The Influences of Moisture and Fluorine on the Characteristics of Fluorinated Silicate Glass for Copper Metallization

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In this study, the impacts of moisture and unstable fluorine on the fundamental properties of fluorinated silicate glass (FSG) are discussed. Specific thermal treatment and water-soaking treatment are applied to the FSG dielectric layer. The influences of the moisture and fluorine outgassing from the FSG layers on the integrity of the Cu/TaNx.0/Ta/FSG/OSG/IMD/CMP multilayer structure are investigated using transmission electron microscopy, Rutherford backscattering spectroscopy, and secondary ion mass spectroscopy. The results indicate that the formation of voids at the interface between the metallization layer and FSG film is correlated with the moisture and unstable fluorine in the FSG dielectric layer. Nevertheless, both of them can be eliminated by baking the FSG dielectrics prior to the subsequent metallization. Meanwhile, the dielectric constant and leakage current characteristics of the FSG film can be improved by driving out the moisture and unstable fluorine of the dielectric layer after baking in N2 at ambient conditions.

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As the dimensions of the integrated circuits (ICs) are scaled down continuously, the interconnect resistance–capacitance (RC) time delay has become the dominant factor in determining the interconnect performance. To reduce RC time delay, the traditional Al/SiO2 structure is replaced by the Cu/low-k material below 90 nm technology node. Several materials with low dielectric constants have been proposed in the literature, including poly-arylethers (PAEs),1 hydrogen silsesquioxane (HSQ),2 fluorinated silicate glass (FSG),3,4 organosilicate glass (OSG),5 and porous methylsilsesquioxane (MSQ).6 To reduce the dielectric constant of SiO2-based intermetal dielectric (IMD), the introduction of carbon in the form of methyl (CH3) groups and/or mesopores is effective to reduce the dielectric constant from about 4 to a value less than 3. However, the mechanical strength can be significantly degraded, resulting in yield issues because of possible damage from subsequent chemical mechanical polishing (CMP) processing steps.7 Though the effective k value of FSG is slightly above 3, FSG has satisfactory mechanical strength such that it is still the most popular material with low dielectric constant used at the 90 nm technology node.

FSG possesses lower dielectric constant than SiO2 due to the incorporation of fluorine into SiO2 films.8 The introduction of fluorine into SiO2 leads to a less dense, more porous film by creating voids in the SiO2 matrix. Meanwhile, the fluorine alters the electronic polarizability of the SiO2 film.9 The above two reasons contribute to a lower dielectric constant of the FSG dielectric layer. However, the drawbacks of doping fluorine into SiO2 film, including the increase of the number of interface traps and decrease of the adhesion strength of the metal/FSG interfaces, are the major concerns for using in the IC application.10,11 According to our previous study, the FSG film is hydrophilic.12 It indicates that moisture is absorbed by the FSG film as storing in the room ambient, and the absorbed moisture is released during thermal annealing. Moisture outgassing from the FSG layer is a serious issue, because it will degrade the integrity of IC circuits severely. Moisture in the FSG dielectric film also serves as the “water-related traps,” which result in the increase of the negative charges in the oxide layer.13 Therefore, in this study, to eliminate the deterioration caused by the fluorine and moisture, two kinds of thermal treatments are applied to the FSG films. The roles of fluorine and moisture in the FSG films and the influences of the thermal treatment on the dielectric layers are also discussed.

Experimental

The substrates used in the present study are p-type Si(100) wafers with resistivity of 8–12 Ω cm. The fluorinated silicate glass, 100 nm in thickness, was deposited onto silicon wafers in a single-wafer chemical vapor deposition (CVD) chamber with SiH4 + SiF4 + N2O. The dielectric constant of the FSG film measured right after deposition is 3.7 by the mercury-probe method. After deposition, three types of FSG, denoted as FSG–, FSG+ and FSG°, were prepared. FSG– represents the FSG stored in the laboratory ambient without any additional treatment before sputtering the metallic layers by sputtering. Ta and TaNx.0.5 layers were prepared by radio frequency (13.56 MHz) sputtering, using a Ta metal target (99.95% purity), and their thicknesses are 2 and 10 nm, respectively. The TaNx.0.5 film prepared with 1% of nitrogen flow ratio [N2/(N2 + Ar)] has amorphous structure. More detailed information about the Ta–N films can be found in our previous work.14 Cu films (180 nm) were then deposited on Ta–N films using dc sputtering with a Cu target (99.99% purity).

