Modifications of Low Dielectric Constant Fluorinated Amorphous Carbon Films by Multiple Plasma Treatments

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This study investigated the material and electrical characteristics of hydrogen, nitrogen plasma-treated fluorinated amorphous carbon (a-C:F) films in relation to their thermal stability. Experimental results indicate that the nitridation passivation layer and hydrogen passivated chemical bonds on the film surface effectively suppress thermal decomposition during high temperature annealing. Accordingly, a multiple plasma treatment on a-C:F films was proposed. In this treatment, nitrogen plasma nitridation was performed not only to passivate the a-C:F films against copper diffusion, but also to prevent the fluorine contents from penetrating into copper intermetals. Hydrogen plasma treatment then recovered unstable bonds formed during the nitridation process, thus yielding stable chemical structures and inducing hydrophobic characteristics of the film surface. The multiple plasma-treated a-C:F films demonstrated the desired performance as interlayer dielectrics.

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Low dielectric constant (low-k) materials as interlayer dielectrics (ILDs), deposited either by chemical vapor deposition (CVD) or spin-on techniques,1 encounter similar difficulties, such as integration issues,2 weak resistance to copper diffusion, and the requirement of blocking corrosion species that would otherwise penetrate into intermetals.3 Low-k materials such as black-diamond Si-C films4 and fluorinated amorphous carbon (a-C:F) films5 are attracting increasing interest since they can be deposited by conventional plasma-enhanced chemical vapor deposition (PECVD) methods. The gaseous mixture containing fluorocarbon and hydrocarbon is a precursor for depositing a-C:F films,5 making the deposition of a-C:F films as easy as preparing fluorinated SiO₂ (SiOF) films.

Several attempts have been made to address and improve critical areas regarding material properties of a-C:F films in the interconnect processes.6–12 Yang et al. elucidated the structural evolution of the a-C:F film during thermal annealing.7 Yokomichi further indicated that the dangling bond density increased after annealing a-C:F films at 400°C.9 Optimizing the processing parameters enables a-C:F films with better characteristics to be deposited as an ILD.10 However, the electrical characteristics of a-C:F films become degraded even after annealing at several hundred degrees, typically about 400°C,11 as most of the low-k materials. This intrinsic, fatal problem seriously limits their application as ILDs.

Previous studies have demonstrated that plasma post-treatment is an effective means of modifying as-deposited dielectric films.13–17 Hydrogen plasma treatment can typically recover unstable bonds, or defect sites, into stronger chemical structures.14–16 The treated films exhibited better resistance to moisture uptake and even copper diffusion, and unaffected electrical characteristics when annealed.15,16 On the other hand, the NH₃-plasma nitridation on interlayer films can block the penetration for copper into ILD, and hinder the hygroscopic behaviors of low-k films.17 However, relevant integration issues for fluorinated dielectrics, such as a-C:F, SiOF, include the degassing of fluorine into nearby metals, or dielectric layers, causing metal corrosion or etching of the dielectrics.14–18 The extent of the precipitation of fluorine in the a-C:F film greatly exceeds that of SiOF, requiring additional shielding.

This work demonstrates the feasibility of applying multiple plasma treatment to a-C:F films. Nitrogen plasma nitridation is performed not only to passivate the a-C:F films against copper diffusion, but also to block the erosive fluorine contents from penetrating into copper intermetals via the nitridation passivation layer. Hydrogen plasma treatment then recovers unstable bonds formed during the nitridation process, thus yielding stable chemical structures. The postdeposition parameters can be separately optimized since multiple plasma treatment is performed. The proposed approach can recover the electrical degradation caused by nitrogen plasma post-deposition and prevent a large amount of hydrogen, as decomposed from NH₃ plasma, from bonding with fluorine species, and then degassing via the HF structure. Combining the postdeposition of N₂ and H₂ yields a better performance over that of conventional single plasma, or mixed plasma treatments.

