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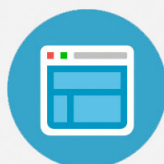
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Effect of fluorine flow and deposition temperature on physical characteristics and stability of fluorine-doped siloxane-based low-dielectric-constant material

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The effects of SiF₄ flow rate and deposition temperature on the physical properties and stability of fluorine-doped organo-silica-glass (OFSG) films were investigated. The porosity of the as-deposited OFSG dielectrics declines as the flow rate of SiF₄ gas and the deposition temperature increase, increasing the dielectric constant. However, newly formed Si–F bonds have less electronic polarizability, reducing the dielectric constant. These traded-off properties yield a minimum dielectric constant of the OFSG film deposited at 250 °C with a SiF₄ flow rate of 100 SCCM (SCCM denotes cubic centimeter per minute at STP). The stability of Si–F bonds in the OFSG films is related to the deposition conditions. OFSG films deposited a higher SiF₄ flow rate (>400 SCCM) or a lower deposition temperature (<300 °C) have lower thermal stability and are less well protected against moisture because of the instability of Si–F bonds. Therefore, more attention should be paid to the conditions for depositing fluorine-doped OFSG dielectrics. © 2010 American Vacuum Society. [DOI: 10.1116/1.3383402]

I. INTRODUCTION

To reduce resistance-capacitance (*RC*) delay of ultra-large-scale integrated circuits, copper, and low-*k* materials ($k < 3.9$) have replaced traditional aluminum and SiO₂, respectively.^{1–3} Among all low-*k* materials in copper metalization, fluorinated silicate glass (FSG) (Si_xO_yF_z) has been extensively applied. However, FSG does not have a low enough *k* value ($k = 3.4–3.7$) to meet the requirements of the next generation.^{4,5} Therefore, carbon-doped silicates or organo-silica-glass (OSG) films with dielectric constants of 2.7–3.2 have become the major candidates for intermetal dielectric applications in ultra-large-scale integrated circuits.^{6–8} However, their poorer mechanical strength and adhesion ability than those of standard SiO₂ films are limiting factors from a process integration point of view.

Our previous works combined FSG and OSG low-*k* film properties to produce fluorine-doped organo-silica-glass (OFSG) films with superior electrical and mechanical properties, as well as excellent adhesion to OSG films.^{9,10} However, the stability of fluorine in OFSG films is unclear. The present work studies the effects of the SiF₄ flow and the deposition temperature on the physical and stability properties of OFSG films. The mechanisms of changes in the film structure under various SiF₄ flow rates and deposition temperatures and under thermal and moisture-induced stress are proposed and discussed.

II. EXPERIMENT

The film deposition was carried out with 13.56 MHz operating rf in an applied material DxZ plasma-enhanced chemical vapor deposition system. The substrates were 200 mm-thick B-doped *p*-type silicon wafers with (100) orientation. Films were deposited from reagent mixtures consisting of 150 SCCM (SCCM denotes cubic centimeter per minute at STP) of oxygen (O₂), 600 SCCM of trimethylsilane, and various SiF₄ flow rates from 0 to 600 SCCM. The process pressure and rf power were set to 4 torr and 600 W, respectively. The deposition temperature was varied from 200 to 400 °C.

The thickness and refractive index of the 300–500 nm-thick films were determined by reflectometry and ellipsometry. Atomic composition was determined by x-ray photoelectron spectroscopy (XPS) using a Physical Electronics 5000LS ESCA spectrometer after sputtering with an Ar⁺ beam to remove the top 2 nm of the film. Transmission Fourier transform infrared (FT-IR) spectra were obtained using a Bio-Rad spectrometer at 4 cm⁻¹ resolution. All spectra were averages of 32 scans, background corrected to a silicon reference. Dielectric constant and residual stress were measured using a mercury probe at 1 MHz and a Flexus stress measurement system, respectively.

