



Effect of adding Ar on the thermal stability of chemical vapor deposited fluorinated silicon oxide using an indirect fluorinating precursor

Kow Ming Chang, Shih Wei Wang, Chii Horng Li, Ta Hsun Yeh, and Ji Yi Yang

Citation: [Applied Physics Letters](#) **70**, 2556 (1997); doi: 10.1063/1.118939

View online: <http://dx.doi.org/10.1063/1.118939>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/70/19?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Electrical and reliability performances of nitrogen-incorporated silicon carbide dielectric by chemical vapor deposition](#)

J. Vac. Sci. Technol. B **28**, 573 (2010); 10.1116/1.3425633

[Thermal stability of low dielectric constant porous silica films](#)

Appl. Phys. Lett. **87**, 262909 (2005); 10.1063/1.2159093

[Plasma-enhanced chemical vapor deposition of low-k dielectric films using methylsilane, dimethylsilane, and trimethylsilane precursors](#)

J. Vac. Sci. Technol. A **21**, 388 (2003); 10.1116/1.1539086

[Rapid thermal chemical vapor deposition of zirconium oxide for metal-oxide-semiconductor field effect transistor application](#)

J. Vac. Sci. Technol. B **19**, 1782 (2001); 10.1116/1.1396639

[Thermal stability enhancement of Cu/WN/SiOF/Si multilayers by post-plasma treatment of fluorine-doped silicon dioxide](#)

J. Appl. Phys. **85**, 473 (1999); 10.1063/1.369410

The logo for AIP Chaos is centered on a red background with a geometric, low-poly pattern. The letters 'AIP' are in a large, white, sans-serif font, followed by a vertical orange bar and the word 'Chaos' in a smaller, white, sans-serif font.

CALL FOR APPLICANTS

Seeking new Editor-in-Chief

Effect of adding Ar on the thermal stability of chemical vapor deposited fluorinated silicon oxide using an indirect fluorinating precursor

Kow Ming Chang, Shih Wei Wang, Chii Horng Li, Ta Hsun Yeh, and Ji Yi Yang
*Department of Electronic Engineering and Institute of Electronics, National Chiao Tung University,
National Nano Device Laboratory, Hsinchu, Taiwan*

(Received 4 November 1996; accepted for publication 10 March 1997)

For a low dielectric constant intermetal dielectric application, fluorinated silicon oxide (F_xSiO_y) films were deposited in an electron cyclotron resonance chemical vapor deposition system, with SiH_4 , O_2 , and CF_4 as the reaction gases. Since the CF_4 is an indirect fluorinating precursor, the fluorinating mechanism resembles that of the oxide etching by a fluorocarbon plasma. Thermal stability of the incorporated fluorine (and hence, the dielectric constant) relies heavily on the deposition parameters and technologies. According to experimental results, adding Ar gas during deposition can improve the thermal stability of incorporated fluorine. Such an improvement is due to the fact that Ar sputtering enhances the removal of weakly bonded silicon fluoride on the as-deposited film surface, thereby elevating the mean bonding strength of fluoride remaining in the oxide. © 1997 American Institute of Physics. [S0003-6951(97)00219-2]

Chemical vapor deposition of inorganic fluorinated silicon oxide (F_xSiO_y), having various inexpensive precursors and easily integrated properties, has received extensive use in low dielectric constant (k) intermetal dielectric (IMD) applications.¹ Research has shown that a higher fluorine content in the oxide implies a lower k value.^{1,2} However, incorporating too much fluorine leads to an unstable film, particularly when using indirect-fluorinating precursors such as CF_4 and C_2F_6 . When using these etching gases as fluorinating sources, the incorporated fluorine originates from the nonvolatile silicon fluoride, which has a formation mechanism similar to etching of the oxide. Our previous reports have demonstrated that films deposited at a low temperature have a higher F concentration (lower k) but lower thermal stability than those deposited at a high temperature.^{3,4} Such a discrepancy is apparently due to the residual nature of weakly bound or physically adsorbed $-F$ bonds buried in the film where the bonds break and diffuse out upon heating. The outgassing of fluorine not only causes the k value to increase, but reliability problems (e.g., the leaching of $-H$ contained oxide and adhesion degradation) occur as well.⁵ In this letter, Ar gas was added during deposition of F_xSiO_y film, with SiH_4 , O_2 , and CF_4 as the reaction gases in an electron cyclotron resonance chemical vapor deposition (ECR-CVD) system. Experimental results indicate that enhancing the depletion of weakly bound fluorine improves the thermal stability of the F_xSiO_y film by the simultaneous sputtering effect of the Ar plasma, with a similar effect seen when increasing the deposition temperature.

