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Effect of NH_3/N_2 ratio in plasma treatment on porous low dielectric constant SiCOH materials

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This study investigates the effect of the NH_3/N_2 ratio in plasma treatment on the physical and electrical properties as well as the reliability characteristics of porous low- k films. All of the plasma treatments resulted in the formation of a thin and modified layer on the surface of porous low- k films, and the properties of this modified layer were influenced by the NH_3/N_2 ratio in the plasma. Experimental results indicated that pure N_2 gas plasma treatment formed an amide-like/ nitride-like layer on the surface, which apparently leads to a higher increase in the dielectric constant. Plasma treatment with a mixture of NH_3/N_2 gas induced more moisture uptake on the surface of the low- k dielectric, degrading the electrical performance and reliability. Among all plasma treatment with NH_3/N_2 mixed gas, that with pure NH_3 gas yielded low- k dielectrics with the worse electrical and reliability characteristics. © 2014 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4868631>]

I. INTRODUCTION

As feature sizes of integrated circuits continuously shrink to submicro, interconnect resistance–capacitance (RC) delay begins to dominate overall device speed as compared to gate delay.^{1–3} To further decrease RC delay time, low resistivity copper (Cu) layer and ultralow dielectric constant materials ($k < 2.6$) are widely used as conductor and insulator, respectively, in the backend interconnect system.^{3–6} To obtain the ultralow dielectric constant materials, introducing porosity into a dielectric film has become an attractive method to produce porous low- k film.^{6–8} However, compared with traditional SiO_2 dielectric film, porous low- k films with a decreasing dielectric constant value have unstable thermal, mechanical, and electrical properties. Therefore, integration of porous low- k films would induce some problems, such as high leakage current, low breakdown voltage, high moisture uptake, and weak tolerance against the chemical mechanical polishing process.^{8–10}

During Cu/low- k interconnect fabrication manufacturing, plasma treatments are indispensable steps, such as etching, resist stripping, Cu barrier film deposition, and Cu oxide (CuO_x) reduction.^{11–13} During the plasma treatment process, low- k films surrounded with the Cu interconnects was also exposed in the plasma condition, resulting in the modification of low- k dielectrics. Moreover, the low- k surface may suffer from damage in this plasma process, resulting in a degrading electrical and reliability performance. Therefore, understanding of the plasma damage mechanism on the low- k materials is one of the key factors for successful

integration. In these plasma treatment processes, hydrogen (H_2), nitrogen (N_2) ammonia (NH_3), and oxygen (O_2) gases were commonly used and had been reported.^{12–16} However, these studies only focused on the film properties, rarely on the electrical performance and reliability. Consequently, we investigate the effects of the plasma treatment using mixture of NH_3 and N_2 gas on porous low- k film properties in this paper. The ratio of the NH_3/N_2 gas in the plasma treatment was the main parameter, and correlation of electrical properties and reliability characteristics of the porous low- k film with the chemical structure of the film was studied.

II. EXPERIMENT

The porous low- k dielectric films were deposited on a p-type (100) silicon substrates by plasma-enhanced chemical vapor deposition. The porous low- k films were deposited from diethoxymethylsilane and alpha-terpiene as a matrix and porogen precursor, respectively. A small amount of oxygen was also introduced as an oxidant. The deposition temperature, pressure, and power were 300 °C, 7.5 Torr, and 600 W, respectively. After deposition, UV curing with 200–450 nm wavelength was performed to remove the organic porogen to form porous low- k dielectric film with pore size and porosity of 1.4 nm and 15%, respectively. The resulting thickness and dielectric constant are about 300 nm and 2.56, respectively. Then, the porous low- k film (blanket wafer) was tested by NH_3/N_2 plasma treatments with various ratios, ranging from 0 to 1, in an inductive-coupled plasma chamber. The temperature, pressure, RF power, and treatment time in NH_3/N_2 plasma treatment were 300 °C, 2.0 Torr, 30 W, and 30 s, respectively. After plasma treatment, regular pattern of Al metallization with 100 nm thick

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were thermally evaporated to form ohmic contact on the dielectric films through the shadow mask. All processes and analyses were conducted in a clean room with dry air atmosphere. All analyses were performed within 1 day after performing NH₃/N₂ plasma treatment to reduce air exposure effect.