III. RESULTS AND DISCUSSIONS

Figure 1 plots the deposition rates of OFSG films as functions of the SiF₄ flow rate and the deposition temperature. In

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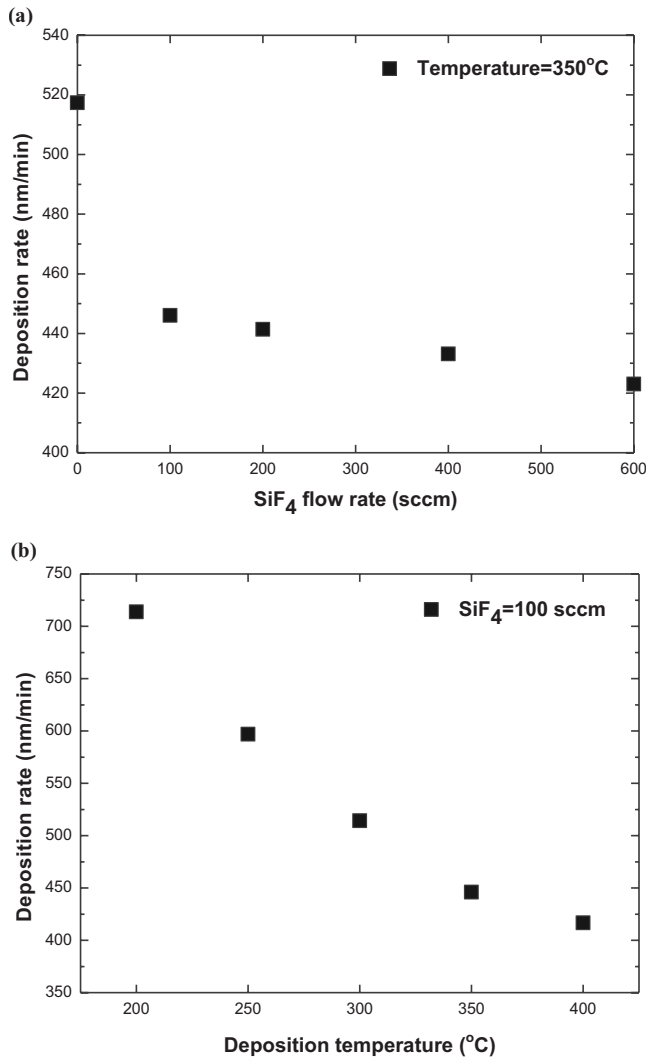


FIG. 1. Deposition rate of OFSG films as function of (a) SiF₄ flow rate and (b) deposition temperature.

both cases, the deposition rate declined as the SiF₄ flow rate and the deposition temperature increased. The decrease in the deposition rate with the deposition temperature reveals a desorption or decomposition-dominated deposition mechanism. Additionally, as shown in Fig. 1(a), as SiF₄ was introduced into the reactor to form the OFSG film, the deposition rate declined from 517 to 446 nm/min, and thereafter decreased slightly as the SiF₄ flow rate was further increased. This result suggests that the deposited OFSG film underwent structural changes because of the introduction of the SiF₄ process gas. In addition, SiF₄ may also act as an etchant in the process of deposition, making the deposition rate of OFSG lower than that of OSG process.

Figure 2 plots the refractive index (633 nm wavelength) of the as-deposited OFSG film as functions of the SiF₄ flow rate and the deposition temperature. The refractive index increases with increasing the SiF₄ flow and deposition temperature. It was reported that the refractive index of dielectric films with constant composition and bonding structure can be used to determine film density.¹¹ Hence, a higher refrac-

