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Effect of water absorption on the residual stress in fluorinated silicon-oxide thin films fabricated by electron-cyclotron-resonance plasma-enhanced chemical-vapor deposition

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Fluorinated silicon-oxide (SiOF) films were produced by electron-cyclotron-resonance plasma-enhanced chemical-vapor deposition. The effect of water absorption on the film properties was studied by measuring the residual stress as a function of exposure time to room air. The residual stress shows an increase of the compressive component as the film absorbs water. However, the chemical bonding structure does not change after the water absorption. The residual stress returns to the initial value when the film is dried. It is suggested that the water absorption occurs entirely by physical adsorption of H_2O molecules to Si–F bonds. © *2001 American Institute of Physics.*
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In modern ultra-large-scale integrated circuits technology, the operating speed of devices is delayed by the capacitance of intermetal dielectrics.[1] To reduce the capacitance, many low-dielectric constant materials, such as polyimide, parylene, hydrogen silsesquioxane, and fluorinated silicon-oxide (SiOF), are being studied.[2] Among these materials, SiOF has some strong points as low-k dielectrics. The relative dielectric constant of fluorinated silicon-oxide (SiOF) film is lower (3.0–3.7) than that of SiO_2 (>4.2), which is currently used as intermetal dielectrics.[2,3] There have been many studies about SiOF films because of their similar properties to those of SiO_2 films and the ease of application to the Si process.[3]

Except for the low dielectric constant, an important issue is how to maintain the other desired properties for intermetal dielectrics.[2] The SiOF film shows an instability of the properties when it is exposed to humid atmosphere.[3–6] Many researchers have studied the detrimental effects of water absorption on the properties of SiOF films. The absorbed water causes the formation of a Si–OH bond.[3–6] The unstable Si–F bond reacts easily with H_2O and forms the Si–OH bond. It has been explained that the formation of the Si–OH bond is the origin of the water absorption and the degradation of the film properties. Yoshimaru, Koizumi, and Shimokawa observed that the water absorption in SiOF films originates from two mechanisms using thermal desorption spectroscopy analysis.[4] One is a chemical reaction and the other is physical adsorption. The former is the formation of Si–OH and the latter is physical adsorption of H_2O on the films. Most of the reports have been concentrated on the former effect. The effects of Si–OH bond formation on film properties are well understood.[3–6] However, the explanation about the physical adsorption and its effect on the film properties are not clear yet.

It is well known that residual stress is very sensitive to the water absorption in the case of SiO_2 films.[7–9] Haque, Naseem, and Brown[8] insisted that three factors affect the variation of the residual stress in the case of SiO_2 films deposited by the plasma-enhanced chemical-vapor-deposition (PECVD) technique—water adsorption on the surface, Si–OH formation, and the interaction between adsorbed water dipoles. According to Park *et al.*,[9] the change of the residual stress is composed of irreversible and reversible components. The reversible and irreversible components result from the change of the chemical bonding structure and water absorption, respectively.

In the present work, the effect of water absorption on the properties of the SiOF films was studied by measuring the variation of the residual stress. The change of the chemical bonding structure with water absorption was also studied using Fourier transformed infrared (FTIR) spectroscopy analysis. The compressive residual stress increased with the water absorption and returned to the initial value when the films were kept in dry air. Experimental results indicate that the water absorption occurs significantly without any change in Si–F bond and the formation of the Si–OH bond. That means the major water absorption mechanism in our study is the physical adsorption on the film surface.

1000-Å-thick SiOF films were deposited on chemically cleaned 4 in., ⟨100⟩, Si wafers using electron-cyclotron-resonance (ECR) PECVD. The flow rate of SiF_4 was varied from 1 to 5 sccm, whereas those of Ar and N_2O were fixed at 5 and 30 sccm, respectively. The pressure was kept at 2 m Torr and the microwave power was 600 W. The substrate was not heated intentionally. FTIR analysis was performed using a Bio Rad FTS 6000 system. The residual stress was measured by a Flexus stress measurement system. The analyses were carried immediately after the deposition process. The change of residual stress was measured as a function of storage time in room atmosphere [25 °C, 45% relative humidity

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TABLE I. Variations of $I_{Si-F}/(I_{Si-O}+I_{Si-F})$ intensity ratio, dielectric constant, residual stress, and *P*-etch rate with different SiF_4 flow rates.