Experimental

As-deposited a-C:F films were deposited by PECVD. The basic precursor gas was a mixture of CH₄, and CF₃ (CF₂, C₂F₆, or C₃F₈). As in our previous work,10 the optimum deposition parameters for a-C:F films were CF₃/CH₄~10, radio frequency (rf) plasma power 200 W, process pressure 550 mTorr, and deposition temperature 250°C. The total gas flow used for depositing the a-C:F films was 300 standard cubic centimeters per minute (scm). In this experiment, another class of samples was the NH₃, N₂, and H₂ plasma-treated a-C:F films. For simplicity, STD represents the as-deposited a-C:F films, whereas N-3, N-6, and N-9 represent as-deposited a-C:F films with N₂ plasma treatments of 3, 6, and 9 min, respectively. Additionally, H-3, H-6, and H-9 represented as-deposited a-C:F films with H₂ plasma treatment for 3, 6, and 9 min, respectively. The postdeposition parameters of NH₃, N₂, and H₂ plasma treatments were rf plasma power 200 W, process pressure 100 mTorr, substrate temperature 250°C, and flow rate 200 scm. Table I lists the deposition and postdeposition parameters. Thermal stability was then examined by curing those a-C:F films in a furnace at elevated temperatures for 30 min in N₂ ambient at a flow rate of 10 L/min. The thicknesses and refractive indices of those films were determined by a n and k analyzer. Before and after each treatment, the Fourier transform infrared (FTIR) absorption spectra and X-ray photoelectron spectroscopy (XPS) of each film were examined to monitor structural changes. Secondary ion mass spectroscopy (SIMS) was carried out to analyze not only the degrees of copper diffusion in the a-C:F films, but also the outgassing of fluorine contents into the intermetals. Thermal desorption spectroscopy (TDS) determined the extent of desorption of various bonding classes (such as H₂O) in the a-C:F films, to compare the effects of the postdeposition parameters on thermal stability and the resistance to moisture. Finally, electrical measurements were taken by using metal-insulator-semiconductor (MIS) capacitors.

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Table I. Deposition and postdeposition parameters.

<table>
<thead>
<tr>
<th>Deposition parameter</th>
<th>Postdeposition parameter</th>
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<tr>
<td>Reactant gases</td>
<td>CF&lt;sub&gt;4&lt;/sub&gt; with CH&lt;sub&gt;4&lt;/sub&gt;, NH&lt;sub&gt;3&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt;, and H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>RF plasma power</td>
<td>200 W</td>
</tr>
<tr>
<td>Process pressure</td>
<td>550 mTorr</td>
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<tr>
<td>Temperature</td>
<td>250°C</td>
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<tr>
<td>Flow rate</td>
<td>300 sccm</td>
</tr>
<tr>
<td>Stress</td>
<td>−45 Mpa</td>
</tr>
<tr>
<td>Stress</td>
<td>−25 Mpa</td>
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Results and Discussion

**Fundamental characteristics of plasma modified low-K a-C:F films.**—Tables IIa and b list the basic characteristics for as-deposited a-C:F films, indicating that the best performing a-C:F films are deposited by a mixture of CH<sub>4</sub> and C<sub>4</sub>F<sub>8</sub>. The dielectric constant is as low as 2.35, and the leakage current can be maintained below \( I_d = 6.0 \times 10^{-9} \text{ A/cm}^2 \) at a bias electric field of \( E_{bias} = 1.0 \text{ MV/cm} \). All a-C:F films discussed in this study were deposited by a mixture of CH<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. After annealing at 450°C, the dielectric constant and leakage current markedly increased to 3.68 and \( I_d = 5.0 \times 10^{-8} \text{ A/cm}^2 \) respectively, although the film shrinkage was below 2.5%. Closely examining XPS spectra in Table IIb reveals that the calculated fluorine/carbon (F/C) ratio also decreased from 0.98 to 0.83. Therefore, an additional modification such as plasma treatments on as-deposited a-C:F films was required in addition to the optimization of deposition conditions.

Figure 1a illustrates the film shrinkage of a-C:F films after NH<sub>3</sub>, N<sub>2</sub>, and H<sub>2</sub> plasma treatments at various process times (films’ thickness, ~5000 Å). The NH<sub>3</sub> plasma treatment is not applicable to a-C:F films since its refractive index, thickness changed by more than 9% in the 1.5 min process time, although NH<sub>3</sub> plasma effectively modified many materials. Therefore, nitrogen and hydrogen plasma treatments were adopted herein. Figure 1b indicates that the N<sub>2</sub> plasma-treated a-C:F films can maintain their thickness after 450°C annealing (1% thickness loss in the best case). Figure 1c displays the dielectric constants of N<sub>2</sub>-treated a-C:F films as a function of annealing temperature. Although the dielectric constants of N<sub>2</sub>-treated a-C:F films did not change, Fig. 2a indicates that the leakage currents of N<sub>2</sub>-treated samples slightly increased. We can infer that this phenomenon is owing to the formation of a few unstable bonds on the film surface during nitrogen plasma treatment. Nevertheless, the dielectric constants of the bulk films of the as-treated samples remained unaffected. Thus, FTIR spectra for the chemical structures of those samples are the same as those of the as-deposited samples, as shown in Fig. 3a.