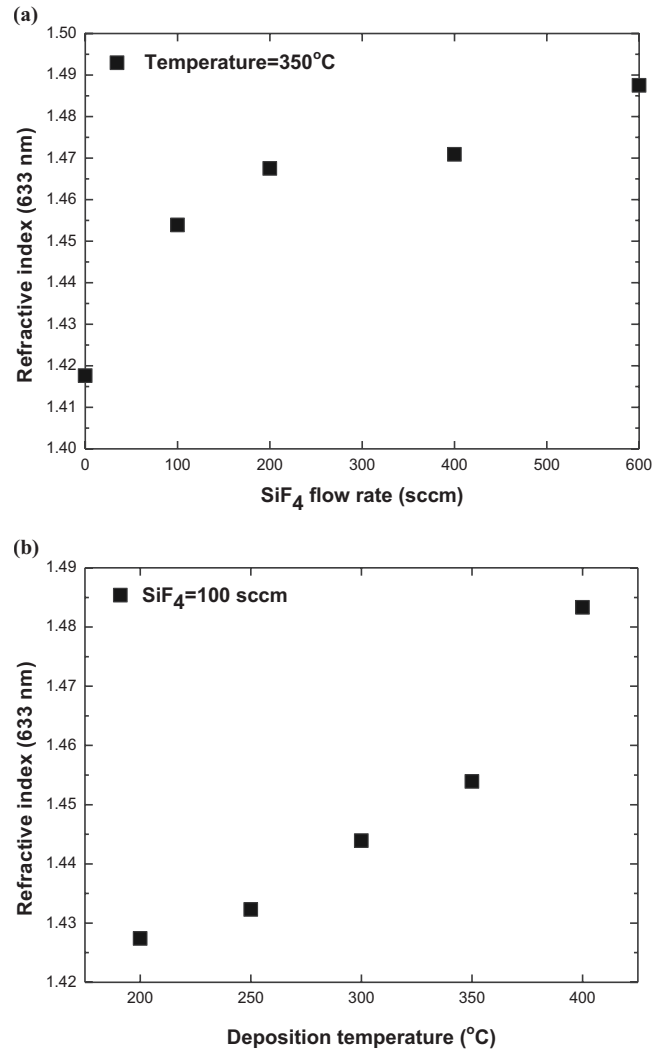


FIG. 2. Refractive index of OFSG films at 633 nm wavelength as function of (a) SiF₄ flow rate and (b) deposition temperature.

tive index represents a higher film density, and thus lower porosity. Therefore, increasing the SiF₄ flow rate or deposition temperature may destroy the porous structure in the deposited films.

To evaluate the reduction in the porosity by the introduction of the SiF₄ gas or an increase in the deposition temperature during OFSG film deposition, the compositions of as-deposited OFSG films were analyzed by XPS and FT-IR. As SiF₄ gas was added into the reactor and its flow rate was increased, the film's fluorine content increased, the carbon content decreased, and the silicon to oxygen concentration ratio varied little, as shown in Fig. 3. Calculating the FT-IR bonding peak intensity of the OFSG films, as presented in Table I, reveals that the absorption peak of Si-H bonding almost disappears when the SiF₄ gas participates in the reaction. Then, the peak intensity of Si-CH₃ bonding declined and that of Si-F bonding increased as the SiF₄ gas flow was increased, indicating that most of the Si-H and Si-CH₃ bonds are replaced by Si-F bonds and that the Si-H bonds are replaced first. With respect to the deposition temperature