The Cu/TaNx.0.5/Ta/FSG° (or FSG+)/(Si) (the symbol “(Si)” represents the single-crystalline silicon substrate) samples were followed by postmetallization annealing (PMA) in vacuum (2.5 × 10−5 Torr) at 400°C for 60 min to investigate the thermal stability. High-resolution transmission electron microscopy (HRTEM) was used to examine the reactions occurring at the Ta/FSG interfaces. Compositional depth profile analysis was performed with Rutherford backscattering spectrometry (RBS) and secondary ion mass spectroscopy (SIMS). For RBS measurement, the 4He+ ions were accelerated to 2 MeV and the backscattered ions were detected at a

<table>
<thead>
<tr>
<th>Sample Pretreatment</th>
<th>FSG°</th>
<th>FSG+</th>
<th>FSG°</th>
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<tbody>
<tr>
<td>Baked at 400°C in N2 ambient for 30 min</td>
<td>×</td>
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<td>○</td>
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<tr>
<td>Dipped into DI water for 30 min (after baking)</td>
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scattering angle of 160°. SIMS analysis was performed using Cs+ primary ion beam. To avoid knock-on effect, the Cu layer was stripped by acid solution before SIMS analysis. The acid solution is composed of phosphorous, nitric acid, and acetic acid mixed in a proportion of 1:1:1. Water desorption from the dielectrics was analyzed by thermal desorption spectroscopy (TDS).

To obtain the electrical characteristics of the dielectric films, Cu/FSG/(Si) metal-oxide-semiconductor (MOS) capacitors were fabricated. Copper of 200 nm in thickness was sputtered through a shadow mask to obtain circular dots of 0.4 mm diam. To calculate the dielectric constant (k) of the dielectric, capacitance–voltage (C–V) measurement was performed using an HP 4284 LCR meter at a frequency of 100 kHz with an ac small signal of 25 mV. The leakage current densities of the dielectric films prepared by various conditions were also characterized using a computer-controlled HP 4140B pA meter/dc voltage source with a staircase-ramped voltage stress for current–voltage (I–V) curves. The refractive indices of the multilayer structures significantly and helps to prevent Cu and Ta from interdiffusing.

Results and Discussion

Figure 1 depicts cross-sectional TEM bright-field micrographs of the Cu/TaNx−0.5/Ta/FSGx/(Si) and Cu/TaNx−0.5/Ta/FSGy/(Si) multilayer structures, which are as-deposited and after PMA at 400°C in vacuum for 60 min. The FSG without prebaking process is denoted as FSG and denoted as FSG with prebaking treatment (400°C/60 min, in N2) in this study. Figure 1a and b indicate that the interfaces between the TaNx−0.5/Ta bilayers and the dielectric films of the as-deposited samples are smooth, and the barrier layers adhere well to the dielectric films for both FSG and FSG. However, after PMA, voids can be observed at the interface between TaNx−0.5/Ta bilayer and FSG film (Fig. 1c) but cannot be found between TaNx−0.5/Ta and FSG layer (Fig. 1d). The average size of voids is about 20 nm. The origin of these voids is further explored and discussed as follows.

The compositional depth profiles of the Cu/TaNx−0.5/Ta/FSG (or FSG) (Si) specimens, as-deposited and after PMA, were investigated by RBS and the spectra are shown in Fig. 2. Figure 2a gives the comparison of RBS spectra for the Cu/TaNx−0.5/Ta/FSG (Si) specimens, as-deposited and after PMA. Compared to the as-deposited spectrum, the Cu profile in the 400°C/60 min annealed spectrum become more slanted, and so does the Ta profile. This implies that interdiffusion had occurred at both the Cu/TaNx−0.5 and Ta/FSG interfaces after PMA. Nevertheless, for the FSG specimens, the profile of the as-deposited sample overlaps nicely with that of the annealed sample (Fig. 2b). The RBS result proves that prebaking on the FSG dielectric layer improves the thermal stability of the multilayer structure significantly and helps to prevent Cu and Ta from interdiffusing.

