Electrochemical and Solid-State Letters, **8** (1) G11-G13 (2005)
1099-0062/2004/8(1)/G11/3/$7.00 © The Electrochemical Society, Inc.

Effects of Oxygen Plasma Ashing on Barrier Dielectric SiCN Film

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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_2 bonds appear at the surface of SiCN film after O_2 plasma ashing. The formation of the oxidized layer, SiO_xCN, 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 O_2 plasma ashing.
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Manuscript submitted June 9, 2004; revised manuscript received August 5, 2004. Available electronically November 22, 2004.

Low-*k* materials and Cu wiring are currently used to reduce the resistance-capacitance (RC) delay caused by multilevel interconnects.[1] However, copper diffusion in low-*k* dielectrics results in large leakage current and premature dielectric breakdown.[2] 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.[3,4] Dual damascene is the standard structure for Cu metallization.[5] 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. O_2 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.[6-8] 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.[9] In the formation of trench patterning steps, the etch stop layer is always subjected to the O_2 plasma exposure in the via-first or trench-first procedures. In this paper, the effects of O_2 plasma ashing on SiCN barrier dielectrics, with $k = 4.4$, deposited by PECVD, has been demonstrated. The O_2 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 NH_3 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. O_2 plasma ashing was operated at a pressure of 500 mtorr, rf power of 300 W, and with an O_2 gas flow rate of 900 sccm at 300°C in the PECVD chamber. The periods of time of O_2 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 cm^2. 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 O_2 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—CH_2—Si near 990 cm^{-1}, Si—CH_3 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}.[10,11] After the O_2 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.[6-8] Moreover, the Si—O bonding is observed to increase near 1070 cm^{-1} with O_2 plasma ashing for 6 min, as indicated in the inset of Fig. 1. Note that the thicknesses of SiCN were almost unchanged after O_2 plasma treatments. The dielectric constant of the O_2 plasma treated film is decreased from the initial value of 4.4 to 4.2.

XPS spectra were performed to realize the O_2 plasma influence on the surface of SiCN films. The main peaks for Si_{2p} (~100 eV), Si_{2s} (~145 eV), C_{1s} (~285 eV), N_{1s} (~400 eV) and O_{1s} (~534 eV) are evident in Fig. 2. The peak of O_{1s} emerges conspicuously in the samples with O_2 plasma ashing for 2, 4, and 6 min, respectively. On the contrary, the carbon and nitrogen contents of O_2 plasma treated sample are reduced with increasing the O_2 plasma treated time. The enlargement of the Si_{2p} peak of O_2 plasma treated SiCN is shown in Fig. 3. The Si_{2p} spectra of O_2 plasma treated SiCN films are contributed by the peaks, including Si—N bond ($E_b = 102$ eV), Si—C bond ($E_b = 101$ eV), Si—O—C bonds ($E_b = 101.5$ eV), and Si—O_2 bond ($E_b = 103.4$ eV).[12,13] The peak heights of the Si—O_2 bonds significantly rise with the periods of treatment after the O_2 plasma ashing. Also, the intensity of the

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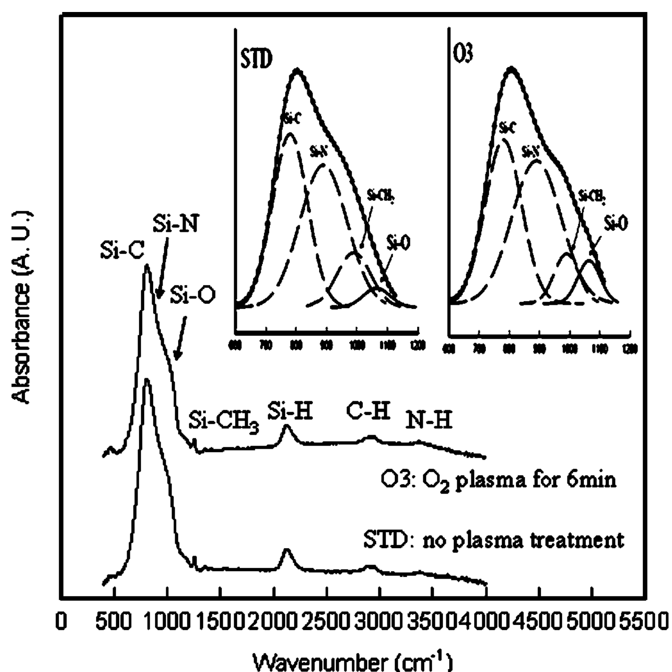