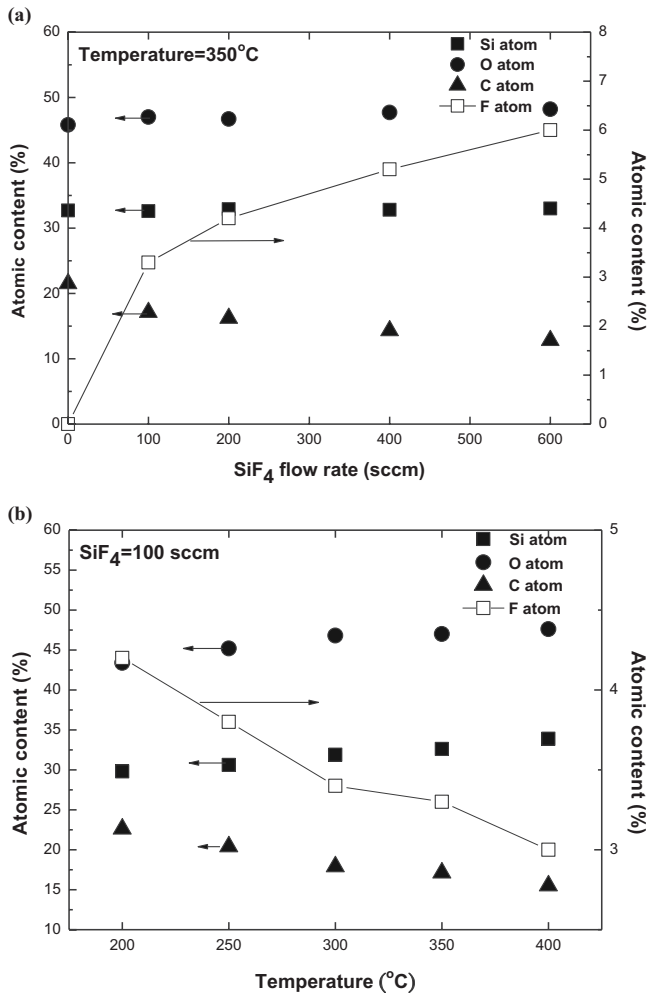


FIG. 3. Composition of OFSG films as function of (a) SiF₄ flow rate and (b) deposition temperature.

TABLE I. Relative S-F, Si-CH₃, and Si-H bond contents incorporated in OFSG films deposited at various SiF₄ flow rates and deposition temperatures. [Note: relative content=peak height for bonds (Si-F, Si-CH₃, and Si-H)/peak height for Si-O-Si bond (at 1050 cm⁻¹).]

Temperature=350 °C			
SiF ₄ (SCCM)	Si-F (%)	Si-CH ₃ (%)	Si-H (%)
0	0	23.40	1.85
100	7.64	17.62	0
200	8.33	15.75	0
400	9.57	13.52	0
600	10.85	12.24	0
SiF ₄ =100 SCCM			
Temperature (°C)	Si-F (%)	Si-CH ₃ (%)	Si-H (%)
200	11.21	24.48	0
250	9.67	21.60	0
300	8.45	18.57	0
350	7.64	17.62	0
400	7.48	15.74	0