Electron cyclotron resonance chemical vapor deposited F_xSiO_y films^{3,4} ($SiH_4/O_2/CF_4=8/85/10$ sccm, Ar=0–16 sccm, MW 300 W, 3 mTorr) were deposited on n -type Si(100) 4 in. wafers to a thickness around 240 nm, at temperatures of 25, 100, 200, and 300 °C. After annealing in a nitrogen ambient atmosphere at various temperatures (400, 500, 600, 700, and 800 °C) for half an hour, the films' thermal stability was analyzed from the variation of the Si–F peak ($\sim 930\text{ cm}^{-1}$) in the Fourier transform infrared spectroscopy (FTIR) spectrum. The dielectric constant (k) of the deposited film was measured from C – V characteristics, us-

ing the metal–insulator–semiconductor (MIS) structure at 1 MHz.

Figure 1(a) compares the thermal stabilities of F_xSiO_y films with and without adding Ar gas (12 sccm). Notably, for the films deposited at 25 °C and without adding Ar, the Si–F ($\sim 930\text{ cm}^{-1}$) peak intensity start decaying at 500 °C ($\sim 88\%$ remaining) after half an hour of annealing.^{3,4} On the other hand, when adding Ar, the F_xSiO_y film can withstand temperatures above 500 °C without degrading the Si–F peak's intensity. Figure 1(b) depicts the thermal stability of the Si–F bond in F_xSiO_y films under different Ar flow rates. F_xSiO_y films can withstand temperature at around 600 °C with only a slight outgassing of fluorine when the Ar exceeds 12 sccm. These results suggest that adding Ar raises the thermal stability.

Previous investigations^{3,4} have indicated that two reactions are primarily responsible for Si–F bonds forming in F_xSiO_y film while adding CF_4 : (1) the homogeneous reaction in the plasma; the active F and O atoms react with SiH_4 , thereby causing the formation of oxyfluoride species and deposition, and (2) the heterogeneous reaction on the film's surface; the active F absorbs (physically and chemically) on the deposited film and, consequently, the nonvolatile fluoride is buried in the film during the subsequent deposition. On the other hand, the volatile fluoride results in simultaneous etching. The fluorine's bonding strength for these nonvolatile species buried in the film determines the stability during subsequent thermal cycles. Most of the volatile fluoride becomes depleted at a high surface temperature during deposition, leading to a low but stable fluorine concentration remaining in the film. According to Figs. 1(a) and 1(b), adding Ar yields an effect similar to that observed by increasing the deposition temperature. As is well known, adding Ar enhances the etching reaction of oxides in a fluorocarbon plasma, due to the depletion of fluoride species on the oxide surface by Ar ion sputtering. Consequently, adding Ar during the ECR-CVD of F_xSiO_y film depletes the weakly bonded fluoride and increases the thermal stability of the remaining F bonds, as increasing deposition temperature does as well.

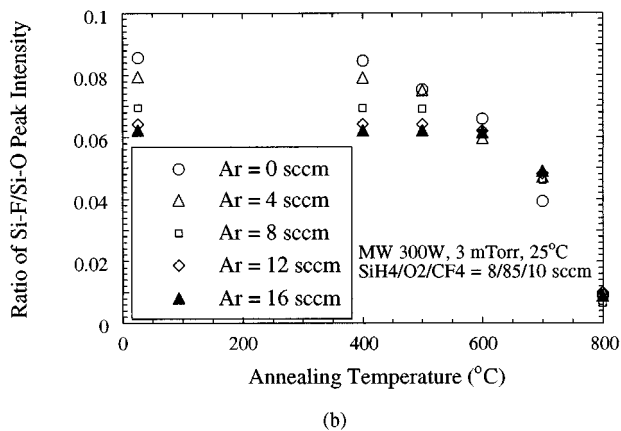
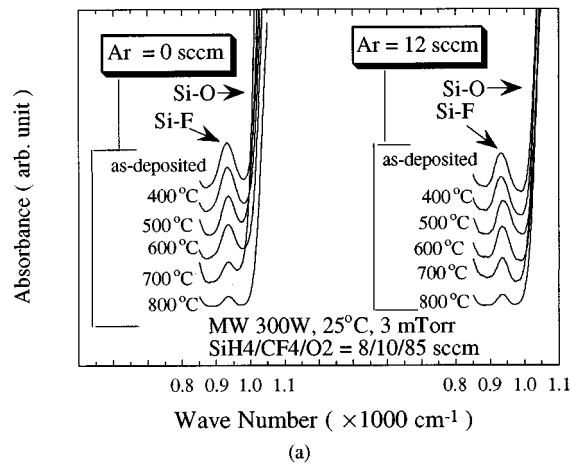


