Effects of Oxygen Plasma Ashing on Barrier Dielectric SiCN Film

C. W. Chen,† T. C. Chang,‡ P. T. Liu,§ T. M. Tsai,‡ and T. Y. Tseng†

†Institute of Electronics, National Chiao Tung University, Hsin-Chu, Taiwan
‡Department of Physics and Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan
§Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan
§Department of Photonics and Display Institute, National Chiao Tung University, Hsinchu, Taiwan
‡National Nano Device Laboratory, Hsin-Chu, Taiwan

Effects of oxygen plasma ashing on barrier dielectric SiCN films have been studied for various ashing conditions. According to X-ray photoelectron spectra analyses, Si−O bonds appear at the surface of SiCN film after O₂ plasma ashing. The formation of the oxidized layer, SiO₂CN, at the surface of the SiCN film effectively reduces the leakage current as a consequence. The leakage conduction of the SiCN films has been investigated to be Schottky emission at the fields between 0.4 and 1.2 MV/cm. Also, the increase of Schottky barrier height between SiCN and the metal is calculated to be 42 meV after O₂ plasma ashing.

© 2004 The Electrochemical Society. [DOI: 10.1149/1.1833666] All rights reserved.

Low-k materials and Cu wiring are currently used to reduce the resistance-capacitance (RC) delay caused by multilevel interconnects. However, copper diffusion in low-k dielectrics results in large leakage current and premature dielectric breakdown. Thus, copper interconnect lines must be encapsulated from the surrounding barrier dielectric layers to provide reliable products. Some reports show that SiC-based dielectrics own good barrier capability and are suitable for back-end-of-line (BEOL) manufacturing. Dual damascene is the standard structure for Cu metallization. Two patterning and two etch steps are currently implemented in dual-damascene to fabricate the trench and via structures in dielectrics prior to metal deposition and chemical mechanical polishing (CMP) steps. The required patterns transferred to the dielectric thin films are fabricated by lithography and plasma etching techniques. O₂ plasma ashing applied to photoresist removal usually causes silica-based low-k materials to increase both leakage current and dielectric constant due to the oxidation of Si−CH or Si−H groups. However, the major functional groups of SiC-based barrier dielectrics are Si−CH, Si−C−Si, and Si−H bonds. The barrier dielectric films, SiCN, are also used as the etch stop in dual-damascene structure for Cu wiring. In the formation of trench patterning steps, the etch stop layer is always subjected to the O₂ plasma exposure in the via-first or trench-first procedures. In this paper, the effects of O₂ plasma ashing on SiCN barrier dielectrics, with k = 4.4, deposited by PECVD, has been demonstrated. The O₂ plasma ashing process was applied to the sample of SiCN to investigate its impact on the SiCN film during photoresist stripping.

Experimental

The SiCN films were deposited with a tri-methyl-silane source and NH₃ using a plasma-enhanced chemical vapor deposition (PECVD) system. The deposition temperature was 350°C. The pressure in the chamber was kept at 3 Torr during the deposition processes. The SiCN films were deposited on p-type silicon wafers with a resistivity of 15−25 Ω-cm. O₂ plasma ashing was operated at a pressure of 500 mtorr, rf power of 300 W, and with an O₂ gas flow rate of 900 sccm at 300°C in the PECVD chamber. The periods of time of O₂ plasma applied to as-deposited SiCN were 2, 4, and 6 min. After the plasma treatments, material analyses including the Fourier transform infrared spectrometer (FTIR) and n&k analyzer were employed to identify the chemical structure and film thickness. The thickness of SiCN films in this study is 100 nm as determined by the n&k analyzer. The X-ray photoelectron spectra (XPS) were recorded by a VG Escalab MKII spectrometer using Mg Kα (1253.6 eV) radiation, and it was utilized to study the surface composition of SiCN films. The infrared spectrometry was performed from 400 to 4000 cm⁻¹ using a FTIR spectrometer calibrated to an unprocessed bare p-type wafer as the background, for determining the chemical structure of the SiCN film. The dielectric constants and leakage current of the SiCN films were investigated using capacitance-voltage (C-V) and current-voltage (I-V) measurements on metal-insulator-semiconductor (MIS) structures, Al/SiCN/Si, with a gate electrode area of 0.0053 cm². A Keithley model 82 C-V meter at 1 MHz was used to measure the dielectric constant of the films. The current-voltage characteristics of the SiCN films were investigated by an HP4156.

