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# Moisture resistance and thermal stability of fluorine-incorporation siloxane-based low-dielectric-constant material

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**Abstract**

The low dielectric constant (low-*k*) of organo-silica-glass (OSG) and fluorine-incorporated OSG (OFSG) materials produced from plasma-enhanced chemical vapor deposition of trimethylsilane are thermally stable to greater than 600 °C. FTIR analysis indicates that Si–$CH_3$ bonds and Si–F bonds remain intact to temperatures well above that normally encountered during integrated circuit manufacture, allowing these materials to maintain a low-*k* value. While OFSG materials proved to have less hydrolytic resistant than their non-fluorinated analogs during high pressure, high temperature water exposure (pressure cooker test), their leakage current was found to be lower than OSG films before and after wafer exposure. The measured properties of OFSG blanket films suggest that this material is sufficiently robust to ensure stability of reliability after the fabrication.
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*Keywords:* Organo-silicate-glass; Heat resistance; Moisture resistance; Low dielectric constant (low-*k*)

## 1. Introduction

Low parasitic capacitance multilevel interconnects using low dielectric constant interlayer dielectrics are essential for high-speed ultra large-scale integrated circuits [1–3]. Organo-silica-glass (OSG, $k=2.8$–3.3) deposited by plasma-enhanced chemical vapor deposition (PECVD) has received more attention recently due to their potential to fit into existing processing schemes [4,5]. It is the reduced mechanical strength of OSG materials as a result of replacement of oxygen from the silicate network with organic groups such as Si–$CH_3$ bonds that is the main issue for integrated circuit fabrication [6]. Here we study that the heat and moisture resistance of a newly developed low-*k* material, organofluorosilicate glass (OFSG), within fluorine is incorporated into the structure as Si–F only. The resulting material is endowed with higher mechanical strength, providing enhanced resistance to cracking of multi-layer structures and film peeling due to chemical–mechanical planarization.

To ensure high process yield, device performance and reliability over its lifetime, the electrical properties (dielectric constant, breakdown voltage and leakage current) of interlayer/intermetal dielectric materials were resistant to thermal and moisture stresses. The heat resistance is necessary since wafers are exposed to temperatures over 400 °C during fabrication of upper-level interconnects. Since thermal treatment is required after completion of each level of the interconnect structure, the lower level interlayer dielectrics are subjected to many hours of heating [7]. Additionally, moisture resistance is necessary for long-term reliability after packaging. In real operating conditions, the ILDs are subjected to moisture penetrating from the outside environment. The effect of this moisture penetration is commonly evaluated by accelerated humidity tests.

The effects of heat and moisture exposure on OSG and OFSG films are investigated in this paper. The

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Table 1
Process conditions and film properties of OFSG and OSG film

| | OFSG | OSG |
|---|---|---|
| *Process conditions* | | |
| 3MS (sccm) | 540 | 540 |
| $O_2$ (sccm) | 150 | 150 |
| $SiF_4$ (sccm) | 250 | |
| RF power (W) | 600 | 600 |
| Pressure (Torr) | 4 | 4 |
| Temperature (°C) | 4 | 4 |
| *Film properties* | | |
| Refractive index | 1.45 | 1.41 |
| Dielectric constant | 3.2 | 3.3 |
| Modulus (GPa) | 12.5 | 8 |
| Hardness ($H$, GPa) | 1.98 | 1.76 |
| Deposition rate (mm/min) | 450 | 670 |

effect of fluorine addition to the silicate network is assessed by physical and reliability properties of these films. The result of the relationships between the dielectric constant stability, surface chemical composition and electric properties are reported and discussed.

