

Effect of deposition temperature and oxygen flow rate on properties of low dielectric constant SiCOH film prepared by plasma enhanced chemical vapor deposition using diethoxymethylsilane

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Abstract

Low dielectric constant (Low- k) films (SiCOH) were deposited from diethoxymethylsilane [DEMS; SiH(CH₃)(OC₂H₅)₂] which has two ethoxy groups along with one methyl group attached to the silicon atoms. The deposited films have been characterized for different oxygen flows, ranging from 50 to 250 standard cubic centimeters per minute (scm). The growth rate is increased with the increasing oxygen (O₂) flow. The absorbance spectrum of Fourier transform infrared spectroscopy shows that the frequency of Si–O stretching vibration mode in the SiCOH film is shifted to a higher wave number with the increase of oxygen flow. It is deduced that the oxygen does not participate in a simple oxidative mechanism, and has no apparent impact on the methyl content even if the relative Si–O content of the deposited films is up to an O₂/DEMS flow rate ratio of 1:1. Also, the refractive index is decreased with increasing the oxygen flow and slightly increased with the deposition temperature. The dielectric constant of the SiCOH is investigated between 2.7 and 3.2, depending on the deposition temperature and O₂/DEMS flow rate ratio, which is lower than that of the current OSG films ($k=2.9–3.3$). SiCOH films deposited with DEMS only exhibit higher mechanical hardness and lower leakage current than those deposited with both DEMS and oxygen.

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1. Introduction

To mitigate the signal propagation delay, crosstalk, and dynamic power consumption due to resistance and parasitic capacitance, new materials of metal lines and inter-metal-dielectric (IMD) layers are being developed to replace conventional aluminum and SiO₂, respectively, to improve the performance of decreasing the device sizes [1–3]. This requires the introduction of low resistivity conductors such as copper and insulators with lower dielectric constant (k). Therefore, the ongoing effort has been invested to develop reliable low- k materials to implement copper metallization.

Recently, one of the low- k candidates is the material comprised mainly of Si, C, O, H, and/or F prepared by plasma enhanced chemical vapor deposition (PECVD) method. These include F-doped oxide, or fluorinated silicate glass (FSG, Si_xO_yF_z); and C-doped oxides, or organosilicate glass (OSG, SiCO:H) [4]. The former, FSG ($k=3.4–3.7$), with a slightly lower dielectric constant than conventional undoped silicate glass ($k=3.9–4.1$) [5–7], has successfully demonstrated its benefits as a feasible low- k material [8–12] into IMD application with suitable fluorine concentration (<5%) [13,14]. The latter, the OSG film, has become one of the main candidates for potential applications in 130 nm technology node due to its lower dielectric constant ($k=3.0–2.1$) [15–17] with good thermal and mechanical stability.

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Many precursors have been studied for the deposition of PECVD SiCOH films, such as trimethylsilane, tetramethylsilane, tetramethylcyclotetrasiloxan, dimethyldimethoxysilane, and hexamethyldisiloxane [18–20]. However, from the point of view of process integration, this new low- k material, which has low density and high porosity, has not demonstrated sufficient mechanical properties, such as high hardness and elastic modulus that are required to withstand the mechanical stress imposed by the chemical–mechanical polishing process. Additionally, it needs to possess high resistance to stress migration and dry etching, without raising the dielectric constant.

In this study, DEMS was selected as a precursor for the deposition of SiCOH film. It has been suggested that the precursor provides the best balance between the electrical and mechanical properties [21]. The SiCOH films were deposited at various oxygen flows, and the optical refractive index, bonding configuration, mechanical properties, and electrical strength of the films were investigated in this study. The structural alteration mechanism that leads to the improved mechanical properties and lower dielectric constant are proposed and discussed in this contribution.