The thickness and refractive index (at a 633 nm wavelength) of as-deposited films were analyzed on an optical-probe system with an ellipsometer (Film Tek™ 3000SE). The water contact angle (WCA) was determined as the average of five measurements (Reme Hardt, Mode 100-00-230). The reflectance of the low-*k* films was measured using ultraviolet-near-infrared spectrometer (UV-NIR; Hitachi-U3900H). Chemical bonding of the film was investigated using Fourier transform infrared spectroscopy (FT-IR; Bio-Rad Win-IR PRO]. The compositions of the film surfaces were identified using x-ray photoelectron spectroscopy (XPS; VG Scientific Microlab 350). The electrical characteristics of low-*k* films were examined by capacitance–voltage measurements at 1 MHz using a semiconductor parameter analyzer (HP4280A). Leakage and breakdown time measurements were done at room temperature (25 °C) on the metal–insulator–silicon (MIS) structure. The breakdown time is defined as the stressing time at a sudden rise of at least three decades of the leakage current.

III. RESULTS AND DISCUSSION

Figure 1 presents the change in the thickness of porous low-*k* films after plasma treatment as a function of the NH₃/N₂ gas ratio in the plasma. We used a bilayer model of ellipsometry measurement to measure the thickness of the top modified layer and the bottom bulk low-*k* film. As shown, a thin modification layer was formed on the top of the porous low-*k* films after plasma treatment. The variation in the thicknesses of the top modification layer is less than 2 nm among all NH₃/N₂ plasma treatment conditions. This value is within the experimental error, revealing that the penetration depth that is caused by the plasma treatment depends less on the NH₃/N₂ gas ratio than on the plasma treatment time, power, and method.¹⁷ Additionally, the total thicknesses shrink after

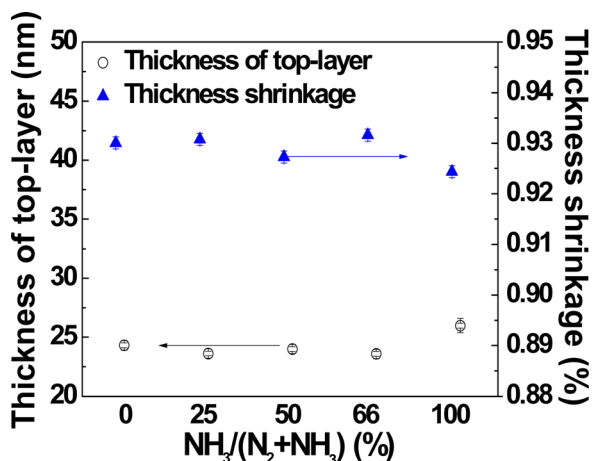


FIG. 1. (Color online) Thickness variation of porous low-*k* films after various NH₃/N₂ plasma treatments.

performing the plasma treatment, suggesting that the porous low-*k* films were densified by vacuum ultraviolet radiation, radical etching, and ion bombardment in the plasma with NH₃/N₂ mixed gas. Furthermore, the sample was treated with pure NH₃ gas exhibited slightly higher thickness shrinkage than the others.

The reflectance of the pristine and plasma-treated low-*k* films was measured using UV-NIR, as displayed in Fig. 2. As indicated, the wavelength of maximum reflectance was shifted from 500 nm to 450 nm upon NH₃/N₂ plasma treatment. Moreover, all NH₃/N₂ plasma-treated samples could be divided into two groups based on the reflectance behavior. The reflectance of low-*k* samples that were treated with NH₃ gas remained the same as that of the pristine low-*k* film. However, the reflectance of pure N₂ gas plasma-treated low-*k* films was reduced by approximately 20% relative to that of the plasma-treated sample with NH₃ gas, revealing that NH₃ gas in the plasma process differently modified the top surface of the porous low-*k* films.