## 2. Experimental

The deposition of the OSG and OFSG films were carried out in an enhanced plasma PECVD system with 13.56 MHz operating r.f. The substrates used in this study were B-doped p-type 200-mm silicon wafers with (1 0 0) orientation. The deposition temperature was both maintained at 350 °C; process pressure and r.f. power were set at 4 mm Torr and 600 W, respectively. Except for the addition of $SiF_4$, both materials were deposited using trimethylsilane (Z3MS™) and oxygen under similar conditions. The optimized process conditions and film properties are shown in Table 1. Films 300–500 nm thick were analyzed for thickness and refractive index (RI, at 248 and 633 nm) by reflectometry (SCI Film Tek 2000) and/or ellipsometer (Nano-Spec 9100). Transmission FTIR spectra were measured using Bio-Rad spectrometer at 4/cm resolution. All spectra are an average of 32 scans and were background corrected to a silicon reference. Dielectric constant and leakage current were measured by mercury probe at 1 MHz frequency. Atomic composition was determined by X-ray photoelectron spectroscopy using a Physical Electronics 5000LS ESCA spectrometer after sputter with $Ar^+$ beam to remove the top 20 A of film.

Thermal stability of the films was assessed by 1 h furnace anneal in nitrogen ambient at temperature ranging from 300 to 700 °C. Thermal cycling 7 times for 1 h at 425 °C in nitrogen ambient was used to mimic stress encountered during copper alloy process. Moisture resistance was determined by exposing films to 120 °C, and 100% relative humidity at 2 atmosphere pressure for up to 168 h.

## 3. Results and discussions

The results of different times of heating tests at 425 °C for 1 h are shown in Figs. 1–3. The thickness of the OSG and OFSG films decreases continuously upon 425 °C heating tests (Fig. 1). The maximum thickness reduction was found after the first time heating test, decrease slightly for each subsequent cycle, with OSG films showing higher shrinkage than OFSG films. The dielectric constant of OSG and OFSG films was essentially stable after thermal cycling (Fig. 3). The change

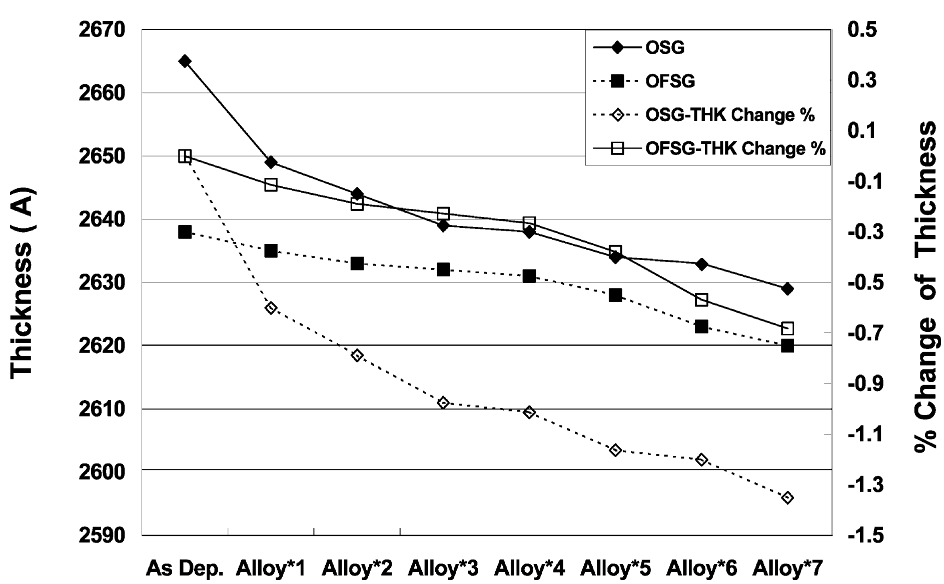


Fig. 1. Heating test (425 °C alloy) on thickness change for OSG and OFSG films.