2. Experiment

The deposition of the SiCOH films was performed in a PECVD system with the operating rf of 13.56 MHz. The thin films were deposited on p -type 200 mm silicon wafers with (100) orientation diethoxymethylsilane (DEMS, Air Products and Chemical, Inc.) was carried in vapor phase by inert helium (He) gas to the reaction chamber. The flow rate of He gas and DEMS flow were controlled at 300 sccm and 1500 mg min⁻¹ (equal to 250 sccm), respectively. The DEMS precursor gas was mixed with oxygen (O₂) in the deposition process. The pressure and RF power were maintained at 533 Pa and 500 W, respectively, throughout the deposition process. The deposition temperature and O₂/DEMS flow rate ratio were varied between 350 °C and 425 °C and 0–1, respectively, where O₂ flow rate was varied from 0 to 250 sccm.

The thickness and refractive index (at 633 nm wavelength) of the as-deposited films were analyzed for by reflectometer and/or ellipsometer using the Nano-Spec® 9100. Forty-nine-point measurements were performed on each wafer to acquire the mean value. Chemical bonding and composition of the film were investigated using Fourier transform infrared spectroscopy (FT-IR) [Bio-Rad Win-IR PRO], and photoelectron spectroscopy (XPS), respectively. FT-IR was performed at a resolution of 4 cm⁻¹, each spectrum being the average signal over 64 scans with the background corrected to a silicon reference. An MTS Nano Indentor XP system was utilized to measure the nano-hardness and modulus of the deposited SiCOH films. The sample thickness for nano-hardness measurement was approximately 1 μm. The penetration depth was about 100

nm at ~0.3 mN down force, and each hardness entry is the average over 5 measurements. In electrical characterization, the dielectric constant and leakage current of the SiCOH films were measured by capacitance–voltage measurements with a SSM Inc. Hg probe 5100 CV system at 1 MHz. The errors of the capacitance and the mercury electrode area are less than 1%.

3. Results and discussion

Fig. 1 shows the deposition rate of SiCOH films deposited at different temperatures (350 °C and 425 °C) as a function of the O₂/DEMS flow rate ratio. The deposition rate is increased with O₂/DEMS flow rate ratio and decreased with the deposition temperature. In the PECVD process, the deposition rate depends on the activated reactant concentration on the substrate surface. The increase of the oxygen flow rate in the deposition process induces the increase in reactivity of DEMS, and a higher proportion of plasma-generated species having sufficient bonding energy has been incorporated into the film. In addition, as O₂/DEMS flow rate ratio is increased beyond 0.4, the effect of oxygen content on the growth rate of SiCOH films becomes significantly obvious. Moreover, it is found that the growth rate is increased by a factor of 4 times as the O₂/DEMS flow rate ratio up to 1.0. The change in deposition rate at different deposition temperatures can be explained by the changes in desorption of the reactant with different temperatures. The deposition rate of the SiCOH films exhibits a decreasing tendency with temperature, indicating that this deposition process is surface reaction control, and the sticking coefficient of the precursor-mediated molecules on the silicon surface is decreased with increasing the temperature. Fig. 2 exhibits the refractive index of the SiCOH films deposited at various temperatures and oxygen flows. The refractive index of SiCOH films is averaged over 49 measured points per wafer which exhibits a decreasing trend with the O₂/DEMS flow rate ratio

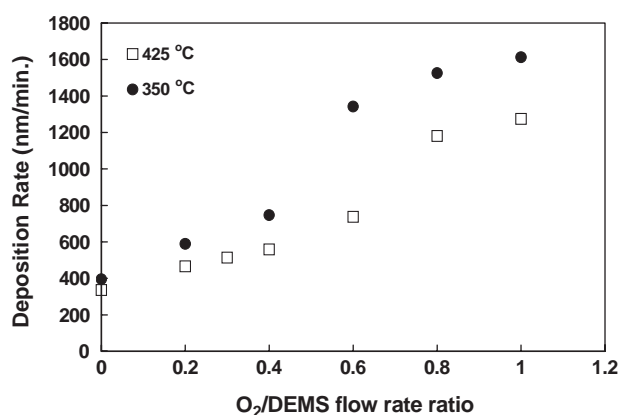


Fig. 1. Deposition rate as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature.