To investigate further the properties of the plasma-modified layer that were induced using various NH₃/N₂ ratios, diluted HF solution (1% volume) was used to etch the plasma-treated low-*k* films with various times. The etching rates of bulk films in all plasma-treated low-*k* samples were similar to that of the pristine low-*k* film, indicating that the bulk film in the plasma-treated low-*k* material was not affected by the plasma treatment. However, the etching rates of the top modified layer of the plasma-treated low-*k* films were higher than that of the pristine low-*k* film, as shown in Fig. 3. Moreover, the etching rates of the modified top layer depend on the NH₃/N₂ ratio in the plasma. The etching rate has its minimum value at the NH₃/N₂ ratio of 1.

FT-IR spectra of plasma-treated porous low-*k* films were analyzed to study the change of bonding structures upon plasma treatment. The obvious peaks in the FT-IR spectra of the porous low-*k* films are in the regions: ~1020–1050 cm⁻¹, 1250 cm⁻¹, 2200–2250 cm⁻¹, 2850–3100 cm⁻¹, and 3200–3500 cm⁻¹, corresponding to Si-O-Si bridging, Si-CH₃ stretching, Si-H bending, C-H_X stretching, and Si-OH/H-OH peak, respectively.¹⁸ Figure 4 plots the absorbance of these peaks relative to those of the pristine low-*k* film as a function

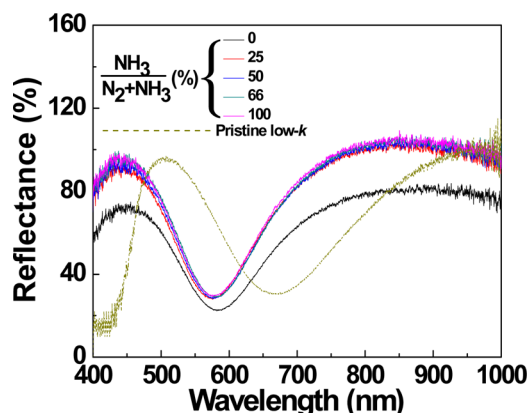


FIG. 2. (Color online) Reflectance of porous low-*k* films after various NH₃/N₂ plasma treatments.

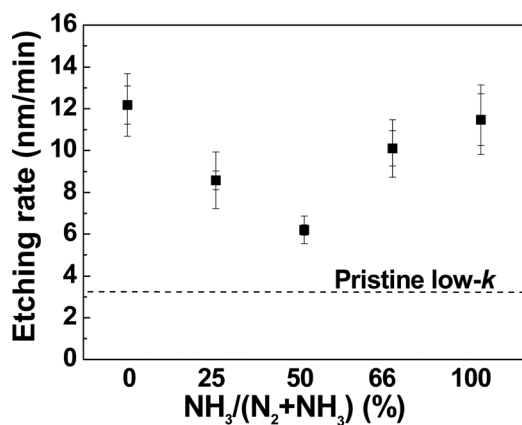


Fig. 3. Wet etching rate of various NH₃/N₂ plasma-treated low-*k* films.

of NH₃/ (N₂+ NH₃) ratio in the plasma. The intensities of Si-O-Si bridging in the NH₃/N₂ plasma-treated low-*k* films remain unchanged for all conditions. However, the peak intensities of Si-CH₃ stretching and C-H_x stretching are slightly lower than those of the pristine low-*k* film, whereas the Si-OH/H-OH (3200–3500 cm⁻¹) peak intensity is higher. The maximum change is observed in the plasma-treated low-*k* film with pure NH₃ gas, indicating that pure NH₃ gas in the plasma induces more replacement of Si-CH₃ bonds by Si-OH/H-OH bonds.