FIG. 1. Changes of (a) FTIR spectrum, and (b) Si-F bond absorbance peak intensity (normalized with the of Si-O peak intensity, stretching mode, $\sim 1070 \text{ cm}^{-1}$) with different annealing temperatures, for $F_x\text{SiO}_y$ films deposited at 25°C with various Ar flow rates.

Adding Ar also influences the deposition rate of $F_x\text{SiO}_y$ films. Figure 2 depicts the variation of the $F_x\text{SiO}_y$ film's deposition rate with CF_4 flow rate, at different deposition temperatures and Ar flow rates. The deposition rates generally decrease with an increasing CF_4 flow rate and

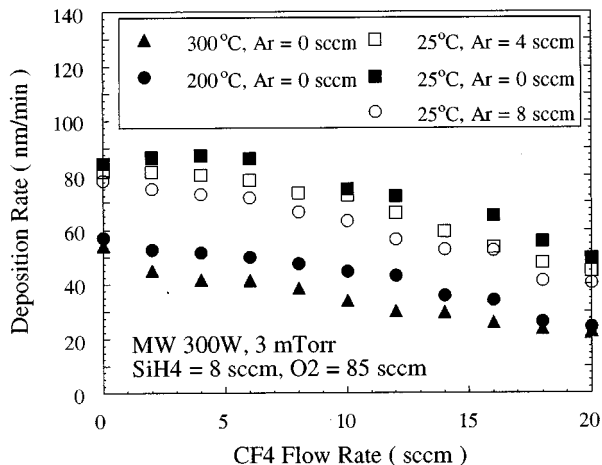


FIG. 2. Deposition rate of $F_x\text{SiO}_y$ film as a function of CF_4 flow rate, with different deposition temperatures and Ar flow rates.

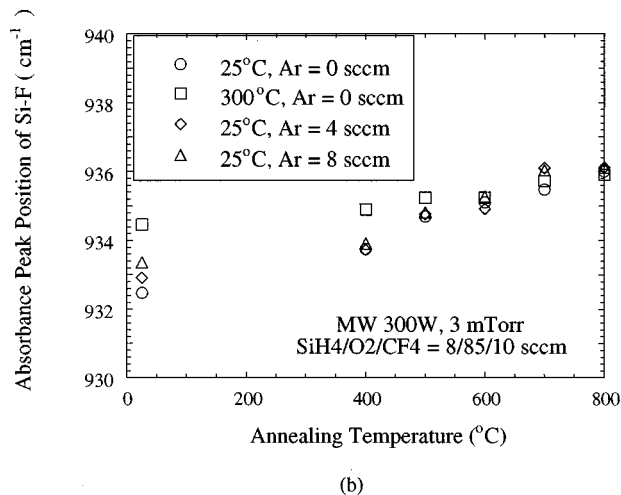
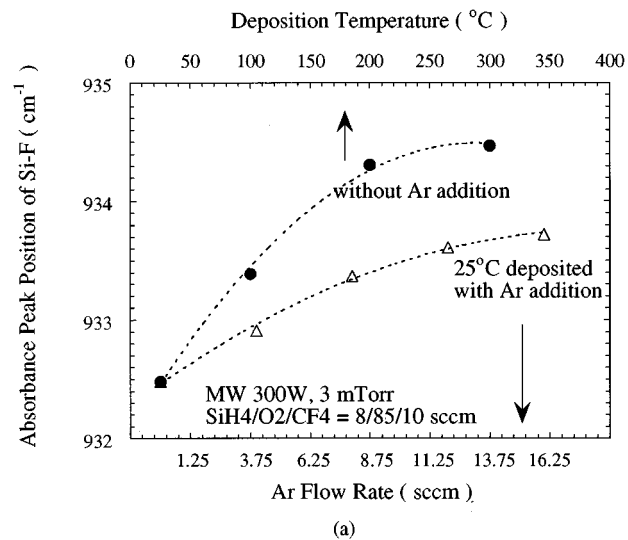