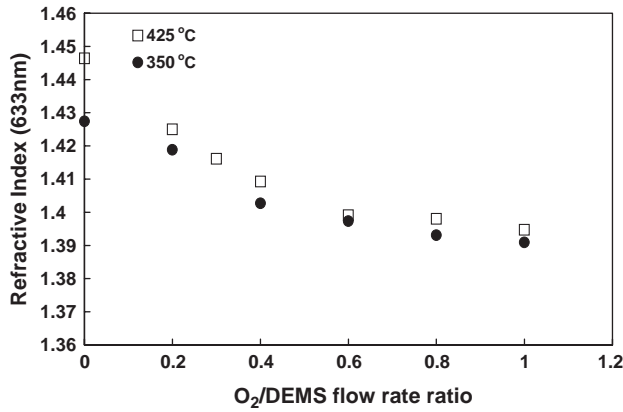


Fig. 2. Refractive index (633 nm wavelength) as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature.

regardless of the deposition temperature. The results suggest that the properties of the deposited films, such as composition, density, and bonding configuration, have been significantly changed by the addition of oxygen. It is well known that the refractive index is closely related to the density of materials, being lower at lower density [22]. A lower density is attributed to the higher porosity within the film. Therefore, the difference of the refractive index with O₂/DEMS flow rate for SiCOH films in this study is attributed to the variation of film density which is caused by Si–O–Si caged structure variation obtained from FT-IR measurements.

To further investigate the variation in growth rate and refractive index, the bonding states of the SiCOH composite films were analyzed by IR absorption spectra over the range of 400–4000 cm⁻¹. Fig. 3 shows the FT-IR raw spectra for a series of SiCOH film of 300 nm thickness deposited at 425 °C. The Si–O stretching cage-structure peak near 1132

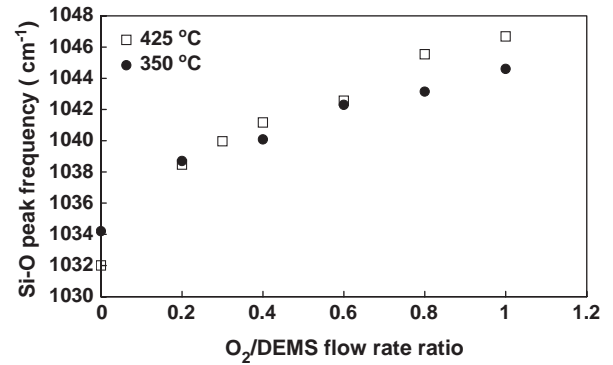


Fig. 4. Si–O peak frequency as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature.

cm⁻¹, Si–O network stretching network peak is near 1040 cm⁻¹, Si–O bending cage-like peak near 863 cm⁻¹, and the Si–O bending network peak is near 830 cm⁻¹. In addition, the Si–CH₃ stretching and bending peaks are near 1270 cm⁻¹ and 802 cm⁻¹, respectively. The weakly absorption methylene bridged silicon stretch is located at 1360 cm⁻¹. CH_x peak is near 2975 cm⁻¹, and the weakly absorbing Si–H bands are located at 2240 and 2170 cm⁻¹ due to (Si–O₃)–H and R–(Si–O₂)–H, respectively.