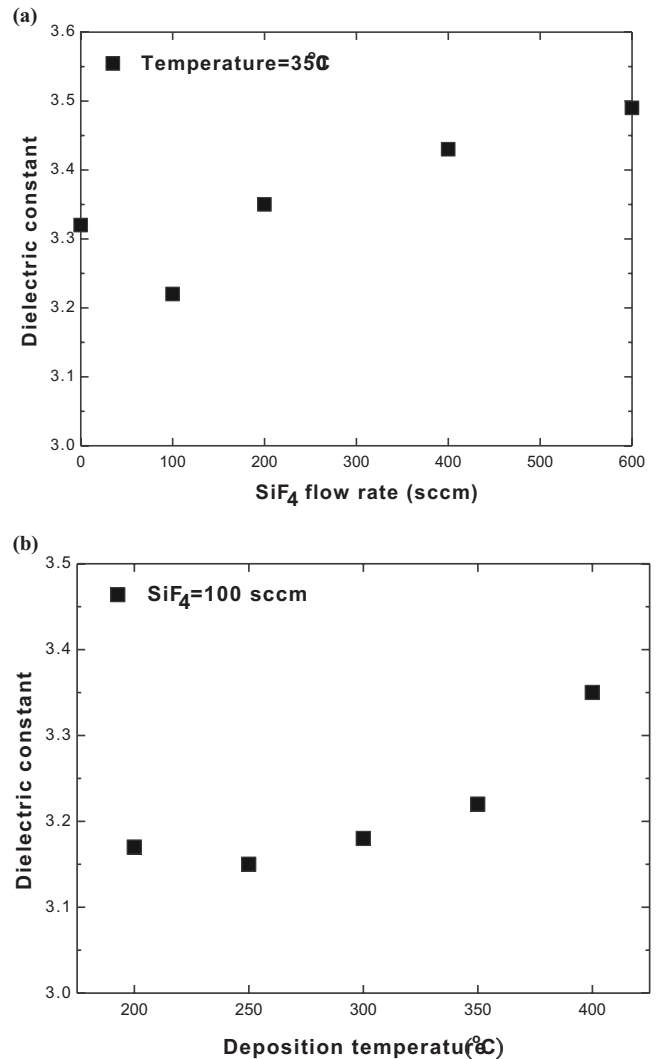


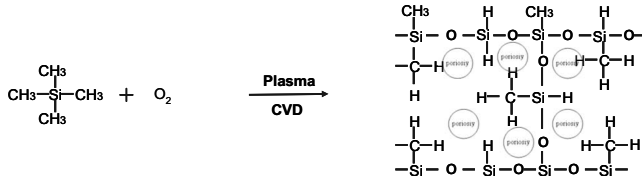
FIG. 4. Dielectric constant of OFSG films at 633 nm wavelength as function of (a) SiF₄ flow rate and (b) deposition temperature.

effect that is shown in Fig. 3(b), the fluorine and carbon contents of the OFSG films decreased slightly, while the silicon and oxygen contents increased as the deposition temperature increased. Additionally, the peak intensity of the Si-F stretching mode decreases upon increasing the deposition temperature. This result suggests that the Si-CH₃ and Si-F bonds in the OFSG films are replaced by Si-Si and Si-O bonds at a higher deposition temperature. Moreover, the decreasing magnitude of Si-F bonds revealed by a decrease in FT-IR peak intensity with increasing the deposition temperature differs from the results of XPS analysis, suggesting that more fluorine reacts with carbon to form C-F bonds at a lower deposition temperature. This result is verified by F(1s) XPS analysis with the observation of C-F bonding. It is also observed that the peak position of Si-O-Si shifts to a higher wave number and the stretching mode of the Si-O-Si cagedlike structure at 1130 cm⁻¹ (Refs. 12 and 13) decreases as the deposition temperature increases, indi-

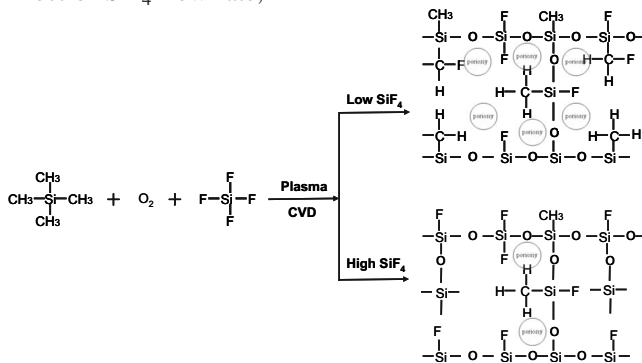
ating that the Si–O–Si bond strength is restored to be similar to SiO₂ and the porosity structure is reduced as the deposition temperature increases.

Based on the aforementioned results, the possible chemical reactions responsible for the deposition of the OFSG films with the effects of SiF₄ flow rate and the deposition temperature can be described as the following reactions:

Without SiF₄,



Effect of SiF₄ flow rate,



Effect of deposition temperature

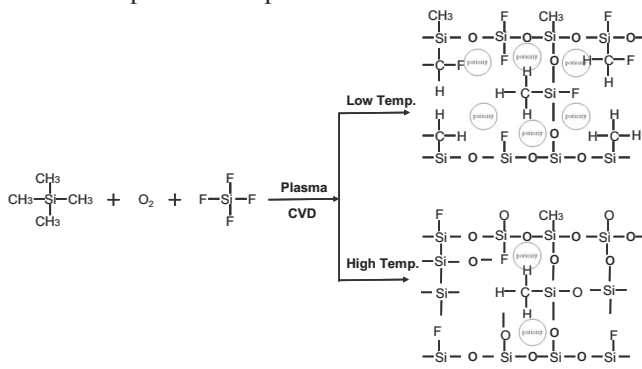


Figure 4 plots the dielectric constant (relative permittivity) of the as-deposited OFSG film as a function of the SiF₄ flow rate and the deposition temperature. The dielectric constant is lowest at 250 °C with a SiF₄ flow rate of 100 SCCM; it increased with increasing the SiF₄ flow rate and the deposition temperature. These results are attributable to the porosity and polarizability effects of the as-deposited OFSG films. The porosity arises from the deteriorated Si–O–Si tetrahedral network by the presence of terminal CH₃, CH_x, or H groups. Consequently, OFSG films deposited at lower SiF₄ flow rates or lower deposition temperatures contain more porous structures. Studies of FSG films^{14,15} have shown that Si–F bonds replace Si–O bonds in the SiO₂ matrix in the FSG films, reducing the dielectric constant due to less electronic polarizability of Si–F bonds. In the deposited OFSG film in this study, Si–F bonds mainly replaced Si–CH_x or Si–H bonds. Pauling found that fluorine is significantly less polarizable,¹⁶ thus produces a film with a lower dielectric constant. As a result, the contributions of porosity and polar-

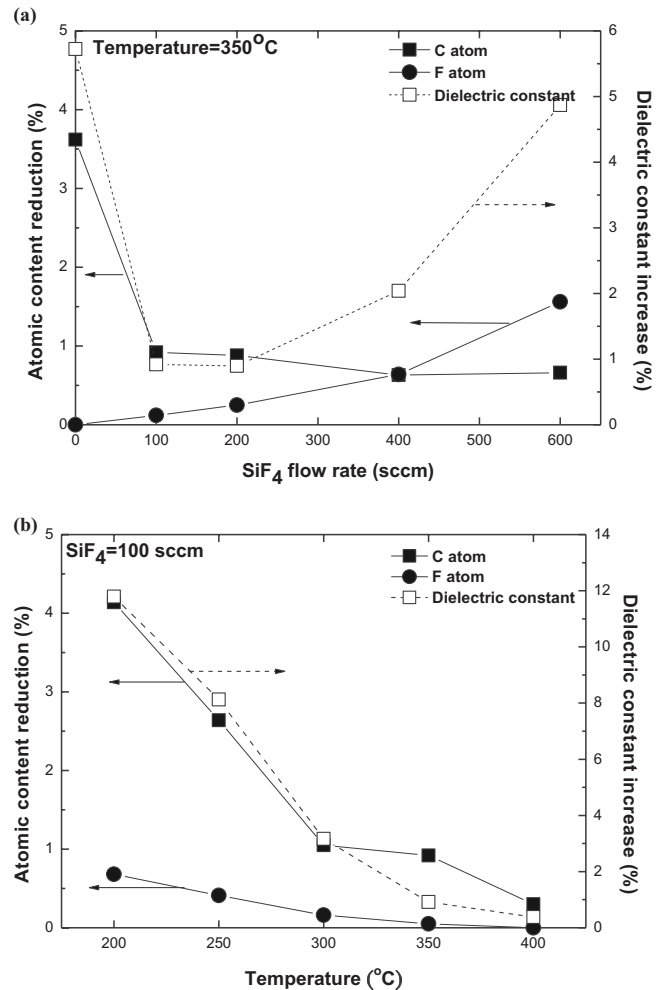


Fig. 5. Change in composition and dielectric constant for OFSG films upon seven cycles of annealing at 500 °C for 1 h each as function of (a) SiF₄ flow rate and (b) deposition temperature.

izability to the dielectric constant of OFSG films are traded-off as Si–F bonds replace Si–CH_x bonds. Therefore, when fluorine is introduced into the matrix of OSG films, the dielectric constant decreases because the Si–F bonds with lower electronic polarizability are formed and the porosity of the structure is not destroyed since the Si–F bonds initially replace Si–H bonds. Further increasing the amount of fluorine would clearly destroy the porous structure and thereby increases the dielectric constant.