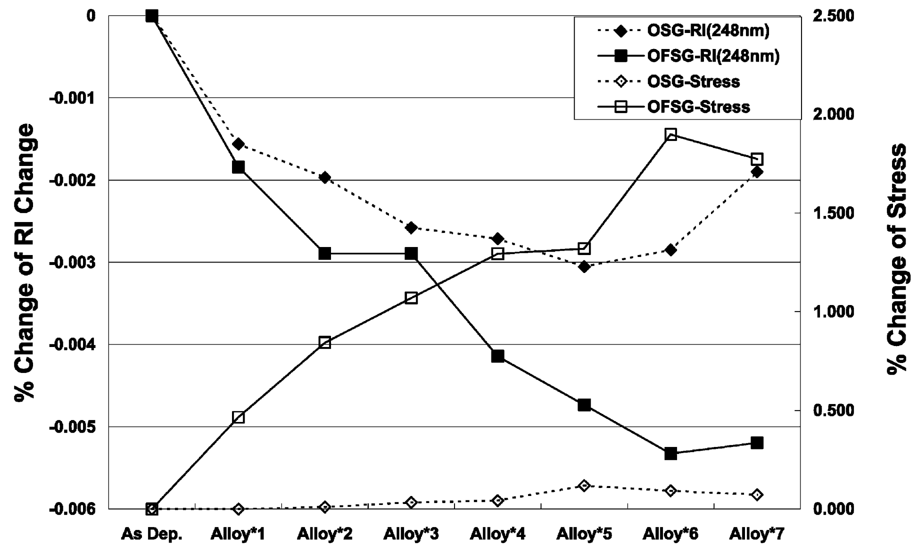


Fig. 2. Heating test (425 °C alloy) on RI and stress change for OSG and OFSG films.

of RI and stress for OSG and OFSG films (Fig. 2) indicates that magnitude of change for RI of OFSG films is actually larger than that for OSG films. While the trends in RI and stress differ in direction, the relative change is in good agreement.

The possible explanation is that OFSG films have higher bonding strength to against the heating tests. The stability of film properties upon thermal cycling suggests that both OSG and OFSG films would retain their desirable properties through the thermal stresses experienced as a result of the copper alloy process. This clearly indicates that the OSG and OFSG films are suited for intermetal dielectrics on semiconductor since there is at least 7–8 layers interconnect fabrication process and 400 °C is a minimal backend process for an interconnect fabrication process.

Figs. 4 and 5 show the change of thickness, RI and dielectric constant for furnace anneals from 300 to 700 °C for 1 h. The *k*-value for both of the OSG and OFSG films were stable ($k=3.2$–$3.3$) up to 600 °C, however, exposure to temperature of 700 °C resulted in sharp increase in the *k*-value for both films. We infer that specific bonds in OSG and OFSG films, such as Si–$CH_3$ and Si–F, do not decompose at least up to 600

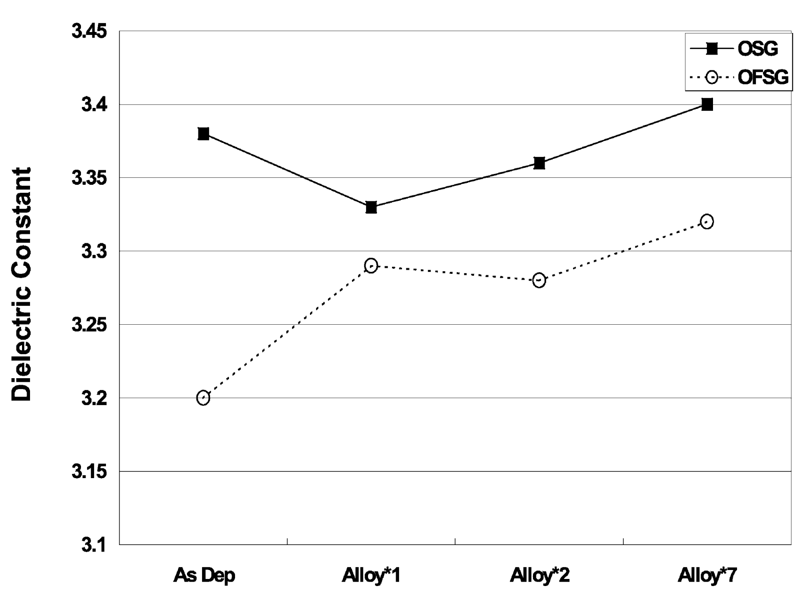


Fig. 3. Effect of heating test (425 °C alloy) on dielectric constant for OSG and OFSG films.