Results and Discussion

Figure 1 shows the FTIR spectra of as-deposited SiCN and the sample with O₂ plasma treatment for 6 min, respectively. The main peaks of the SiCN films are the Si−C stretching bond at 780 cm⁻¹, Si−N at 890 cm⁻¹, Si−CH₂−Si near 990 cm⁻¹, Si−CH₃ bending near 1245 cm⁻¹, Si−H stretching near 2100 cm⁻¹, C−H stretching near 2960 cm⁻¹, and N−H stretching near 3340 cm⁻¹. After the O₂ plasma ashing process, the intensity of the main peaks remains as before plasma treatments, which makes the surface of the SiCN film hydrophobic and is unlike general low-k films that are degraded in insulating characteristics and become hydroscopic. Moreover, the Si−O bonding is observed to increase near 1070 cm⁻¹ with O₂ plasma ashing for 6 min, as indicated in the inset of Fig. 1. Note that the thicknesses of SiCN were almost unchanged after O₂ plasma treatments. The dielectric constant of the O₂ plasma treated film is decreased from the initial value of 4.4 to 4.2.

XPS spectra were performed to realize the O₂ plasma influence on the surface of SiCN films. The main peaks for Si₂p (−100 eV), Si₂p₂ (−145 eV), C₁s (−285 eV), N₁s (−400 eV) and O₁s (−534 eV) are evident in Fig. 2. The peak of O₁s emerges conspicuously in the samples with O₂ plasma ashing for 2, 4, and 6 min, respectively. On the contrary, the carbon and nitrogen contents of O₂ plasma treated sample are reduced with increasing the O₂ plasma treated time. The enlargement of the Si₂p peak of O₂ plasma treated SiCN is shown in Fig. 3. The Si₂p, spectra of O₂ plasma treated SiCN films are contributed by the peaks, including Si−N bond (E₀ = 102 eV), Si−C bond (E₀ = 101 eV), Si−O−C bonds (E₀ = 101.5 eV), and Si−O₂ bond (E₀ = 103.4 eV). The peak heights of the Si−O₂ bonds significantly rise with the periods of treatment after the O₂ plasma ashing. Also, the intensity of the
Si—O—C bond is inferred to increase with increasing O$_2$ plasma ashing time. On the contrary, the peak heights of both the Si—N and Si—C bonds are decreased after O$_2$ plasma ashing.

Leakage current density-electric field curves (J-E) of O$_2$ plasma treated SiCN films are shown in Fig. 4. Note that the leakage current of O$_2$ plasma treated samples become smaller than that of the standard curve. This phenomenon is distinctly different from the general silica-based low-$k$ dielectric materials which possess Si—C and Si—H bonds and are easily degraded and result in large leakage after O$_2$ plasma exposure. 6-8

Electrical analyses are implemented by transforming J-E characteristics into an ln J vs. $E^{1/2}$ plot. Figure 5 shows that a logarithm of leakage currents of STD and O$_2$-treated samples are linearly related to the square root of the applied electric field, which corresponds to a Schottky mechanism. 14,15 The Schottky-Richardson emission gen-

Figure 1. FTIR spectra of SiCN films and the main function groups in the film are labeled as Si—C (780 cm$^{-1}$), Si—N (890 cm$^{-1}$), Si—CH$_3$ (990 cm$^{-1}$), Si—O (1070 cm$^{-1}$), Si—CH$_2$ (1245 cm$^{-1}$), Si—H (2100 cm$^{-1}$), C—H (2960 cm$^{-1}$), and N—H (3340 cm$^{-1}$). Sample STD: no plasma treatment; sample O3: O$_2$ plasma treatment for 6 min. With the O$_2$ plasma ashing, the Si—O bonding gets strengthened.

