×10^{-7}
500	1.34×10^{-8}	1.50×10^{-6}
600	1.29×10^{-8}	1.97×10^{-6}
700	1.19×10^{-8}	3.17×10^{-5}
800	1.06×10^{-8}	3.11×10^{-4}

3.2. Dielectric constant

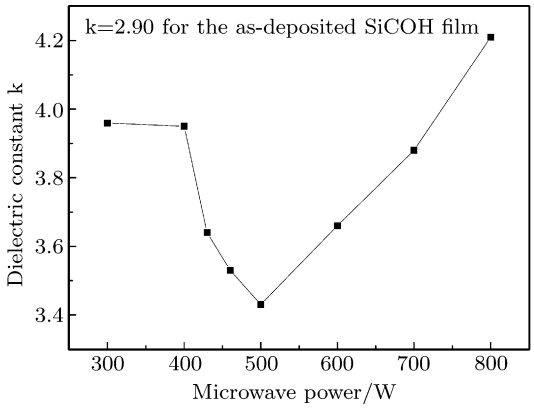


Fig.2. Dielectric constant k as a function of the O_2 plasma treatment power.

The dielectric constant (k value) variation of the SiCOH films with the O_2 plasma treatment power is shown in Fig.2. The k value of as-deposited film is 2.90, which is similar to the result of Wang.[10] After the O_2 plasma treatment, the k values of the SiCOH films are in the range of 3.4–4.2 and are all larger than those of the as-deposited films.

In the cases of low treatment powers (300–400 W), the k value increases to nearly 4.0, and then with the power increasing to 500W, the k value decreases gradually to 3.4. As the power further increases, the k value increases again. When the treatment power reaches 800 W, the k value is close to 4.2, which is similar to that of SiO_2.

3.3. Bonding configurations

The electric and dielectric properties of the SiCOH films are closely related to the bonding configurations of the films. Figure 3 shows the FTIR spectra of porous SiCOH films before and after O_2 plasma treatment. It can be seen that in the absorption peaks included are C-H_3 in $SiMe_2$ (796 cm^{-1}), H-Si-O (888 cm^{-1}), Si-O-Si (1038 cm^{-1}), Si-CH_3 (1272 cm^{-1}), C=C (1635 cm^{-1}), C-H_3 and C-H in sp^3 CH_3 (2964 and 2927 cm^{-1}) and Si-OH (3366 cm^{-1}). By deconvolving the Si-O-Si (1038 cm^{-1}) peak in Gaussian profile, the Si-O network (1030 cm^{-1}) and Si-O cage (1130 cm^{-1}) can be obtained. The Si-O cage is responsible for the introduction of closed air gap. Using Spectra Analysis program, the relative content of the groups is calculated from the peak area according to Beer's law. The change in relative content of the groups with treatment power is shown in Fig.4. It can be seen that by comparing with the as-deposited film, the relative contents of the groups have no obvious change except for Si-O cage.

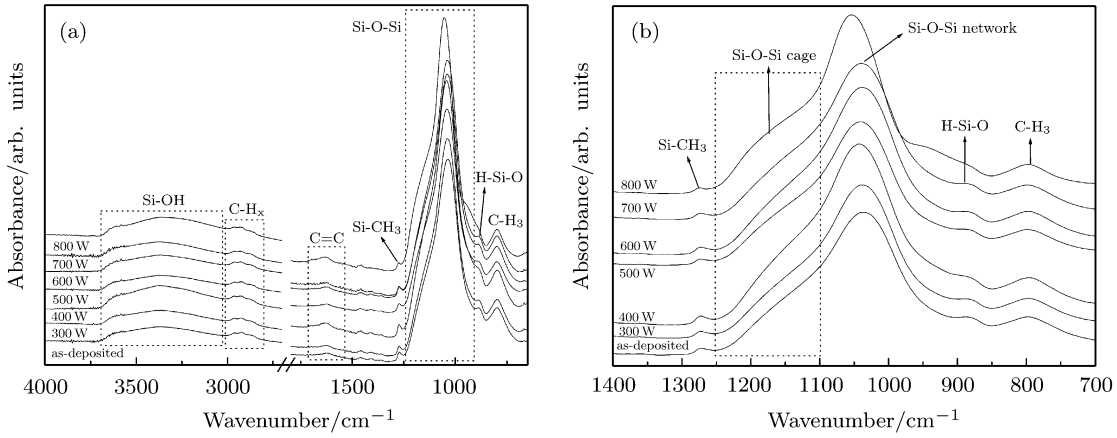


Fig.3. FTIR spectra of porous SiCOH films before and after O_2 plasma treatment.

At the surface of porous SiCOH films, the terminal groups are the -CH_3 and -OH groups and Si dangling bonds. After O_2 plasma treatment, the possible change of film bonding configuration comes from the oxidization of -CH_3 and the linkage of Si dangling bonds through O. The oxidization reaction of -CH_3 is[19]

$$-\mathrm{Si}-\mathrm{CH_3}+\mathrm{H_3C}-\mathrm{Si}-+\mathrm{O}\rightarrow-\mathrm{Si}-\mathrm{OH}+\mathrm{HO}-\mathrm{Si}-+\mathrm{CO}+\mathrm{H_2O}. \quad (1)$$

As a result of the reaction, the content of Si-OH group increases. However, the relative content of Si-OH group almost keeps the same as that of as-deposited film except for the 400 W case, and the relative content of C-H_3 group has no change obviously. The results show that the oxidization of -CH_3 is not the main reaction taking place in the O_2 plasma. For the Si dangling bonds, Si-O chains, Si-O networks and Si-O cages may form by linking Si dangling bonds through O. However, no obvious increase of relative content of Si-O networks can be seen. Only for the Si-O cage peaks, can the obvious increase of relative content with the increase of O_2 plasma treatment power be seen. The result means that the Si dangling bonds link up with each other through O and form Si-O cages, which seal the open pores at the surface of porous SiCOH films.