The surface roughness of the treated porous low-*k* films was examined using AFM. Figure 5 shows the AFM images and the average root-mean square (rms) value is also presented in Fig. 5. The pristine low-*k* film had an rms value of 0.34, while the plasma-treated low-*k* films had higher values, and the rms value also increased as the NH₃/N₂ ratio decreased. The low-*k* films that were plasma-treated with pure N₂ gas had the highest rms value of 0.41, possibly because this plasma condition produces the most nitrogen active species in the plasma, which heavily bombarded the surface of the film.

XPS was used to investigate the changes in the surface composition of the porous low-*k* films following NH₃/N₂

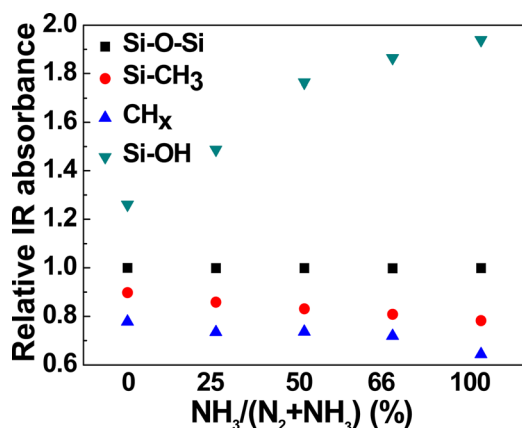


Fig. 4. (Color online) Relative absorbance of Si-O, Si-CH₃, CH_x, and Si-OH/H-OH bonds of various NH₃/N₂ plasma-treated low-*k* films.

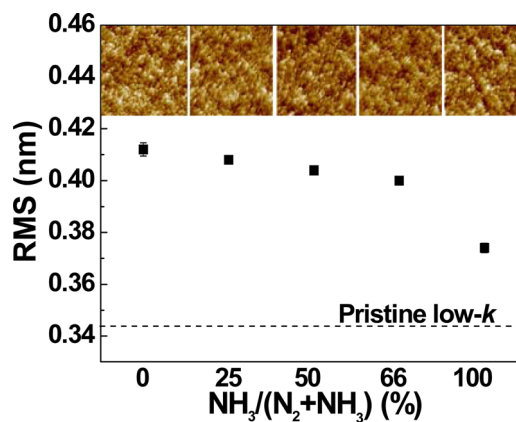


Fig. 5. (Color online) AFM images and rms values of various NH₃/N₂ plasma-treated low-*k* films.

plasma treatment. The three elements of Si, O, and O were observed in the as-deposited low-*k* film. Another element of N was detected in the low-*k* films that were treated by a mixture of NH₃ and N₂ gases. Additionally, the plasma-treated low-*k* film with pure N₂ gas yielded the strongest N1s signal. The bonding energy of the N1s peak is ~399.0 eV, which is attributed to Si-N and sp³ C-N bonds.^{16,19,20} Moreover, C 1s XPS spectrum shifts to a higher binding energy at ~289.0 eV, which is assigned to N-C=O structures. The relative atomic percentages of these elements in the porous low-*k* films were calculated using the relative elemental sensitivity factor method. Figure 6 plots the C and N atomic percentages relative to the Si atomic percentage as functions of the NH₃/N₂ gas ratio. The figure reveals that plasma treatment with a higher NH₃/N₂ ratio caused severe carbon depletion on the porous low-*k* film surface, whereas treatment with pure N₂ gas resulted in a much N incorporation.

One of the most important concerns associated with plasma treatment is surface hydrophobicity. Measurements of the WCA are commonly used to evaluate the hydrophobicity of low-*k* films. Measurements were made at five sites on every sample, and Fig. 7 plots the averaged results. The untreated as-deposited porous low-*k* film had a WCA of ~90°, larger than those of the treated films, indicating that this as-deposited porous low-*k* film seems to be hydrophobic.