Figures 1d and 2c summarize the corresponding measurements for H<sub>2</sub>-treated samples. In contrast to N<sub>2</sub>-treated a-C:F films, both the dielectric constants and leakage currents of a-C:F films treated by H<sub>2</sub> plasma remain unchanged. The hydrogen plasma can deeply penetrate into a-C:F films and recover the unstable bonds or defect sites, into stable chemical bonds. Consequently, the leakage currents and dielectric constants of H<sub>2</sub>-treated films can be improved or at least maintained. FTIR spectra for the chemical structures of such films are the same as those of the as-deposited samples, as shown in Fig. 3c.

Notably, a-C:F films are also characterized by the slight increase of their compressive stresses from −10 to −12 Mpa after N<sub>2</sub> and N<sub>2</sub>/H<sub>2</sub> postdepositions because of the formation of more dense films by postdeposition treatment. Also, stresses of the H<sub>2</sub>-treated...
Figure 1. (a) Film shrinkage and index of a-C:F films as a function of plasma treatment time for N₂, H₂, and NH₃ postdeposition. (b) Film shrinkage (c) Dielectric constant of N₂-treated a-C:F films as a function of annealing temperature. (d) Dielectric constant of H₂-treated a-C:F films as a function of annealing temperature.

Figure 2. Leakage currents of N₂-treated a-C:F films (a) before annealing, (b) after annealing at 450°C for 30 min. Leakage currents of H₂-treated a-C:F films (c) before annealing, (d) after annealing at 450°C for 30 min.
a-C:F films are maintained at the same level as those of untreated films because the hydrogen gases have less of a densification effect on a-C:F films than nitrogen gases do. This nitrogen plasma bombardment introduces either steric strains or nonoptimum bond angles in the a-C:F films, resulting in fewer unstable bonds in the N$_2$-treated a-C:F films. Damage incurred from the nitrogen plasma is more serious than that from the hydrogen plasma owing to the heavier nitrogen atoms and radicals of the former. In addition, some dangling bonds caused by deposition, postdeposition processes or thermal stresses may temporarily exist on the film surface. Those unstable sites tend to react with other species, i.e., moisture from the environment, thus degrading the electrical characteristics for formation of C=O. However, the effect of imperfect bonds on degrading electrical characteristics can be decreased by either an inert passivation layer on the film surface or formation of stable bonding structures (hydrogen passivated bonds).

**Thermal stabilities of modified low-k a-C:F films.**—Figures 1c and d for the N$_2$- and H$_2$-treated a-C:F films reveal that the dielectric constant increases from 2.35 to 2.8 as the annealing temperature increases to 450°C. In comparison, the untreated sample abruptly changes its electrical characteristics, and its dielectric constant rises to 3.7 such that the thermal stability of the dielectric constants of a-C:F films is significantly improved after treatment with H$_2$ or N$_2$ plasma. Some interesting observations can be made about improvements of those two processes. First, at lower annealing temperatures...
(<400°C), the resistance of as-deposited films to thermal stresses is better than that of N₂-treated samples. In contrast, the H₂-treated samples exhibited better thermal stability than that of untreated samples. Second, the modifications of a-C:F films by both of these postdeposition processes saturate at specified times, at which the N-6, H-6 samples behave like N-9 and H-9 samples, respectively. Finally, the H₂-treated samples exhibit a higher resistance to thermal stresses than the N₂-treated samples do, as observed from Fig. 1c, d and 2b, d.