It had been reported that Cu diffuses rapidly into dielectrics primarily due to oxidation of copper caused by the moisture absorbed in the dielectric film. Additionally, the cross-sectional TEM image (Fig. 1c) reveals the formation of voids at the interface between TaNx−0.5/Ta bilayer and the FSG film after PMA. To clarify if the TEM and RBS results correlate with the moisture contained in the dielectrics, FSG single layer (FSG) was analyzed by thermal desorption spectroscopy (TDS). A constant heating rate of 20°C per minute was used during the measurement. The mass-to-charge ratio (m/e) = 18, corresponding to water (H2O) molecules, was recorded. The TDS result of water desorption from the FSG and FSG films is shown in Fig. 3. A blank Si wafer was also

![Figure 1. Cross-sectional TEM micrographs of (a) as-deposited Cu/TaNx−0.5/Ta/FSGx/(Si), (b) as-deposited Cu/TaNx−0.5/Ta/FSGy/(Si), (c) 400°C/60 min annealed Cu/TaNx−0.5/Ta/FSGx/(Si), and (d) 400°C/60 min annealed Cu/TaNx−0.5/Ta/FSGy/(Si).](image)

![Figure 2. RBS spectra of the (a) Cu/TaNx−0.5/Ta/FSGx/(Si) and (b) Cu/TaNx−0.5/Ta/FSGy/(Si) specimens, as-deposited and after annealing at 400°C in vacuum for 60 min.](image)
investigated as a reference. Figure 3 demonstrates that the FSGO film contains a significant amount of water, whereas the FSG* dielectric layer does not. Degradation of the multilayer, as shown by TEM and RBS analysis, is thus connected with moisture absorbed in the FSG layer.

To understand the impacts of moisture on the chemical composition of FSG, the FTIR absorption spectra of the FSGO films, as-prepared and after annealing at 400°C in vacuum and in N2 ambient, is shown in Fig. 4. It has been reported that absorbed H2O in dielectric film shows a broadband at 3400–3200 cm⁻¹. Therefore, the appearance of a wide peak centered around 3350 cm⁻¹ is associated with the vibration of Si–OH bonds in the as-prepared FSGO film. A minor peak located around 3650 cm⁻¹ is also observed and it should be attributed to the OH stretching vibration in Si–OH bonds. However, it can be found that the Si–OH bonds disappear after annealing of FSGO in vacuum and in N2 ambient. This indicates that the absorbed water in the FSGO films are driven out after thermal treatment.

Because the role of moisture in degradation of the multilayer structure has been confirmed, the degradation caused by the “unstable fluorine” is discussed in the next section. In this study, the unstable fluorine indicates the weakly bonded or unbonded fluorine in the FSG film which is released from the dielectric layer after thermal annealing. Therefore, we would like to discuss the influences of prebaking treatment on the stability of fluorine content in the Cu/TaN(0.5)/Ta/FSGO (or FSG*)/(Si) structure.

Figure 5 shows the SIMS depth profiles of F signals of various (Cu)/TaN(0.5)/Ta/FSGO (or FSG*)/(Si) specimens. The “(Cu)” symbol denotes that Cu films on the multilayer specimens had been removed by acid solution before performing SIMS analysis. In Fig. 5, we can find an accumulation of F at the Ta/FSGO interface of the (Cu)/TaN(0.5)/Ta/FSGO/(Si) specimen due to the high reactivity of Ta with F. We have demonstrated that tantalum fluoride forms at the Ta/FSGO interface after annealing at 400°C, observed by X-ray photoelectron spectroscopy (XPS). It had been reported that the interaction between the Ta layer and unstable fluorine released from the dielectric layer affects the adhesion by occupying the dangling bonds at the interface. Nevertheless, the profile of F signals in the FSG film remains similar even after annealing at 400°C for 60 min. SIMS analysis suggests that prebaking treatment “stabilizes” the FSG film. The desorption of fluorine from FSG films has also been measured by TDS analysis (not shown) at temperatures ranging from room temperature to 800°C. It is found that the amount of fluorine driven out from the FSG films decreases drastically after prebaking treatment in N2 and reduces further after annealing in vacuum. Though the exact amount of fluorine driven out cannot be quantified, the result indicates that, besides residual moisture, unstable fluorine in the FSG film is also driven out by prebaking at 400°C in N2 ambient for 30 min prior to the subsequent metallization. Accordingly, the interaction between the metallization layer and unstable fluorine can be prevented effectively. Meanwhile, the degradation of the specimens via outgassing are reduced significantly.

To further understand the characteristics of Si–O and Si–F bonds in the FSG dielectric layers, Fig. 6 shows the FTIR absorption spectra of the FSGO, FSG*, and FSG** films as-prepared and after annealing at 400°C in vacuum. In Fig. 6, the spectra exhibit the absorption of the Si–O bending vibrational mode [denoted by Si–O(s)], the Si–F stretching vibrational mode [denoted by Si–F(l)], and the Si–O stretching vibrational mode [denoted by Si–O(s)], respectively. It could be found that the peak position of Si–O(s) mode shifted slightly to the higher frequency side (blueshift) after thermal treatment, which suggests a reduction of film density (discussed later).