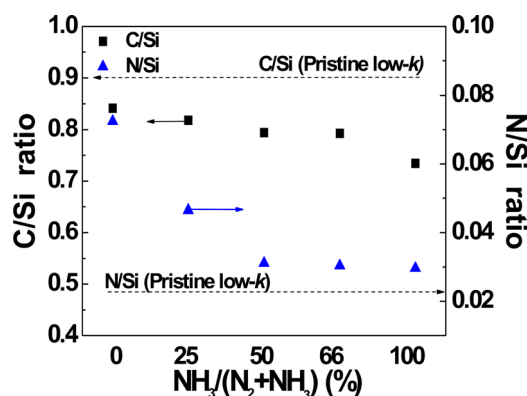


Fig. 6. (Color online) C/Si and N/Si atomic percentages of various NH₃/N₂ plasma-treated low-*k* films.

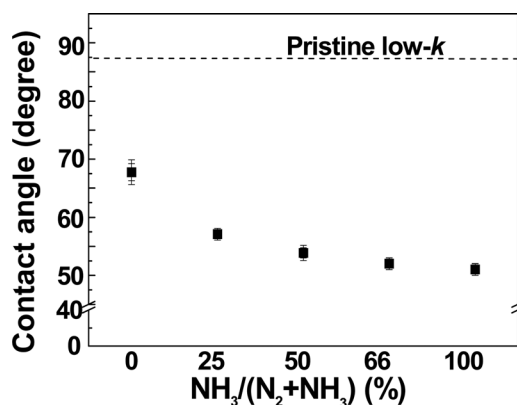


FIG. 7. Water contact angle of porous low-*k* films after various NH₃/N₂ plasma treatments.

Upon NH₃/N₂ plasma treatment, the treated porous low-*k* film had a lower WCA value, indicating that this treated porous low-*k* film was susceptible to the absorption of moisture. Moreover, the decrease in this value increases as the NH₃/N₂ ratio increases, suggesting that the porous low-*k* film is more hydrophilic following the NH₃/N₂ plasma treatment with a higher NH₃/N₂ ratio. This trend is consistent with the results of FT-IR and XPS analyses, which reveal that the porous low-*k* films that were plasma-treated with pure NH₃ gas resulted in the formation of more Si-OH/H-OH bonds and a larger subtraction of C atoms.

MIS structures were constructed herein to evaluate the dielectric property of porous low-*k* films under various NH₃/N₂ plasma treatment conditions. The change in the dielectric constants of porous low-*k* films following plasma treatment at various NH₃/N₂ gas ratios was calculated from the measured accumulation capacitance of the MIS structure. The changes in the dielectric constants of NH₃/N₂ plasma-treated low-*k* films upon O₂ plasma treatment for 1 min were also evaluated, as presented in Fig. 8. The dielectric constant of the as-deposited pristine low-*k* films is 2.56. After NH₃/N₂ plasma treatment, the dielectric constant of the plasma-treated low-*k* films increases. Under pure NH₃ or pure N₂ gas plasma treatment conditions, the increase is larger, being 0.55 and 0.71, respectively. This can be

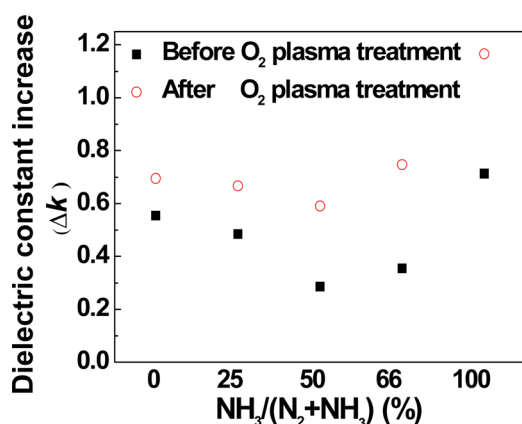


FIG. 8. (Color online) Change in dielectric constant of porous low-*k* films after NH₃/N₂ and O₂ plasma treatments.

attributed to more formation of Si-OH bonds or Si-N/C-N bonds on the surface layer for pure NH₃ or pure N₂ gas plasma treatment, respectively. Treatment with O₂ plasma increases the dielectric constants of all NH₃/N₂ plasma-treated low-*k* films by the replacement of Si-CH₃ and Si-H bonds with Si-O bonds.¹² However, the magnitude of the increase depends on the NH₃/N₂ gas ratio in the plasma. The increase in the dielectric constant becomes larger with the NH₃/N₂ gas ratio. The pure N₂ gas plasma-treated sample exhibits a smaller increase in the dielectric constant owing to the formation of protective Si-N/C-N layer. This layer suppresses the penetration of oxygen radical into the low-*k* film.