As mentioned earlier, unstable bonds in N₂-treated samples appeared. By increasing the hydrophilic nature of the film surface, these bonds facilitate the uptake of moisture and increase the dielectric constants of the samples, especially under thermal stresses. In addition to confirming the more hydrophilic nature of the surfaces of the N₂-treated samples, TDS spectra in Fig. 4a also verified that the desorption abundance of H₂O of the N-9 sample was higher than for any other sample. Therefore, the N₂-treated samples exhibited a worse thermal stability than did the as-deposited samples at lower annealing temperatures (<400°C), as shown in Fig. 1c. However, the dielectric constants of N₂-treated a-C:F films increased only from 2.35 to 2.8 as the annealing temperature rose to 450°C. In comparison, the dielectric constant of the untreated sample abruptly increased to 3.7. These results correspond to those in Fig. 2b, which shows that the leakage currents of the N-6 and N-9 samples were also markedly lower than those of the N-3 and STD samples at this higher annealing temperature of 450°C. The leakage current of the N-6 sample only increased from $I_d \approx 6.0 \times 10^{-7}$ A/cm² to $I_d \approx 3.8 \times 10^{-6}$ A/cm² (at $E_{bias} = 1.0$ MV/cm) after thermal annealing at 450°C. In comparison, the leakage currents of N-3 and STD samples increased to $I_d \approx 1.0 \times 10^{-5}$ and $I_d \approx 5.0 \times 10^{-7}$ A/cm², respectively. These results suggest that N₂-treated a-C:F films are involved in mechanisms other than the creation of a few unstable bonds by nitrogen plasma.

In fact, the N₂-plasma treatment on a-C:F films simultaneously forms fewer unstable bonds and nitridation layers on the film surface. SIMS measurements and investigations of copper diffusion verify the formation of a nitridation passivation layer. This passivation layer on the film surface effectively suppresses the degradation due to accompanying unstable bonds. Therefore, at low temperature annealing, the defects of the N₂-treated samples cause a worse performance of the electrical characteristics than those of untreated ones. In contrast, for annealing temperatures exceeding 400°C, the highly nitried samples (N-6, N-9) exhibited better electrical characteristics than did the lightly treated sample (N-3), or the untreated sample since the chemical structures of weakly passivated samples (N-3, STD) seriously decomposed at higher thermal stresses.

Figure 3b indicates that the major FTIR spectral peaks of CF₃ (980-1350 cm⁻¹) and C-H (2873-2954 cm⁻¹) of the annealed N-6 and N-9 samples are similar to those of the STD samples. However, few defect sites due to damage of annealed N-6 and N-9 samples from nitrogen plasma still induce slightly hydrophilic characteristics in the film surface when the higher temperature stresses are applied to those films. Hence, a peak shape was observed for C=O bonds (1650 and 1850 cm⁻¹) in the FTIR spectra, as compared to the obtuse shape observed for the STD samples in Fig. 3a. On the other hand, weakly passivated N-3 STD samples begin to decompose their chemical bonds, some of which are reconstructed at higher annealing temperatures (above 400°C). The appearance of a small bulge located at the C—H bond confirms thermal decomposition of annealed STD and N-3 samples, because the ratio of C=C bonds in a-C:F films decreased and the related dielectric constants increased after annealing at 450°C. The C=O ratio in Table IIb confirm the reduction of the ratio of C=O bonds in a-C:F films. In fact, a higher C=O peak in the FTIR spectrum was also detected for the a-C:F films deposited at lower C/N CH₄ ratios (data not shown here). Finally, the N-6 sample exhibited thermal stabilities better than the N-9 sample as their dielectric constants (Fig. 1c), leakage currents (Fig. 2b), and TDS spectra (Fig. 4a) are compared. In sum, the nitridation passivation competes with the degradation from accompanying unstable bonds. This effect is believed to be a major mechanism.