Figure 2. XPS spectra at the surface of all samples. The main peaks are Si$_{2p}$ (~100 eV), Si$_{2s}$ (~145 eV), C$_{1s}$ (~285 eV), N$_{1s}$ (~400 eV), and O$_{1s}$ (~534 eV). The intensity of O$_{1s}$ rises obviously with O$_2$ plasma ashing.

Figure 3. Enlargement of XPS spectra of Si$_{2p}$ at the surface of the non-plasma-treated and O$_2$ plasma treated SiCN films. The Si—O$_2$ (103.4 eV) and Si—O—C (101.5 eV) bonding significantly increase after O$_2$ plasma ashing.

Figure 4. J-E curves of all samples. The reduction of leakage current of O$_2$ plasma treated sample was found. The inset shows an energy band-diagram scheme of the O$_2$-treated sample. An oxidized layer, SiO$_x$CN, is formed between the metal and SiCN films after the O$_2$ plasma ashing, which contributes to a high energy barrier.
The current density can be formulated by

\[ J = A^*T^2 \exp \left( \frac{\beta_s E^{1/2} - \phi_S}{K_BT} \right) \]  

[1]

where \( \beta_s = \left( e^2/4\pi\varepsilon_0\varepsilon_r \right)^{1/2} \), \( A^* \) the effective Richardson constant, \( \phi_S \) the contact potential barrier, \( K_B \) the Boltzmann constant, \( e \) the electronic charge, \( E \) the applied electric field, \( \varepsilon_0 \) the dielectric constant of free space, and \( \varepsilon_r \) is the relative dielectric constant. The intercept of \( \ln J \) in Fig. 5 is proportional to the contact potential barrier, \( \phi_S \), between the metal and SiCN. The difference in the intercept values of \( \ln J \) of the non-plasma-treated and \( O_2 \)-treated samples is considered as \([ (\phi_S^2 - \phi_{S1})]/K_BT \] in accordance with the Schottky mechanism where \( \phi_{S1} \) and \( \phi_{S2} \) are the Schottky barrier heights of the non-plasma-treated and \( O_2 \)-treated samples, respectively. Therefore, the difference in potential barrier height between the non-plasma-treated and \( O_2 \)-treated samples in our study is estimated to be around 42 meV. This is consistent with the XPS spectra indicating that the formation of a SiO-bond-rich layer at the surface of the \( O_2 \)-treated SiCN films. It is well known that the barrier height of SiO, for electrons is larger than that of the SiC or SiN. As a consequence, the reduction of leakage current of the SiCN films is obviously observed in the \( O_2 \) plasma treated samples.

**Conclusion**

We have studied the \( O_2 \) plasma ashing effects on SiCN barrier dielectrics for intermetal applications. XPS spectra show that the Si—O and Si—O—C bonds appear at the surface of SiCN after \( O_2 \) plasma ashing. With increasing the \( O_2 \) plasma ashing time, both the signals of Si—O and Si—O—C bonds are significantly strengthened. Additionally, the reduction of leakage current of \( O_2 \)-treated SiCN film is observed due to the formation of a SiO-bond-rich layer, SiO\(_x\)CN, at the surface and the increase of the Schottky barrier height between the metal and SiCN in Schottky emission conduction.

**Acknowledgment**

This work was performed at National Nano Device Laboratory and was supported by National Nano Device Laboratory under contract no. 92A0500001 and the National Science Council of the Republic of China under contract no. NSC93-2112-M-110-008 and NSC92-2215-E-110-006.

*National Sun Yat-Sen University assisted in meeting the publication costs of this article.*

**References**