It is observed from Fig. 3 that there is little change in the Si–O stretching mode while the Si–O stretching cage-like mode is increased as the O₂/DEMS flow rate ratio is increased. The network structure reduces the density of the SiCOH film. Influences of process parameters on absorption of Si–O–Si stretching mode in the films are shown in Fig. 4. It can be found that the absorption of Si–O–Si stretching mode shifts to a higher wave number with increasing the O₂/DEMS flow rate ratio, and to slightly a lower wave number with decreasing the deposition temperature. The increasing wavenumber of the Si–O absorption is due to a changing

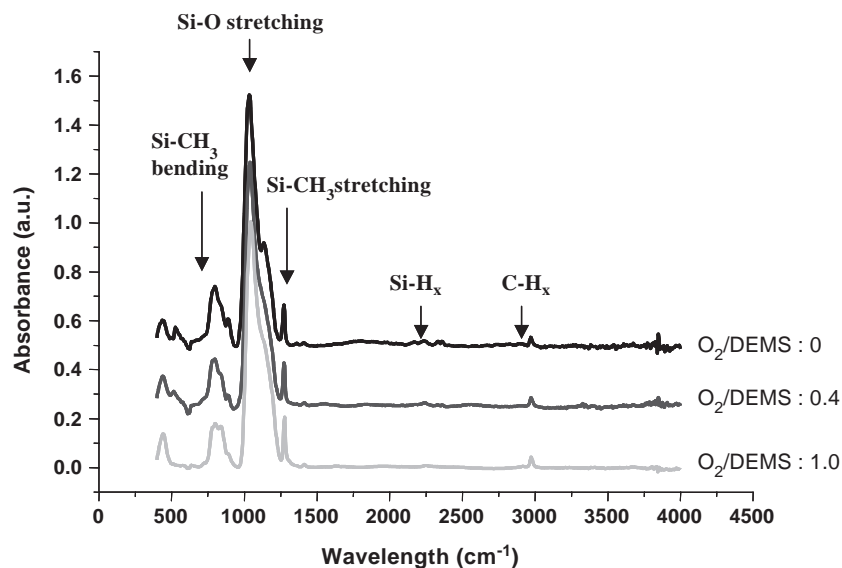


Fig. 3. FT-IR spectra of the SiCOH films with varying O₂/DEMS flow rate ratio.

bond angle of the Si–O network, approaching to that of SiO₂. As a consequence, the Si–O–Si bonds are weakened and become less rigid and more stretchable, resulting in a higher stretching frequency as shown in Fig. 4. In this case, a higher deposition temperature increases the frequency of the stretching Si–O–Si bonds in the structure of SiCOH films. This implies that the electronic defects are reduced and bond angle are adjusted at high deposition temperature so that the Si–O–Si bond strength is restored to certain degree, and the effect of oxygen is enhanced.

As further investigated in 950–1250 cm⁻¹ wavenumber, it reveals that the Si–O–Si stretching peak is divided into two peaks, the main peak at around 1070 cm⁻¹ (Si–O network), and the shoulder peak at around 1130 cm⁻¹. Si–O (cage) is typically the main cause for the shoulder at higher wavenumbers, but has C–O groups and other species that are obscured by the strong Si–O absorbance. It becomes increasingly difficult to differentiate the two peaks at higher O₂ ratio due to the blue-shift and the overlap of shoulder peak with the main peak. Pai et al. [23] suggested that the shoulder peak is due to in-phase and out-of-phase movements of the Si–O–Si bond. Grill et al. [20] and Chou et al. [22] proposed that the shoulder peak is related to the porosity of an oxide with caged Si–O bonds and the reflection of enhanced porosity in the films. The addition of oxygen results in microvoids that account for the appearance of the shoulder peak.

The peak intensity of CH_x-group (around 1270 cm⁻¹ and 2900 cm⁻¹) shows no significant change or trend with increasing O₂/DEMS flow rate ratio (Fig. 5). However, the addition of oxygen in the deposition process slightly increases the organic contribution (CH_x-group), which decreases electrical and ionic polarization of the deposited films. Therefore, the dielectric constant of the deposited film is slightly decreased with the addition of oxygen in the deposition process.