The unstable bonds of the untreated samples are few, and can thus resist thermal stress up to 250°C, as shown in Fig. 1d. Above that temperature, the decomposition of C—C=O bonds in untreated a-C:F films begins. H₂-treated samples are almost unaffected at such low temperatures. Furthermore, strongly H₂-passivated samples (H-6, H-9) were more stable than other samples at all annealing temperatures. After thermal annealing at 450°C for 30 min, the leakage currents of H-6 and H-9 samples were also much lower than those of H-3 and STD samples, as depicted in Fig. 2d. Therefore, hydrogen plasma treatment plays a role in stabilizing chemical structures of a-C:F films. This effect is due to a formation of hydrogen passivated chemical structures in the films and this modified characteristic for H₂-treated a-C:F films can suppress the uptake of moisture and reduce thermal decomposition during high temperature annealing. TDS spectra in Fig. 4b verified the presence of more hydrophilic surfaces in the H₂-treated samples than in the others, and that the desorption abundance of H₂O of the H-9 sample is the least among all samples. Figure 3d also reveals that spectral peaks of CF₃ (980-1350 cm⁻¹) and C-H (2873-2954 cm⁻¹) and the obtuse shape of the C=O bond in the FTIR spectrum of the annealed H-6 and H-9 samples appear as those of the STD sample. In comparison, significant peaks at the C=O and C—H bonds appeared for annealed H-3 and STD samples since reconstruction (C—H bonds) and the moisture uptakes (C=O bonds) occurred in the weakly passivated films. Furthermore, the leakage current of H-6 and H-9 samples only increased from $I_d \approx 6.0 \times 10^{-7}$ A/cm² to $I_d \approx 1.28 \times 10^{-6}$ A/cm² (at $E_{bias} = 1.0$ MV/cm) after thermal annealing at 450°C. The values for annealed H-3 and STD samples are $I_d \approx 5.8 \times 10^{-8}$ and $I_d \approx 5.0 \times 10^{-7}$ A/cm², respectively.

However, Fig. 1d, 2d, 3d, and 4b reveal that the thermal stability of the H-9 sample behaved like that of the H-6 sample. An excess of hydrogen atoms in the H-9 sample, which might break the CF₃ bonds and actively react with fluorine species before outgassing via HF structures at elevated thermal stresses, was believed to be the major reason for the saturation of treatment times. As a result, a small C=H signal for the annealed H-9 sample actually existed, revealing reconstruction in highly H₂-treated samples after annealing. Considering the dielectric constants and leakage currents together, the H₂ treatment time of 6 min is enough to inhibit the degradation caused by thermal stresses and achieve better thermal stabilities than the N₂-treated samples. However, N₂-plasma nitridation performed on a-C:F films before and after thermal annealing at 450°C for 30 min, measured by using the metal/a-C:F/Si metal-insulator-semiconductor (MIS) capacitors with Al and Cu gates.
Inhibition of copper diffusion and outgassing of corrosive fluorine species.—The last section addresses the material and electrical properties of plasma-treated a-C:F films with regard to thermal stabilities, and the optimal postdeposition conditions are obtained. As discussed, both the nitridation passivation layer and hydrogen-passivated bonding structures on surfaces of treated a-C:F films effectively suppress thermal decomposition during high temperature annealing. However, low-k materials are normally employed as interlayers in copper damascene interconnects. Thus, the barrier effect of treated a-C:F films against copper diffusion must be discussed.

Figure 5 shows the leakage currents of annealed N-6 and H-6 samples with Cu and Al electrodes in MIS capacitors. The annealing temperature and process time were 450°C and 30 min, respectively. The behavior of the leakage current of samples with Cu penetration was well explained by the Poole-Frenkel (P-F) mechanism.\(^1\)\(^7\)\(^1\)\(^9\)

\[ I_d \approx 1.28 \times 10^{-8} \text{ A/cm}^2 \] for the Al gate. For the annealed N-6 sample, the change in leakage curves is significantly smaller than that for the H-6 sample, and the relevant values are \( I_d \approx 5.0 \times 10^{-8} \text{ A/cm}^2 \) and \( I_d \approx 3.8 \times 10^{-8} \text{ A/cm}^2 \) for the Cu and Al gates, respectively. For the samples without postdeposition, the leakage current abruptly increases by one order of magnitude higher than that of treated samples. In conclusion, the nitridated surface of a-C:F film efficiently blocks copper diffusion and protects a-C:F films from thermal decomposition.

Figure 6a presents the SIMS analysis of the bare N-6 sample. From this figure, a distribution profile of nitrogen elements near the a-C:F surface was determined. The penetration depth of about 25 nm resembles that given in other studies.\(^1\)\(^7\) In contrast, no obvious nitrogen elements were found in the H-6 sample, as shown in Fig. 6b. Figure 7 illustrates the distribution of copper elements in treated a-C:F films after annealing at 450°C for 30 min. Here, the outgassing of fluorine elements into the capped copper metal is to be measured, and therefore, the capped copper is still maintained on the surfaces of treated a-C:F films after annealing. The copper penetration into N\(_2\)-treated a-C:F films was obviously suppressed below that in the STD and H-6 samples. The resistance of the STD sample to copper diffusion was worse than that of the N-6 and H-6 samples.