FIG. 3. Variations of FTIR Si-F bond absorbance peak position in the (a) as-deposited, and (b) annealed ($400\text{--}800^\circ\text{C}$) $F_x\text{SiO}_y$ films, with different deposition temperatures and Ar flow rates.

deposition temperature. Such an event results from the high surface migration energy of the deposited species at the high surface temperature, resulting in a denser stack. Besides, the etching reaction is also favored at a higher temperature. However, for the 25°C deposited films, the deposition rate slightly increases while adding CF_4 , when the CF_4 flow rate is below 6 sccm. This phenomenon is due to the swelling of the oxide network caused by incorporation of fluorine.^{3,4} Therefore, strictly speaking, the deposition rate of $F_x\text{SiO}_y$ films is determined by the competition among the deposition, etching reaction, and the swelling of the oxide due to F incorporation. Figure 2 also reveals that adding of Ar causes the deposition rate of films deposited at room temperature to monotonically decrease with an increasing CF_4 flow rate, in contrast to those without Ar. Moreover, adding Ar enhances the etching reaction and reduces the incorporated fluorine concentration, both screening the phenomenon of the oxide network expansion due to F incorporation, as the increase of the deposition temperature does as well.

The variation of the FTIR peak position of Si-F bonds also accounts for the change in the thermal stability under different deposition conditions. Figure 3(a) depicts the Si-F

peak position of as-deposited F_xSiO_y films with various process temperatures and Ar flow rates. Notably, that Si–F peak position shifts upward with an increasing deposition temperature and Ar flow rate. This finding suggests that the Si–F bonds with higher vibration frequency possess higher thermal stability. Figure 3(b) presents the peak position of the remaining Si–F bonds after annealing at different temperatures. The Si–F bonds, capable of withstanding a high temperature without outgassing, tend to have the same vibration frequency around 936 cm^{-1} . By simulating the vibration of the Si–F bond simply with Hooke's law, the higher vibration frequency corresponds to a higher force constant and, hence, a higher bonding strength of Si–F. Besides, the strength of the Si–F bond in the $O_{4-x}SiF_x$ local structure tends to decrease with a higher x , due to the repulsive force of fluorine. Consequently, the most stable fluorinated oxide structure (remaining after high-temperature annealing) is in the form of a single fluoride.

In summary, this work demonstrates that the thermal stability of F_xSiO_y films can be improved by adding Ar gas during deposition, when using CF_4 as the fluorinating precursor. The stability can be raised from 400 to 600 °C for films deposited at room temperature. Such a feature is due to en-

hancing the removal of volatile fluorides on the oxide surface by Ar ion sputtering, as the increase in deposition temperature does as well. However, for both of these methods, improving the thermal stability by depleting the excess (weakly bonded) fluorine, yields a higher k value (e.g., $k \sim 3.41$ for 16 sccm of Ar addition, in contrast to $k \sim 3.17$ for that without Ar addition). Besides, adding Ar does not significantly improve the moisture resistance of F_xSiO_y films. A high-temperature ($\sim 300\text{ }^\circ\text{C}$) deposition to derive a denser stack or a capped ECR–oxide layer is still necessary to block moisture absorption.

This work is supported under the Taiwan Republic of China National Science Council Contract No. NSC 86-2215-E-009-047.

¹R. K. Laxman, *Semicond. Int.* **5**, 71 (1995).

²S. W. Lim, Y. Shimogaki, Y. Nakano, K. Tada, and H. Komiyama, *Appl. Phys. Lett.* **68**, 832 (1996).

³K. M. Chang, S. W. Wang, C. J. Wu, C. H. Li, T. H. Yeh, and J. Y. Yang, *First International Symposium on Low and High Dielectric Constant Materials and Technology*, Los Angeles, May 1996.

⁴K. M. Chang, S. W. Wang, C. J. Wu, T. H. Yeh, C. H. Li, and J. Y. Yang, *Appl. Phys. Lett.* **69**, 1238 (1996).

⁵P. Singer, *Semicond. Int.* **5**, 88 (1996).