The relative content of Si–F bonds in the FSG films is calculated by the ratio of peak height of the Si–F stretching mode to the Si–O

![Figure 3. TDS spectra of FSGO and FSG* films showing the H2O⁺ (m/e = 18) ion yield vs temperature. The TDS spectrum of a blank Si wafer is also shown as a reference.](https://example.com/figure3)

![Figure 4. FTIR spectra of the FSGO films before and after annealing at 400°C in vacuum and in N2 ambient. The region of wave numbers corresponding to the vibrational frequencies of Si–OH and H2O is indicated.](https://example.com/figure4)

![Figure 5. SIMS profiles of the F signals in the (Cu)/TaN(0.5)/Ta/FSGO (or FSG*)/(Si) specimens, as-deposited and after annealing in vacuum at 400°C for 60 min. [Note: (Cu) indicates that the Cu layer had been removed before performing the SIMS analysis.]](https://example.com/figure5)
stretches stretching mode and illustrated in Fig. 7. It shows that significant reduction in the relative content of the Si–F bonds can be found after thermal treatment. In Fig. 7, the relative [Si–F(s)/Si–O(b)] peak ratios of the FSG films with thermal treatment (prebaking or 400°C/60 min annealing) are about half of the magnitude as compared with the FSG0 film. The result indicates that unstable fluorine is driven out after thermal treatment, which is consistent with the TDS analysis. Consequently, there is no fluorine piling up at the Ta/FSG interfaces of the prebaked FSG films (FSG*), as shown in Fig. 5.

As we know, the motive of introducing low-k material into IC interconnection is to reduce RC time delay. The RC delay means the signal-propagating time delay which is approximately 0.89/RC, where R is the line resistance and C is the total capacitance associated with the line. Therefore, the variation in the dielectric constants of the dielectrics caused by thermal treatment should be an important concern. In this study, the dielectric constants (k) of the FSG films, with thermal treatment or not, are calculated from the capacitance of Cu/FSG0 (or FSG*)/(Si) MOS structure at the accumulation mode. Furthermore, to clarify the effects of water absorption on the electrical properties of FSG, the FSG* film (prebaked at 400°C in N2 ambient for 30 min followed by soaking in DI water for 30 min) were also prepared and investigated. Whereas the unstable fluorine has been driven out from the FSG films by prebaking treatment, the effects caused by the trapped H2O molecules on the electrical properties of the FSG films can be confirmed by comparing the results of FSG0 with those of FSG*.

Table II sums up the dielectric constants of the FSG0, FSG*, and FSG* for before and after annealing at 400°C in vacuum for 60 min. Meanwhile, the standard deviation numbers for the dielectric constant values are also included. According to Table II, we can find the dielectric constant of the FSG0 film, which is stored in the laboratory ambient and without any thermal treatment, is 4.6. This value is much higher than the dielectric constant of the FSG measured right after deposition (–3.7) and is even higher than that of thermal oxide (–4.0). Nevertheless, the k value of the 400°C/60 min annealed FSG0 would be reduced drastically to 3.6. This indicates that the dielectric constant of FSG increases easily as it is stored in the room ambient, but, after annealing at 400°C for 60 min, the dielectric constant of FSG0 is lowered. Table II also indicates that the k value of the as-prepared FSG0 (3.8) is much closer to the value of the as-deposited FSG (3.7). However, the k value of FSG* could be reduced even as low as 3.2 after annealing in vacuum for 60 min, which is smaller than the k value of as-deposited FSG. Because the unstable fluorine has been driven out of FSG* after baking, the further reduction in the k value of the FSG* layer implies that the dielectric constant is not determined by the unstable fluorine in the film but by some other factors which are discussed later. It includes the content of the moisture in the dielectric film and/or the film density of the dielectric layer. This observation is similar to the conclusion reported by Fuji et al.59

To enhance the amount of H2O molecules in FSG film and prohibit the influence caused by fluorine, the FSG film with prebaking treatment is followed by immersing it into DI water for 30 min and denoted as FSG*. The dielectric constant of as-prepared FSG*, listed in Table II, is 4.2 and reduces to 3.5 after annealing at 400°C for 60 min. Both FSG* and FSG* are prebaked, and the only diversity is the water content in the films. By comparing the k value of the as-prepared FSG* film with that of the as-prepared FSG, the increase of the dielectric constant of the FSG* film can be attributed certainly to the moisture absorption. Because the dielectric constant of water is large (~80 at room temperature), the presence of H2O molecules in the dielectric layer would increase the k value obviously. Moreover, H2O molecules reacting with the unstable Si–F bonds create Si–OH and hydrofluoric (HF) bonds and change the ionic polarization of the FSG film, leading to the increase of the dielectric constant.25