In the FT-IR analysis of 2100–2300 cm⁻¹, there are two obvious peaks observed in 2170 cm⁻¹ and 2240 cm⁻¹, corresponding to R–(Si–O₂)–H and (Si–O₃)–H bonds. As

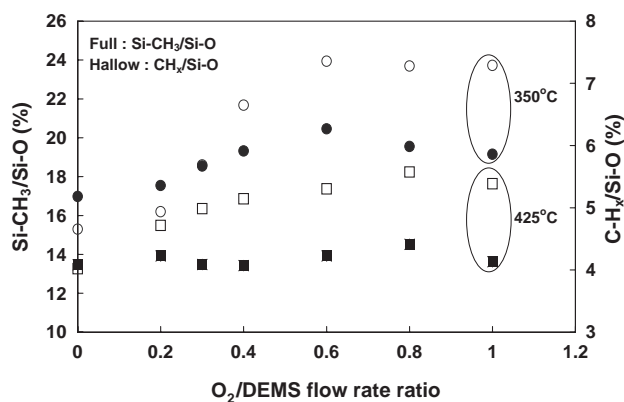


Fig. 5. Si–CH₃/Si–O and C–H_x/Si–O peak ratio in the SiCOH films as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature.

Table 1

XPS result for the SiCOH films as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature

O ₂ /DEMS	Temperature (°C)	O	C	Si
0	425	42.8	24	33.2
0.4	425	45.1	21.9	33
1	425	46.7	20.6	32.7
0	350	41.2	26.4	32.4
0.4	350	43.9	23.6	32.6
1	350	44.8	22.2	33

shown in Fig. 3, there is a significant reduction in the Si–H content with increasing oxygen. It is worth mentioning that the hydrogen reduction is attributed to the reduction of R–(Si–O₂)–H group. Additionally, the shape of the absorbance indicates a shift to more networked as oxygen is added to the deposition process. On the other hand, as comparing the Si–CH₃ absorbance, there is a shift and narrowing of the absorbance with adding and increasing the amounts of oxygen. It is inferred that DEMS contributes more Si–(CH₃)₂ and Si–(CH₃)₃ groups when there is no oxygen in the deposition. As oxygen is added, there is a preference for more Si–(CH₃), or mono-methylsilane groups. This well agrees very well with the ²⁹Si NMR data which shows the same effect when oxygen is added. The amount of methyl groups attached to Si does not change with the addition of oxygen. This indicates that the addition of oxygen does not directly affect the methyl group via oxidation, but it prevents the production of Si–(CH₃)₂ and Si–(CH₃)₃, essentially converting to mono-methylsilane groups. A particular change is the loss of the absorbance at 1360 cm⁻¹, indicating that the influence of addition of oxygen is the reduction of Si–CH₂–Si groups. As a result, when oxygen is added to participate in the deposition process, there are two main outcomes to balance the overall effect on the mechanical properties of the films. One is the loss of Si–H (no contribution to network) and the other is the loss of Si–CH₂–Si (positive contribution to network).

The effects of O₂/DEMS flow rate ratio and deposition temperature on the relative carbon content incorporated into

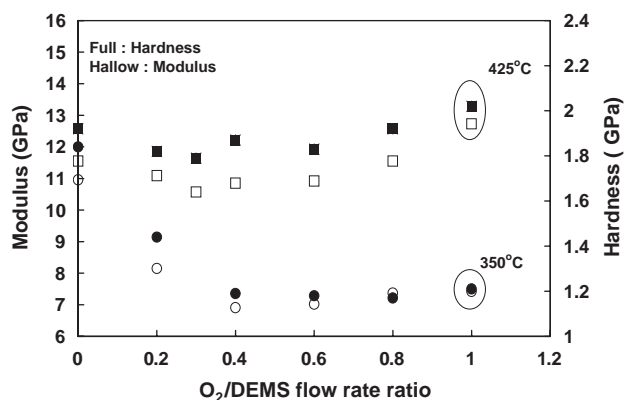


Fig. 6. Hardness and modulus of the SiCOH films as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature.