Figure 9 plots the leakage current densities at 1 MV/cm and 2 MV/cm for the porous low-*k* films treated with various NH₃/N₂ gas ratios. The leakage current densities of the pristine low-*k* films are presented for reference. The leakage current densities of all plasma-treated samples are higher than those of the pristine low-*k* film, suggesting that the top modified layer induced by NH₃/N₂ plasma treatment has a poor insulating property, leading to an increase in the leakage current. In an electrical field of 1 MV/cm, all plasma-treated low-*k* films, except that treated with pure NH₃ gas, exhibit the similar increases in the leakage current. In the elevated electrical field of 2 MV/cm, pure NH₃ or pure N₂ gas plasma-treated low-*k* films exhibited the larger increase in the leakage current; the former exhibited the largest. The largest increase in the leakage current for pure NH₃ gas plasma-treated low-*k* film can be attributable to more absorption of moisture, which provides ionic conduction pathways by releasing mobile ions (H⁺, OH⁻).²¹

Based on the results of the above analyses, the reaction mechanism in the NH₃/N₂ plasma can be described as follows. In pure N₂ gas plasma, only N, N₂, and N₂* active species are generated, no hydrogen species is produced. Physical bombardment by N radicals is favorable, roughing the film's surface. Moreover, the weak bonds in the low-*k* dielectric film, such as Si-H, Si-CH₃, and C-H_x bonds, can be broken by these active species in the plasma, forming Si-N and C-N bonds. As NH₃ gas was added into the plasma, other active species in addition to the N, N₂, and N₂* active

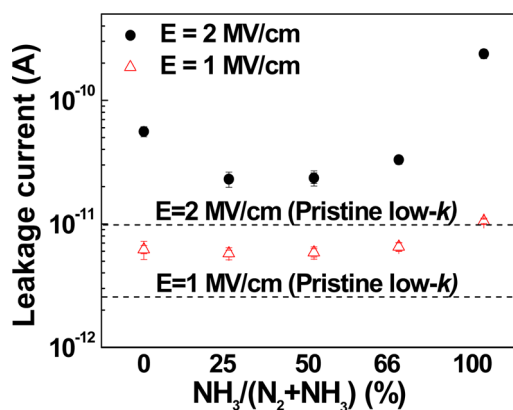


FIG. 9. (Color online) Increase in leakage current density at 1 MV/cm and 2 MV/cm of porous low-*k* films after various NH₃/N₂ plasma treatments in MIS test structures.

species, such as H, NH₂, NH₄, and N₂H, may be generated. The Si-CH₃ group in the low-*k* film is broken to form Si-dangling bonds. This dangling bond easily absorbs H or NH₂ species to form Si-H or Si-NH₂ bonds due to a lower reaction energy, which is thermodynamically favorable.^{22–25} The Si-H and Si-NH₂ bonds are not stable in air and easily react with ambient air to form Si-OH, which is more hydrophobic and has a higher dielectric constant. As the portion of NH₃ in the plasma increases, the number of H and NH₂ active species increases accordingly. At the same time, the amount of the generated N, N₂, and N₂* active species is limited because more energy is required to generate these active species due to a fixed plasma power of 30 W. These changes in the plasma result in the significant replacement of CH₃ groups by H and NH₂ active species, the formation of more Si-OH bonds, and the reduction of Si-N and C-N bonds.