By comparing the k values of as-prepared FSG* (4.6), FSG* (3.8), and FSG* (4.2), it is clear that the main factor altering the k values of FSG is the moisture content. Prebaking (400°C in N2 ambient for 30 min) treatment is effective in driving the moisture out of the dielectrics and the water-soaking process brings the moisture back. Nevertheless, the 400°C/60 min annealing further reduces the k values to be even lower than that of as-deposited FSG (~3.7). By using an ellipsometer, we have realized that the refractive index of the as-prepared FSG0 is 1.464 and it becomes 1.447 after annealing at 400°C for 60 min. In principle, refractive indices
of the materials with similar composition are proportional to the density. It indicates that the film density of the FSG films decreases after annealing. Reduction of film density can also be deduced from an examination of FTIR spectra (Fig. 6), which shows the blueshift of the Si–O(s) vibrational mode after thermal treatment. Lucovsky et al. had reported that the blueshift of the Si–O stretching mode was caused by the decrease in the film density. According to FTIR and ellipsometry analyses suggest that the density of the FSG films decreases after annealing, which consequently leads to the reduction in the dielectric constant of the 400°C/60 min annealed FSG films. The decrease of film density may be due to the loss of fluorine and/or the instability of the FSG structure.25

Figure 8 shows the leakage current density vs electric field (J–E) curves of the Cu/FSG/(Si) MOS capacitors. Ten samples at least were used for the evaluation of leakage current density in each case and the standard deviation error was indicated in Fig. 8 in the electric fields of 1, 2, and 3 MV/cm. According to the magnitude of the leakage current density, these J–E curves can be divided into two groups. The first group includes the FSG* samples only; the second group includes the FSG and FSG’ samples. The results indicate that the leakage current densities of the FSG’ films are higher by 1 order of magnitude than those of the prebaked (400°C/30 min, in N2) FSG and FSG’ films. It had been reported that weak Si–F bonds (the origin of the unstable fluorine) in the FSG film become trapping centers of charges and result in the increase of the leakage current of the MOS capacitors.10,26 In addition, the Si–OH bonds in the FSG film also increase the leakage current. In this study, it is shown that the unstable fluorine can be reduced (i.e., eliminating the weak Si–F bonds) after annealing in N2 ambient and in vacuum. However, it is noticed that the N2 ambient-annealed FSG films (FSG’ and FSG”) possess lower leakage current densities as compared to the vacuum-annealed FSG samples (FSG’). (shown in Fig. 8). The principal residual gas in a vacuum (2.5 × 10−5 Torr) is just H2O vapor; thus, annealing of FSG in vacuum (2.5 × 10−5 Torr) is the same as annealing of FSG in low-pressure H2O vapor. The superiority of prebaking of FSG in nitrogen to annealing of FSG in vacuum (2.5 × 10−5 Torr) is that there is less moisture in the prebaking ambient. By comparing the J–E curve of as-prepared FSG with that of as-prepared FSG’ shown in Fig. 8, it can be found that the leakage current density of FSG’ film is slightly smaller than that of the FSG” sample. The only difference between FSG’ and FSG” is the water content in the dielectric films, and it also indicates that moisture is the main factor in determining the leakage current. The leakage current density of the FSG film increases as water molecules are absorbed in the FSG dielectric layer.

Conclusion

This study investigates the influences of moisture and unstable fluorine on the properties of the FSG dielectric layer and the integrity of the Cu/TaN0.6/Ta/FSG/(Si) multilayer structure. The results indicate that the moisture absorbed in the FSG film increases the dielectric constant drastically. Furthermore, leakage current density of the FSG dielectric layer is affected by the moisture content in the dielectric layer. In this study, both prebaking in N2 ambient and annealing in vacuum can reduce the leakage current densities of the FSG films. However, the effect of prebaking treatment in N2 ambient is superior to that of annealing the FSG film in vacuum. This should be attributed to the less moisture as baking in N2 ambient than annealing in vacuum (2.5 × 10−5 Torr). This study shows that the outgassing process might deteriorate the performance of the IC devices. Therefore, baking the FSG dielectric adequately prior to the subsequent metallization is essential.

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