Thermal stability tests were performed on the OFSG films that were deposited at various SiF₄ flow rates and deposition temperatures in a N₂ environment at 500 °C for 1 h annealing. Figure 5 presents changes in composition and dielectric constant. The carbon content of annealed films declined upon annealing, especially for the OSG film because of a high degree of porosity structure. Additionally, OFSG films formed at a higher SiF₄ flow rate or a lower deposition temperature exhibit a greater drop in fluorine content. Although the bonding strength of Si–F is stronger than that of Si–C (or Si–CH₃) or Si–H, formed Si–F bonds in OFSG films deposited at a higher SiF₄ flow rate or a lower deposition tempera-

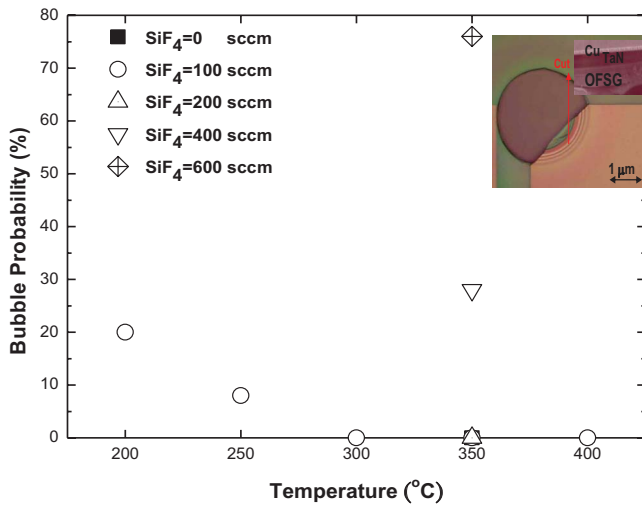


Fig. 6. (Color online) Probability of occurrence of bubble defect for OFSG films deposited at various SiF_4 flow rates and deposition temperatures.

ture are still weak and such bonds are destroyed and decomposed upon annealing at high temperature, producing a larger degradation in dielectric constant.

A stacked film with a $\text{SiCN}/\text{OFSG}/\text{TaN}/\text{Cu}/\text{SiO}_2/\text{Si}$ structure, which OFSG films were prepared under various deposition conditions, was annealed at 500°C for seven cycles, each for 1 h. The film interface state was observed by an optical microscopy. The inset in Fig. 6 presents bubble defects shown in the OFSG films that were formed at a higher SiF_4 flow rate or a lower deposition temperature. Figure 6 presents the probability of occurrence of such bubble defects determined by inspecting 25 sites. Higher failure rates were associated with OFSG films deposited at higher SiF_4 flow rates and lower deposition temperatures. A bubble defect was analyzed by scanning electron microscopy, which indicated that the interface between the barrier metal and the OFSG film was the main location of delamination. One possible cause is that fluorine atoms associated with the unstable Si-F bonds in the OFSG films diffused into the interface during thermal annealing and accumulated there, causing delamination at the interface.