To understand further the dielectric reliability, voltage ramping-up to dielectric breakdown of the porous low-*k* films following plasma treatment under various NH₃/N₂ conditions was measured using MIS test structures. The dielectric breakdown voltage is defined as the voltage at which the leakage current suddenly increases. The dielectric breakdown electric-field was calculated as the measured dielectric breakdown voltage divided by the film thickness. Figure 10 plots the calculated dielectric breakdown electric-fields from 20 sites. As shown in the figure, all NH₃/N₂ mixture gas plasma-treated samples had a poorer dielectric breakdown performance than the pristine low-*k* film. Moreover, the breakdown electric-field of the NH₃/N₂ mixture gas plasma-treated low-*k* films decreases as the NH₃/(N₂ + NH₃) ratio increases. The sample that was plasma-treated with pure NH₃ gas has the lowest breakdown voltage and the highest leakage current.

To investigate the effect of NH₃/N₂ gas ratio in the plasma on the low-*k* dielectric's long term reliability, time-dependent-dielectric breakdown (TDDB) was performed to measure the dielectric breakdown times. Three different electrical-fields were applied to stress Al/porous low-*k*/Si MIS capacitors. Measurements were made on 20 capacitors for each condition and the measured dielectric breakdown times were expressed as a Weibull distribution.

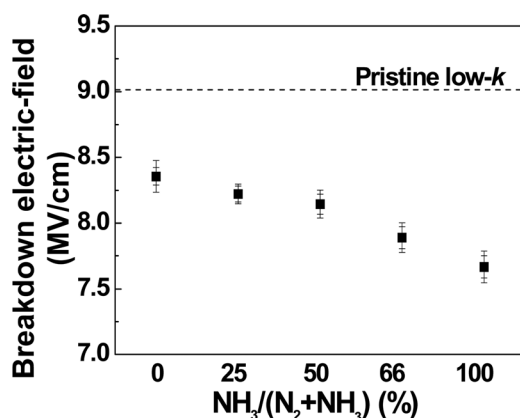


FIG. 10. Dielectric breakdown field of porous low-*k* films after various NH₃/N₂ plasma treatments.

In a Weibull distribution analysis, two important parameters are used to evaluate the reliability of a dielectric film: $T_{63.2\%}$ is the characteristic breakdown time for 63.2% of failure and β is the Weibull slope or shape parameter, which governs the breakdown distribution. Compared to the pristine low-*k* film, all plasma-treated samples had shorter characteristic lifetimes and a smaller β value, indicating that NH₃/N₂ plasma treatment shortened dielectric breakdown time and widened the distribution. The reduction of the dielectric breakdown time may be caused by an accumulation of defects owing to plasma-induced damage. Figure 11 compares $T_{63.2\%}$ values as a function of applied electric-field for the pristine and plasma-treated samples. All plasma-treated samples exhibited reduced characteristic lifetimes, and these reductions were significant in stronger stressing electric-fields. Additionally, in the same applied electric-field, the $T_{63.2\%}$ values of plasma-treated low-*k* films decreased as the NH₃/(N₂ + NH₃) ratio increased. These results were found to correlate well with the moisture contents in the plasma-treated films. Accordingly, the pure NH₃ plasma-treated samples with the highest moisture content show the shortest time-to-failure, indicating that the moisture content in a low-*k* film plays an important role in reducing dielectric time-to-failure. However, the samples that were plasma-treated with pure N₂ gas had the longest time-to-failure, indicating that amide-like or nitride-like layers on the surface retard low-*k* dielectric breakdown. Furthermore, the log of the characteristic lifetimes of the studied low-*k* films is proportional to the electric-field; therefore, the lifetimes can be fitted using E-model (thermochemical model).²⁶ The lifetime of the pristine low-*k* film was found to be well fitted with E-model and the electric-field acceleration factor (γ) was 11.21. However, the lifetimes of all samples that were plasma-treated with various NH₃/N₂ gas ratios were found to deviate significantly from the E-model, especially for the plasma-treated sample with a higher NH₃/N₂ gas ratio. These findings reveal that the plasma-treated samples exhibit an additional failure mechanism in addition to the thermochemical

