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

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For a low dielectric constant intermetal dielectric application, fluorinated silicon oxide (F$_x$SiO$_y$) 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$_x$SiO$_y$), having various inexpensive precursors and easy integrated properties, has received extensive use in low dielectric constant (k) intermetal dielectric (IMD) applications. Research has shown that a higher fluorine content in the oxide implies a lower k value. However, incorporating too much fluorine leads to an unstable film, particularly when using indirect-fluorinating precursors such as CF$_3$ and C$_2$F$_6$. 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. 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. In this letter, Ar gas was added during deposition of F$_x$SiO$_y$ 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$_x$SiO$_y$ 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$_x$SiO$_y$ films with various Ar flow rates. 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 (~930 cm$^{-1}$) in the Fourier transform infrared spectroscopy (FTIR) spectrum. The dielectric constant (k) of the deposited film was measured from C–V characteristics, using the metal–insulator–semiconductor (MIS) structure at 1 MHz.

Figure 1(a) compares the thermal stabilities of F$_x$SiO$_y$ films with and without adding Ar gas (12 sccm). Notably, for the films deposited at 25 °C and without adding Ar, the Si–F (~930 cm$^{-1}$) peak intensity start decaying at 500 °C (~88% remaining) after half an hour of annealing. On the other hand, when adding Ar, the F$_x$SiO$_y$ 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$_x$SiO$_y$ films under different Ar flow rates. F$_x$SiO$_y$ 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 have indicated that two reactions are primarily responsible for Si–F bonds forming in F$_x$SiO$_y$ 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$_x$SiO$_y$ film depletes the weakly bonded fluoride and increases the thermal stability of the remaining F bonds, as increasing deposition temperature does as well.
Adding Ar also influences the deposition rate of F$_x$SiO$_y$ films. Figure 2 depicts the variation of the F$_x$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 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. Therefore, strictly speaking, the deposition rate of F$_x$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, the 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 $936 \text{ cm}^{-1}$. 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 enhancing 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) fluoride, 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 (~300 °C) deposition to derive a denser stack or a capped ECR–oxide layer is still necessary to block moisture absorption.

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