![Figure 6](image)

**Figure 6.** SIMS distribution profiles of nitrogen elements in (a) N\(_2\)-treated a-C:F films, (b) H\(_2\)-treated a-C:F films.

![Figure 7](image)

**Figure 7.** SIMS distribution profiles of copper and fluorine elements in Cu/a-C:F/Si capacitors for as-deposited (\(\triangle\), \(\square\) curves), H\(_2\)-treated (\(\blacksquare\), solid curves), and N\(_2\)-treated (bold-solid, \(\triangle\) curves) a-C:F films, after thermal annealing at 450°C for 30 min. \(\blacklozenge\) shows SIMS distribution of silicon elements in the Cu/a-C:F/Si capacitor.

![Figure 8](image)

**Figure 8.** Dielectric constants for as-deposited, N\(_2\)-treated, and H\(_2\)-treated a-C:F films before and after thermal annealing at 450°C for 30 min, measured by using the metal/a-C:F MIS capacitors with Al and Cu gates.
This finding corresponds to the nitrogen distributions in those samples, as shown in Fig. 6, and explains the changes in measured leakage currents for N2 and H2-treated samples with Al and Cu gates, as shown in Fig. 5.

Another contribution for nitrogen plasma treatments is the inhibition of fluorine contents outgassing into capped copper metals, as depicted in Fig. 7. According to this figure, the intensity of fluorine contents in the N-6 sample is smaller than that in the H-6 sample, while the untreated sample is the worst. The fluorine contents are generally present in the fluorocarbon species (CFx), since these species are the major chemical constituents of a-C:F films and are often observed in TDS spectra, where F, HF is difficult to detect due to the reaction of those gases with Si/SiO2 in the measurement system, leading to the formation of SiF4.12 On the other hand, charged HF species are required by the TDS approach and only a few of them are formed. In general, a portion of the fluorocarbon species in the a-C:F films, as a terminal group, might react with environmental moisture and form corrosive HF which corrodes metals. The stability of the chemical bonds in the H-6 sample cause fewer fluorine species to be desorbed than those from the N2-treated sample. However, the electrical characteristics of N2-treated and H2-treated samples after annealing are similar, likely owing to prevention of the outgassing of fluorine species by the nitridation layer of the N2-treated samples. Although nitridation accompanies bond damage, hydrogen-plasma treatment can recover unstable bonds, and a multiple plasma treatment of a-C:F films is proposed. In this multiple plasma treatment the nitrogen plasma nitridation is performed not only to passivate the a-C:F films against copper diffusion, but also to prevent the erosive fluorine contents from penetrating into copper intermetals. Hydrogen plasma treatment then recovers unstable bonds formed during the nitridation process, thus yielding stable chemical structures. By adopting this novel approach, the leakage current for the multiple plasma-treated samples after annealing declines to $I_d \approx 1.5 \times 10^{-8}$ A/cm² for Cu gates, as shown in Fig. 5. Figure 8 shows the dielectric constants of samples after those different processes. The dielectric constant can be as low as 2.6 for the multiple plasma-treated a-C:F film in the Cu/a-C:F/Si capacitor after annealing at 450°C.

**Conclusion**

This study investigated the thermal stabilities of hydrogen and nitrogen plasma-treated fluorinated amorphous carbon films (a-C:F). The a-C:F films modified by multiple plasma treatments demonstrate the desired characteristics as interlayer dielectrics, including high resistance to pyrolysis, copper diffusion, and penetration of corrosive species into intermetals. The nitrogen plasma nitridation passivates the a-C:F films against copper diffusion. This nitridation passivation layer also prevents the corrosive species of low-k a-C:F films, for example F, from diffusing into copper intermetals. In doing so, additional hydrogen plasma treatment recovers the imperfect bonds formed during the nitridation process, yielding stable chemical structures. Combining postdeposition of N2 with H2 offers remarkable improvements over conventional single plasma, or mixed plasma treatments. This novel approach can be applied to fluorinated dielectrics such as SiOF and a-C:F.

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**References**