The films with more Si-F dipole bonds or more porosity structures were more hydrophilic and exhibited poorer moisture impedance. To investigate the effect of moisture on the OFSG films formed under various deposition conditions, OFSG films made at various SiF_4 flow rates and deposition temperatures were exposed at 120°C , 100% relative humidity, and the pressure of 2 atm for 500 h. The film structure and residual stress changed upon the absorption of moisture. Figures 7 and 8 show the change in residual stress and dielectric constant, respectively, as functions of storage time. The properties of OFSG films degraded more than those of OSG films without incorporated fluorine, suggesting that Si-F bonding may promote the absorption of water beyond that of porous structures. On the other hand, OFSG films deposited at higher SiF_4 flow rates and lower deposition temperatures exhibit a larger shift in residual stress and dielectric

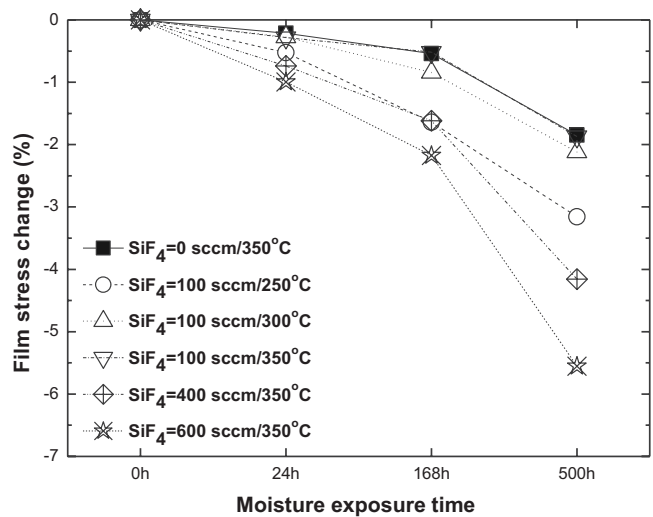


Fig. 7. Change in residual stress for OFSG films deposited at various SiF_4 flow rates and deposition temperatures during the moisture test.

constant, indicating that weak Si-F bonds accelerate the reaction with moisture, which destroys the structure of the film.

IV. CONCLUSION

The effects of SiF_4 flow rate and deposition temperature on the physical characteristics and stability of the OFSG films were studied. The porosity structure of as-deposited OFSG dielectrics, declined as the SiF_4 flow rate and the deposition temperature increased, increasing the dielectric constant. However, newly formed Si-F bonds have less electronic polarizability and therefore reduce the dielectric constant. Therefore, these traded-off properties yield a minimum dielectric constant of the OFSG film at a deposition temperature of 250°C and a SiF_4 flow rate of 100 SCCM. Additionally, the stability of Si-F bonds is related to the deposition conditions. OFSG films deposited at a higher SiF_4 flow rate

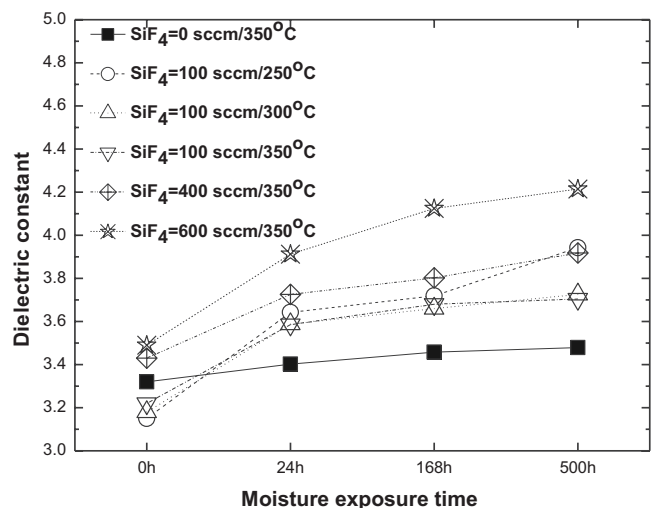


Fig. 8. Change in dielectric constant for OFSG films deposited at various SiF_4 flow rates and deposition temperatures during the moisture test.

(>400 sccm) or a lower deposition temperature (<300 °C) have worse thermal stability and moisture protection resistance because of the instability of Si-F bonds. Consequently, more attention must be paid to the deposition conditions of fluorine-doped organo-silica-glass dielectrics.

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