Figure 1. FTIR spectra of SiCN films and the main function groups in the film are labeled as Si—C (780 cm^{-1}), Si—N (890 cm^{-1}), Si—CH_2 (990 cm^{-1}), Si—O (1070 cm^{-1}), Si—CH_3 (1245 cm^{-1}), Si—H (2100 cm^{-1}), C—H (2960 cm^{-1}), and N—H (3340 cm^{-1}). Sample STD: no plasma treatment; sample O3: O_2 plasma treatment for 6 min. With the O_2 plasma ashing, the Si—O bonding gets strengthened.

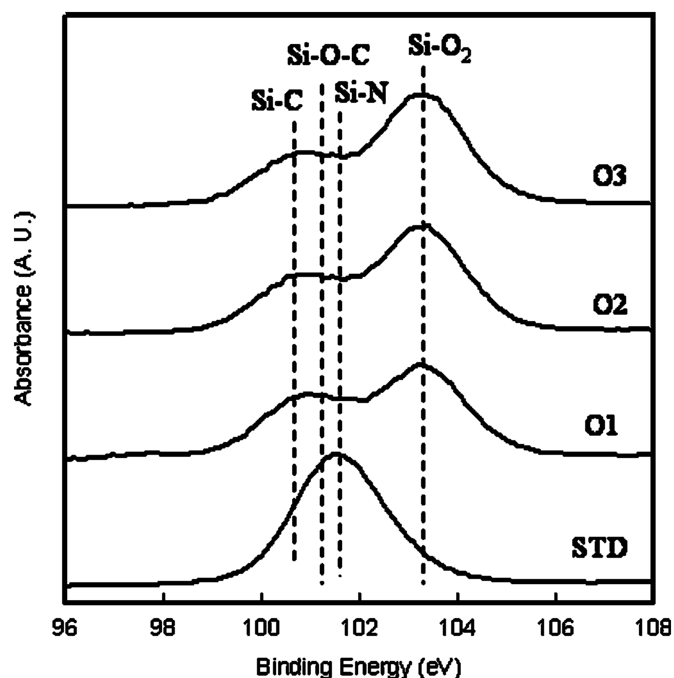

Figure 3. Enlargement of XPS spectra of Si_{2P} at the surface of the non-plasma-treated and O_2 plasma treated SiCN films. The Si—O_2 (103.4 eV) and Si—O—C (101.5 eV) bonding significantly increase after O_2 plasma ashing.

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-

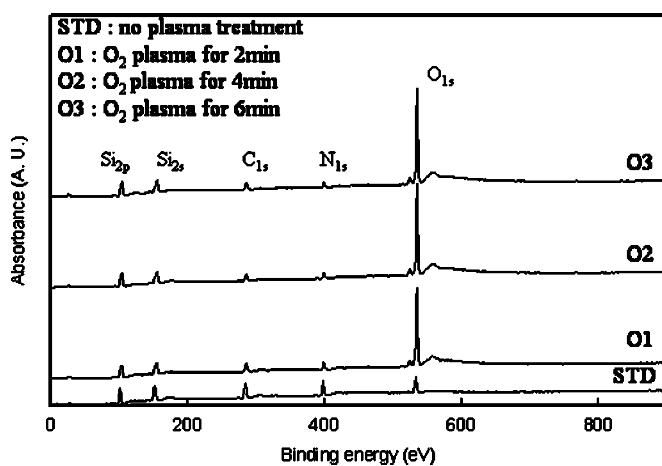

Figure 2. XPS spectra at the surface of all samples. The main peaks are Si_{2p} (~100 eV), Si_{2s} (~145 eV), C_{1s} (~285 eV), N_{1s} (~400 eV), and O_{1s} (~534 eV). The intensity of O_{1s} rises obviously with O_2 plasma ashing.