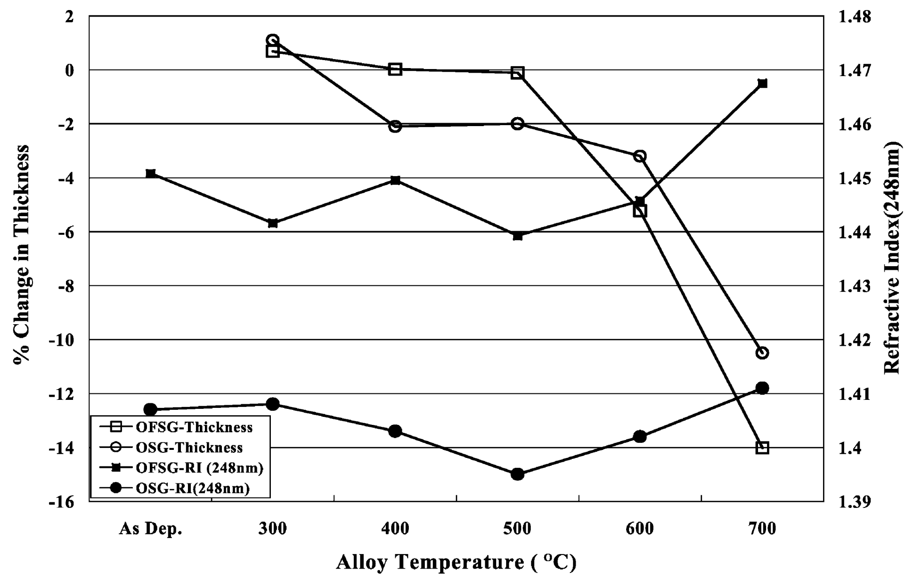


Fig. 4. Effect of different heating test temperature on the change of thickness and RI for OSG and OFSG films.

°C. This further exemplifies that both OFSG and OSG films have sufficient thermal resistance to withstand the normal interconnect fabrication processes which do not typically exceed 400 °C.

The moisture stress test results are shown in Fig. 6. While the *k* values of the OSG film degraded slightly after 168 h PCT test, similar to the result of Takeshi et al. On the other hand, the *k*-value of the OFSG films increase significantly to 3.8 only after the 10 h PCT test. Based on this result, attention should be paid to the moisture penetration when using the OFSG as low-*k* interconnect.

Leakage current tests (Fig. 7) for films pre- and post-PCT test indicate that both OFSG and OSG films increase significantly in current leakage after exposure. Breakdown voltages were also found to decrease from 6.3 and 7.0 MV/cm to 5.6 and 6.6 MV/cm for OSG and OFSG films, respectively. Interestingly, the result