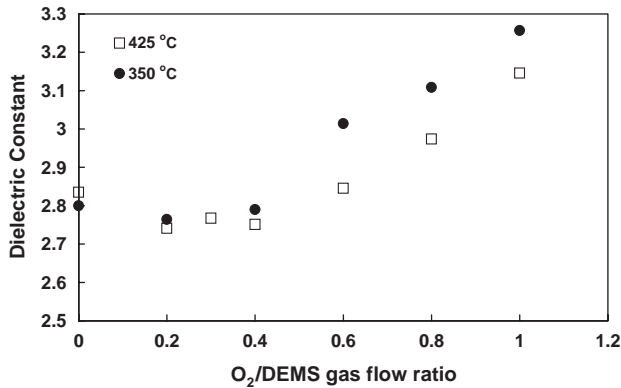


Fig. 7. Dielectric constant of the SiCOH films as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature.

the SiCOH film is shown in Fig. 5. The relative bonding concentration of carbon incorporated in SiCOH films is calculated by the following equation normalized to the peak Area of the Si–O–Si stretch mode:

$$\text{Relative [C] content (\%)} = \frac{A_C}{(A_C + A_{\text{Si-O}})} \times 100\% \quad (1)$$

where $A_{\text{Si-O}}$ and A_C are the peak height of the stretching vibration mode of Si–O–Si at 1060 cm^{-1} and Si–CH₃ at 1270 cm^{-1} , respectively. The carbon content is increased with decreasing the deposited temperature and increasing the oxygen flow. The carbon content is reached saturation as O₂/DEMS flow rate ratio is up to 0.4. On the other hand, from the results of elemental analysis by XPS shown in Table 1, it exhibits a slightly decrease in the carbon element with increasing the O₂/DEMS flow rate ratio. This result suggests that the increase in O₂/DEMS flow rate ratio in the SiCOH films is accompanied with the increase of Si–(CH₃) or mono-methylsilane groups and the decrease of Si–CH₂–Si groups in the SiCOH film.

Mechanical hardness and modulus of elasticity of the resulting SiCOH films are plotted as a function of O₂/DEMS flow rate ratio at 350 °C and 425 °C deposition temperature shown in Fig. 6. The hardness variation with O₂/DEMS flow rate ratio is attributed to the porosity of this film due to the existence of Si–O–Si caged-structure by oxygen incorporation. At the O₂/DEMS flow rate ratio of 0.2–0.3, the film is demonstrated the lowest hardness (1.79 GPa). Due to the reduction of Si–CH₂–Si group, positive contribution to network, the hardness of the film is slightly increased as the O₂/DEMS flow rate ratio is above 0.4. It is worth noting that the hardness (1.7 G ~ 2.2 GPa) of the SiCOH films at 425 °C is higher than that deposited at 350 °C (1.1–1.8 GPa) due to the abundance of Si–O–Si bonds at higher temperatures. This helps the SiCOH films restore part of the bond integrity and tetradral structure of a perfect SiO₂, leading to the improved mechanical properties. Additionally, it is found that the SiCOH film deposited from the DEMS precursor have higher hardness than OSG (~1.5 GPa) deposited by methylsilane precursors.

Dielectric constant is a frequency dependent, intrinsic material property. Fig. 7 shows the dielectric constant (relative permittivity) measured at 1 MHz of the thin films investigated in this study. As shown in Fig. 7, when oxygen is incorporated into the deposition chamber, the dielectric constant is decreased and reaches a minimum value at the oxygen flow rate of 100 sccm (O₂/DEMS flow rate ratio is 0.2). The reduction of the dielectric constant of the SiCOH film caused by the electronic contribution is attributed to a decreased density of the network due to higher Si–O cage structure while the organic content of the film remains unchanged. This reflects the decreased refractive index of the deposited film. Therefore, when the oxygen flow rate reached 100 sccm, the dielectric constant shows a minimum value. While the oxygen flow rate exceeds 100 sccm, the dielectric constant is increased slightly with the increase of the oxygen flow rate. It is deduced that the ionic component