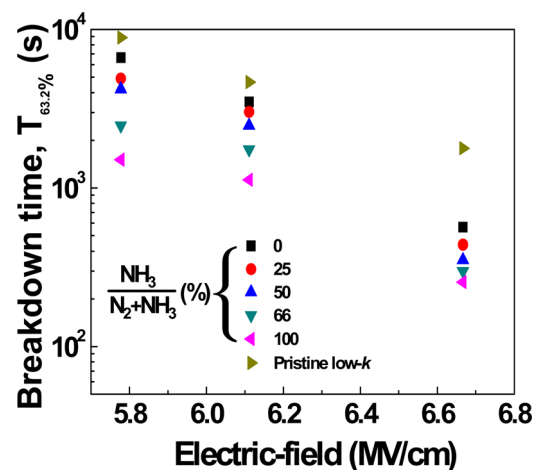


FIG. 11. (Color online) Characteristic dielectric breakdown time at 63.2% failure rate of porous low-*k* films after various NH₃/N₂ plasma treatments as a function of electric-field.

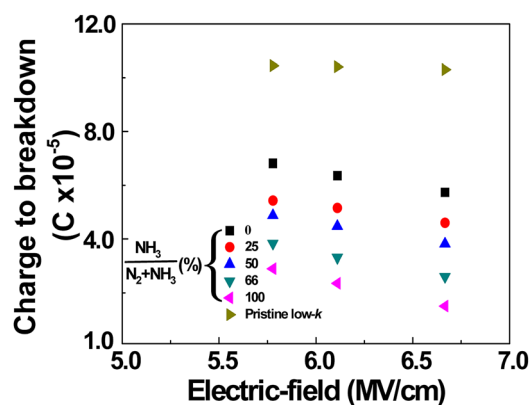


FIG. 12. (Color online) Calculated charge-to-breakdown as a function of electric-field for various NH₃/N₂ plasma-treated low-*k* films.

driven mechanism. The absorption of moisture in the plasma-treated low-*k* films generates mobile ions that may be responsible for this additional failure mechanism.

The charge-to-breakdown (Q_{bd}) data were calculated by integrating the leakage current as a function of time obtained from TDDDB testing until breakdown, which is plotted in Fig. 12. As expected, the pristine samples display the largest Q_{bd} values and remain constant value in the range of the stressing electric-fields that were analyzed in this study. The NH₃/N₂ plasma-treated low-*k* films resulted in a reduced Q_{bd} value and the total Q_{bd} value decreased with increasing the NH₃/N₂ gas ratio. The plasma-treated low-*k* films with pure NH₃ gas had the lowest Q_{bd} value, which was approximately two orders of magnitude lower than that of the pristine sample. This finding also agrees with the likelihood of an additional failure mechanism for NH₃/N₂ plasma-treated low-*k* films. This additional failure mechanism may be associated with the absorption of moisture in plasma-treated samples. Moreover, as the applied electric-field was increased, the total Q_{bd} value observably decreased, revealing that the released mobile ions from the absorbed moisture caused more TDDDB degradation in a stronger electric-field.

IV. CONCLUSIONS

In this study, the impact of various NH₃/N₂ gas mixtures in the plasma on the porous low-*k* dielectrics was investigated. The physical, electrical, and reliability characteristics were compared. Experimental results indicate that all plasma treatments resulted in the formation of a modified layer on the surface of porous low-*k* films, and the properties of this modified layer were affected by the NH₃/N₂ ratio in the plasma. A plasma treatment with pure N₂ gas formed an amidelike/nitridelike layer on the low-*k* film's surface, leading to a higher dielectric constant. Plasma treatment with a mixture of NH₃/N₂ gas induced more moisture uptake on the

surface of the low-*k* dielectric, degrading the electrical performance and reliability. Among all plasma treatment with NH₃/N₂ mixed gas, that with pure NH₃ gas yielded low-*k* dielectrics with the worse electrical and reliability characteristics.

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