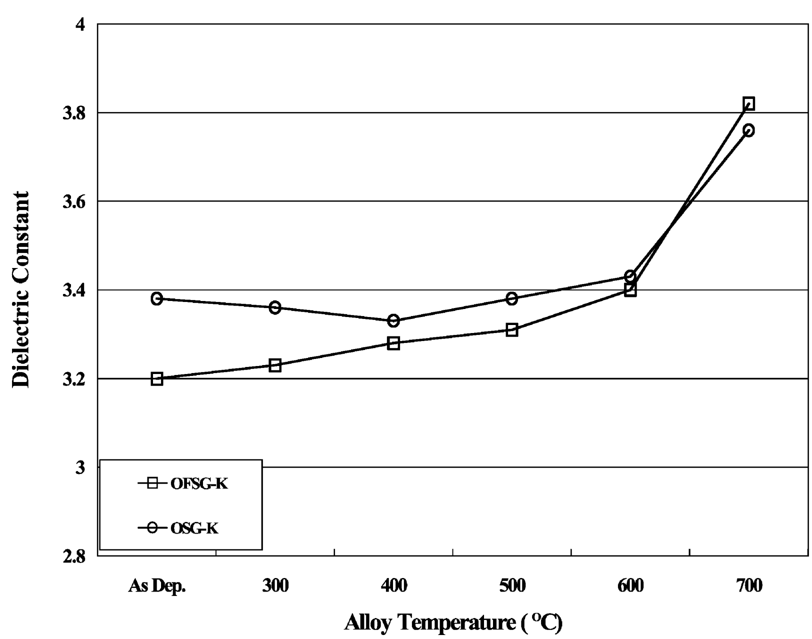


Fig. 5. Effect of different heating test temperature on the change of dielectric constant for OSG and OFSG films.

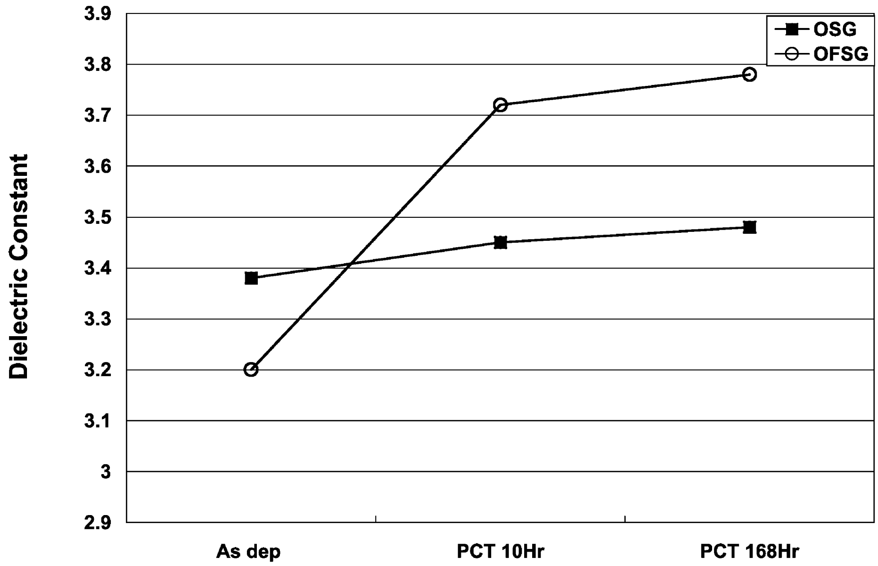


Fig. 6. The change of dielectric constant of OSG and OFSG films for pressure cooker test.

indicates that the leakage current of OFSG films after exposure is still lower than that of OSG film even before the PCT test.

The FTIR spectra of the OSG and OFSG films before and after PCT test are displayed in Figs. 8 and 9, respectively. The FTIR spectrum of OFSG film shows a very weak absorbance at 3500/cm appearing after PCT, suggestive of Si–OH bonds formation. From the analysis result, the 425 °C heating process would cause Si–H bonds to decompose. The decomposition was gradual; the resulting films still contains Si–H bonds, and the films contains a little moisture. During the PCT test, however, the Si–H is found to decompose drastically; at the same time, fewer Si–F bonds is also decomposed due to the moisture absorption. Therefore, it results in much moisture absorption (Si–OH and H–OH). The reactions of Si–F, Si–$CH_3$ or Si–H bonds and $H_2O$ can be expressed as the following formulas, respectively:

$$\text{Si–F} + H_2O \rightarrow \text{Si–OH} + HF \quad (1)$$

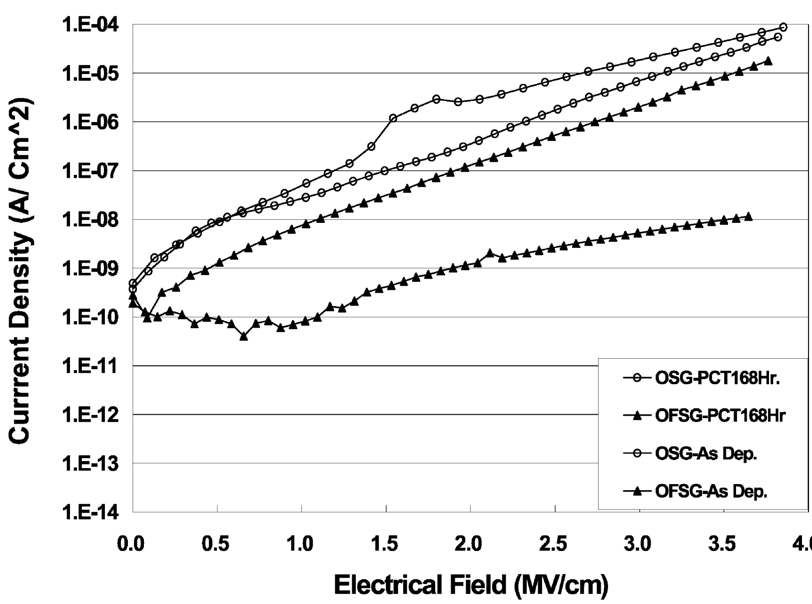


Fig. 7. Effect of PCT test on leakage current for OSG and OFSG films.

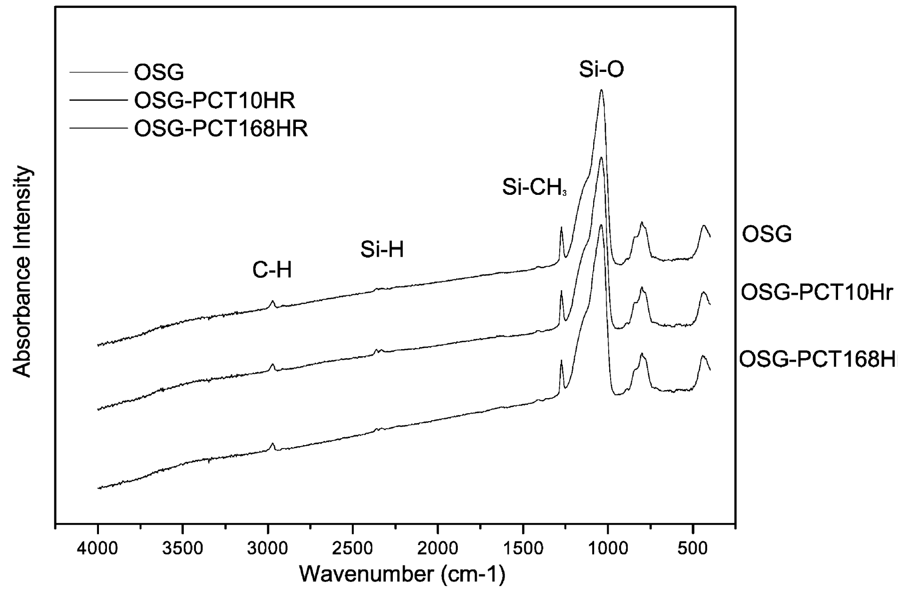


Fig. 8. FTIR spectrum change of OSG film during PCT test.

$$Si–H + H_2O \rightarrow Si–OH + H_2 \quad (2)$$

$$Si–CH_3 + H_2O \rightarrow Si–OH + CH_4 \quad (3)$$

$$2Si–OH \rightarrow Si–O–Si + H_2O \quad (4)$$

During the PCT tests, the greater moisture absorption resulted in drastical decomposition and incomplete condensation. This result significantly increases both the *k*-value and leakage current, so the films degrade as shown in Figs. 5 and 6.