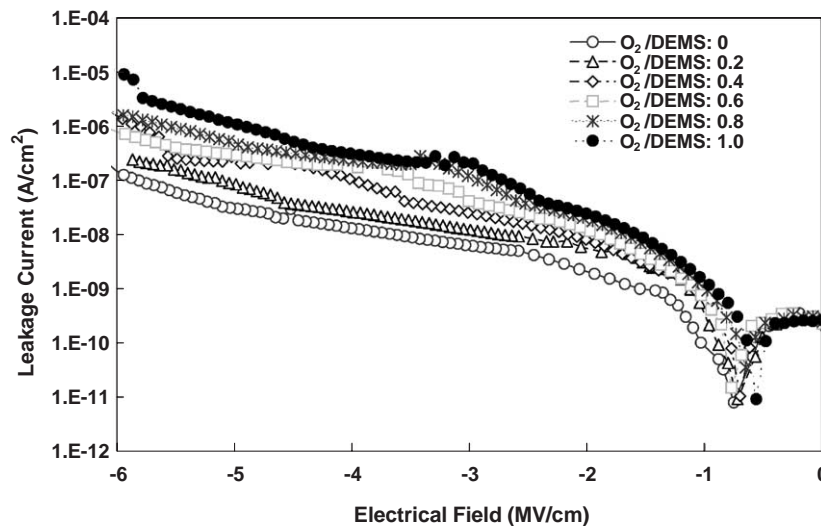


Fig. 8. Leakage current of the SiCOH films as a function of O₂/DEMS flow rate ratio at 425 °C deposition temperature.

increase as the oxygen content increases because Si–O bond is more polarized than Si–C bond [22]. As a result, the dielectric constant of SiCOH films increases as O₂/DEMS flow rate ratio beyond 0.2 although the refractive index decreases. Additionally, an extra benefit is observed as the oxygen is added in the deposition process. Since the non-uniformity in dielectric constant causes the large variation in device performance, depending on the location on the wafers, more uniform dielectric constant across the wafer is essential. As oxygen is incorporated into the reaction, the variation of dielectric constant at the center and edge location of 8-in. Si-wafer is about 0.1–0.2, lower than 0.4 without oxygen addition. It may be caused by the uniform plasma density across the wafer as O₂ is incorporated into the reaction processes. The within-wafer uniformity of thickness and refractive index also reveals the same results.

The leakage currents on the electric field for SiCOH films deposited at varying oxygen flows rate and deposition temperature were evaluated. As shown in Fig. 8, there is an increasing trend of the leakage current with raising the O₂/DEMS flow rate ratio. The leakage currents are in the range of 10⁻⁸–10⁻⁹ A/cm² at 1 MV/cm, depending on the O₂ flow rate. This value is slightly lower than that of other PECVD low-*k* films [23,24]. The reason of increased leakage current by adding O₂ is not clarified yet. However, it is speculated to be the increase of the microvoid structure. As for temperature effect, lower deposition temperature results in more stretchable Si–O–Si bonds, more CH_x groups, and more porosity present in the films. The leakage current of the SiCOH film is, therefore, decreased at a lower deposition temperature.

4. Conclusion

The composition, bonding configuration, mechanical, and electrical properties of SiCOH films using diethoxymethylsilane (DEMS) and oxygen (O₂) as a precursor by PECVD method have been investigated. The refractive index of SiCOH increases with increasing deposition temperature but decreases with increasing oxygen adding to the deposition recipe. The addition of oxygen dramatically enhanced the plasma deposition rate of DEMS. The as-deposited films also show lower dielectric constant and decreased mechanical hardness and modulus. The effect is reduced at higher temperatures. The results can be accounted by the changes in composition and bonding configuration, as determined from FT-IR and elemental analyses.

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