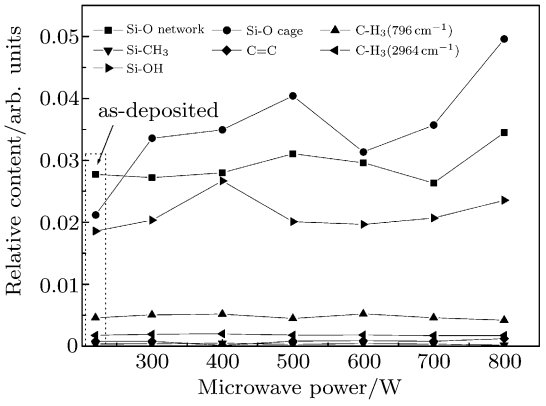


Fig.4. Relative contents of groups vs the treatment power.

The variation of k value is also dependent on the change in films structure. During the film deposition, the breaking of bonds can leave many dangling bonds at the surface.[20] Some of the dangling bonds can form Si-O bonds, Si-O network or Si-OH bonds after exposure of the film to oxygen plasma.[20] The Si-OH bonds can lead to a high dielectric constant. Meanwhile, the plasma treatment can also lead to the bond rearrangement, which increases the density of the film, especially at the film surface.[21] This can also lead to the increase of the dielectric constant. In our experiment, however, the Si-OH bond content has no obvious increase. The possible reason for dielectric constant increase is the increase in surface density.

4. Conclusions

To improve the electric property of Cu/SiCOH porous low-k film integrated structure formed by diffusion of Cu into porous SiCOH low-k films, the effect of O_2 plasma treatment on the leakage current and dielectric constant of Cu/SiCOH integrated structure are investigated. The results show that the leakage current can be reduced obviously at the expense of slight increase in dielectric constant k. By analysing the bonding configuration of SiCOH films after O_2 plasma treatment, the decrease of leakage current is found to be related to the increase of Si-O cage, which makes the open pores sealed and reduces the Cu diffusion to pores.

References

[1] Wolfgang M A 2002 *Curr. Opin. Solid State & Mater. Sci.* **6** 371
[2] Maex K, Baklanov M R, Shamiryan D, Iacopi F, Brongersma S H and Yanovitskaya Z S 2003 *J. Appl. Phys.* **93** 8793
[3] Shamiryan D, Abell T, Iacopi F and Maex K 2004 *Mater. Today* **7** 34
[4] Miller R D 1999 *Science* **286** 421
[5] Ding S J, Wang P F, Zhang W, Wang J T, Wei W L, Zhang Y W and Xia Z F 2000 *Chin. Phys.* **9** 778
[6] Grill A and Patel V 2001 *Appl. Phys. Lett.* **79** 803
[7] Grill A 2003 *J. Appl. Phys.* **93** 1785

[8] Lubguban J, Rajagopalan T, Mehta N, Lahlouh B, Simon S L and Gagopadhyay S 2002 *J. Appl. Phys.* **92** 1033
[9] Yang C S, Yu Y H, Lee K M, Lee H J and Choi C K 2003 *Thin Solid Films* **435** 165
[10] Wang T T, Ye C, Ning Z Y and Cheng S H 2005 *Acta Phys. Sin.* **54** 892 (in Chinese)
[11] Hoyas A M, Schuhmacher J, Shamiryan D, Waeterloos J, Besling W, Celis J P and Maex K 2004 *J. Appl. Phys.* **95** 381
[12] Chen Z, Prasad K, Li CY, Lu P W, Su S S, Tang L J, Gui D, Balakumar S, Shu R and Kumar R 2004 *Appl. Phys. Lett.* **84** 2442
[13] Beyer G, Satta A, Schuhmacher J, Maex K, Besling W, Kilpela O, Sprey H and Tempel G 2002 *Microelectr. Eng.* **64** 233
[14] Yang C S, Yu Y H, Lee K M, Lee H J, Lee K M and Choi C K 2005 *Thin Solid Films* **475** 150
[15] Widodo J, Lu W, Mhaisalkar S G, Sudijono J L, Hsia L C, Shen L and Zeng K Y 2005 *Thin Solid Films* **472** 195
[16] Ye C, Ning Z Y, Wang T T, Yu X Z and Xin Y 2006 *Thin Solid Films* **496** 221
[17] Yu X Z, Wang T T, Ye C and Ning Z Y 2005 *Acta Phys. Sin.* **54** 5417 (in Chinese)
[18] Wei Y X, Qian X M, Yu X Z, Ye C, Ning Z Y and Liang R Q 2007 *Acta Phys. Sin.* **56** (accepted) (in Chinese)
[19] Cheng Y L, Wang Y L, Lan J K, Hwang G J, O'Neil M L and Chen C F 2006 *Surf. Coat. Technol.* **200** 3127
[20] Wang Y H, Kumar R, Zhou X, Pan J S and Chai J W 2005 *Thin Solid Films* **473** 132
[21] Chen C T and Chiou B S 2004 *J Mater. Sci.*: *Mater. Electr.* **15** 139