Compared to the difference between the OFSG films and OSG films, OFSG films have less Si–H bonding and additional Si–F bonding due to mainly Si–H bonding in OSG films that was replaced by Si–F bonding. Therefore, OSG film contains originally the Si–C–Si bonds and Si–O–Si bonds, and also contains fewer Si–H and Si–$CH_3$ bonds. The Si–H bonding content is low

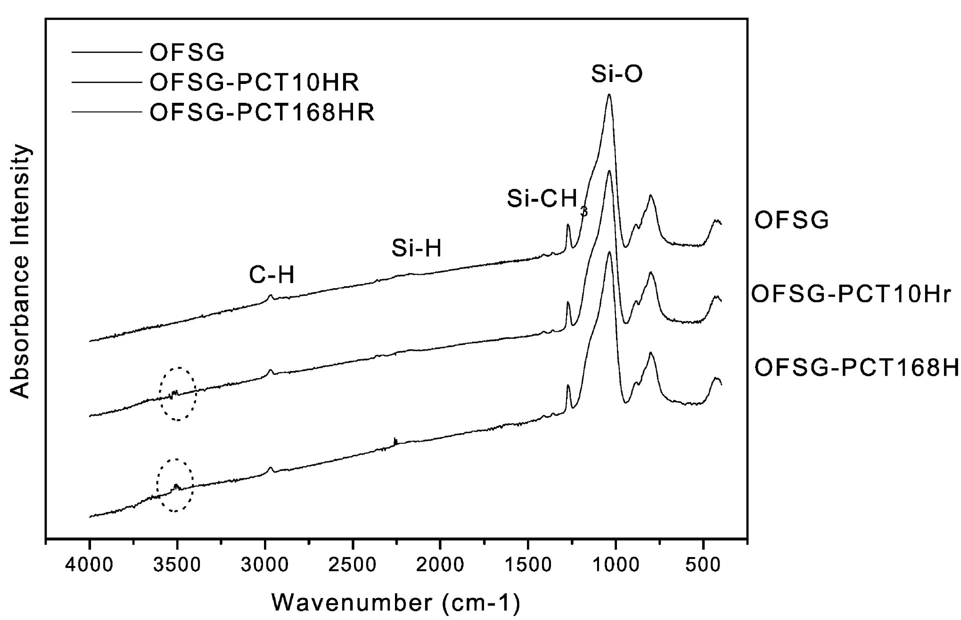


Fig. 9. FTIR spectrum change of OFSG film during PCT test.

enough when compared with the content of Si–$CH_3$ bonding. According to the results of Furusawa et al. [7], the Si–C–Si did not decompose during the heating test at 700 °C or higher. The heat resistance of the films is determined by the decomposition of the Si–H and Si–$CH_3$ bonds; the decomposition temperature of Si–H and Si–$CH_3$ bonds was approximately 700 °C and the bonds will be completely decomposed at higher temperature, no decomposition was observed for Si–C–Si, Si–H and Si–$CH_3$ bonds. On the other hand, partial Si–H bonds were replaced by the Si–F bonds. And Si–F bonds did not decompose until the curing temperature is as high as 700 °C or higher. As a consequence, thickness shrinkage of the OFSG films was less than that of the OSG films. However, the moisture resistance of Si–F bonds is poor, even worse than Si–H bonds. Therefore, the moisture resistance of OFSG films is not strong enough compared to OSG films.

## 4. Conclusions

The resistance of OSG and OFSG films against heat and moisture stress test was investigated. Compared with OSG films, the OFSG films were shown to be thermally stable. The *k*-value was stable after a heating test at 600 °C. However, a degradation of the OFSG films after the PCT test was found due to the un-stability of Si–F or Si–$CH_3$ bonds through the moisture stress test. Consequently, the moisture resistance of the OFSG film should pay more attention to implement this film as low-*k* interconnect dielectrics.

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