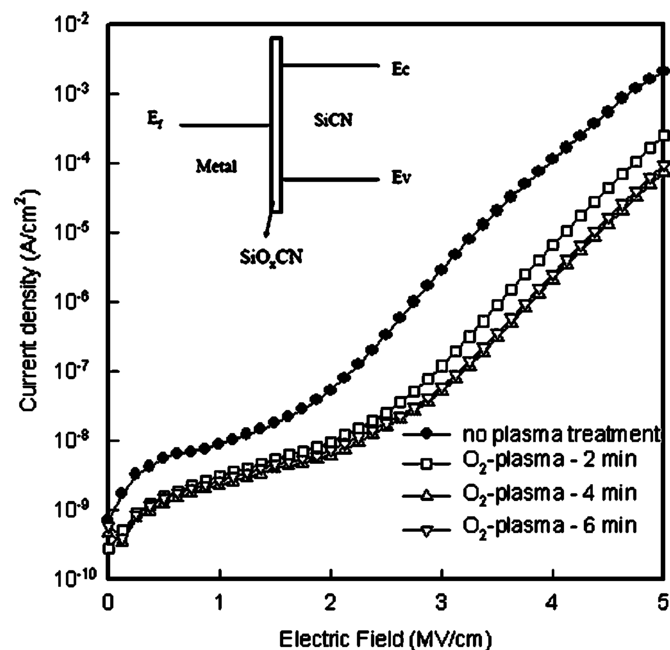

Figure 4. J-E curves of all samples. The reduction of leakage current of O_2 plasma treated sample was found. The inset shows an energy band-diagram scheme of the O_2-treated sample. An oxidized layer, SiO_xCN, is formed between the metal and SiCN films after the O_2 plasma ashing, which contributes to a high energy barrier.

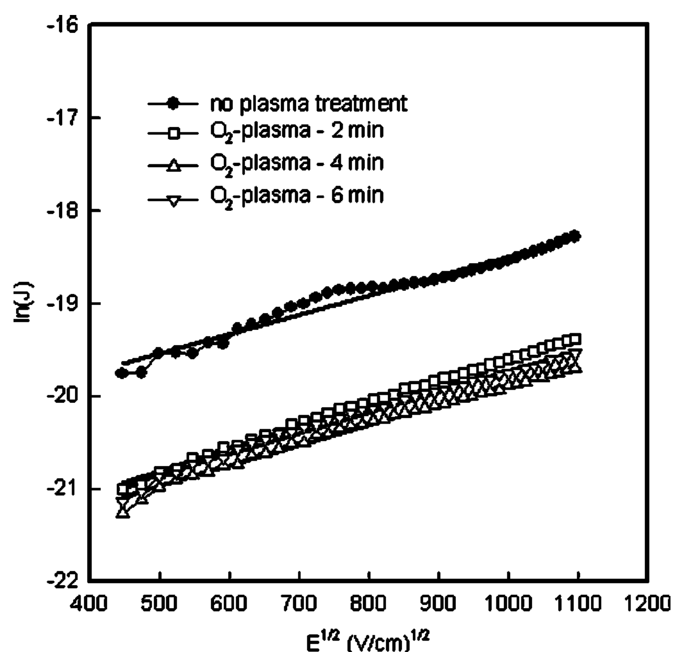

Figure 5. $\ln(J)$ *vs.* $E^{1/2}$ of all samples, showing the Schottky emission type conduction.

erated by the thermionic effect is caused by the electron transport across the potential energy barrier via field-assisted lowering at a metal-insulator interface. The current density can be formularized by

$$J = A^{*}T^{2}\exp\left(\frac{\beta_{S}E^{1/2} - \phi_{S}}{K_{B}T}\right) \quad [1]$$

where $\beta_s = (e^3/4\pi\varepsilon_0\varepsilon)^{1/2}$, A^* the effective Richardson constant, ϕ_S the contact potential barrier, K_B the Boltzmann constant, e the electronic charge, E the applied electric field, ε_0 the dielectric constant of free space, and ε is the relative dielectric constant. The intercept of $\ln J$ in Fig. 5 is proportional to the contact potential barrier, ϕ_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 $[(\phi_{S2} - \phi_{S1})/K_BT]$ in accordance with the Schottky mechanism where ϕ_{S1} and ϕ_{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_x for electrons is larger than that of the SiC_x or SiN_x.[16] As a consequence, the reduction of leakage current of the SiCN films is obviously observed in the O_2 plasmatreated 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_2 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_2 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_xCN, 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.

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