SiF_4 flow rate(sccm)	$I_{Si-F}/(I_{Si-O}+I_{Si-F})$ (%)	Relative dielectric constant, ϵ_r	Residual stress, σ_i (MPa)	*P*-etch rate[a] (Å/s)
1	1.84	3.99	−89.6	5.5
2	3.82	3.94	−89.3	11
3	4.05	3.68	−78.8	18
4	8.02	3.50	−69.1	21
5	10.9	3.40	−66.1	30

[a] *P*-etch solution: 15HF(49%):10HNO_3(70%):300H_2O

(RH) air] for 24 h. Then, the films were exposed to dry air (25% RH air) in a desiccator and the residual stress was measured during drying. The relative dielectric constant (ϵ_r) was measured using a metal–insulator–semiconductor structure at 1 MHz.

For all the films at various SiF_4 flow rates, Si–O (stretching mode, $\sim 1070\,cm^{-1}$; bending, $\sim 805\,cm^{-1}$) and Si–F (stretching mode, $\sim 945\,cm^{-1}$) peaks were observed in the FTIR spectrum. The integrated intensities of Si–O stretching (I_{Si-O}) and Si–F stretching peaks (I_{Si-F}) were used to estimate the content of fluorine atoms. The $I_{Si-F}/(I_{Si-F}+I_{Si-O})$ ratio increases with the SiF_4 flow rate. The film properties with the SiF_4 flow rate are summarized in Table I.

Figure 1 shows the increment of compressive stress with respect to an initial stress value (σ_i), $(\sigma\text{-}\sigma_i)/\sigma_i$ (%), as a function of storage time in 45% RH air. The stress becomes more compressive with the storage time and SiF_4 flow rate. The film deposited at $SiF_4=1$ sccm shows little change. The result indicates that much fluorine promotes the water absorption.

To obtain information about the change in the chemical bonding structure, the film deposited at $SiF_4=5$ sccm was analyzed using FTIR. The variations of the FTIR spectrum are shown in Figs. 2 and 3. Figure 2 shows the variation of Si–O and Si–F stretching bands, however there is very little change in the spectrum. To clarify that the water absorption does not change the FTIR spectrum, the films were kept in deionized water for 2 days. It also shows no evidence that the Si–F bond reacts with water molecules. However, there is another possible reaction that includes water absorption. That is a reaction between the Si dangling bonds and water. It causes the formation of the Si–OH bond in the films.

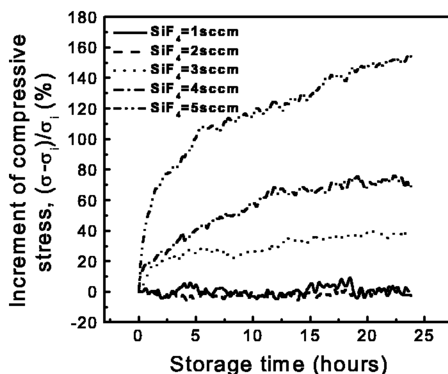

FIG. 1. Increment of compressive stress with storage time in 45% RH air for films deposited with different SiF_4 flow rates.

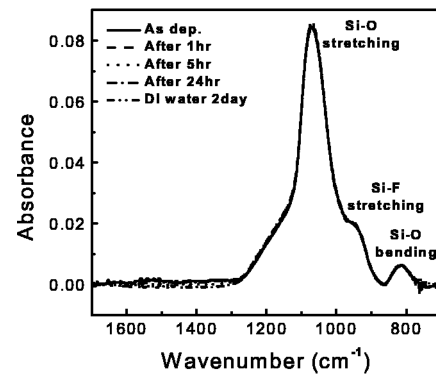

FIG. 2. FTIR spectra of Si–O and Si–F bonds with storage time in 45% RH air for films deposited at $SiF_4=5$ sccm.

Figure 3 shows FTIR spectra in the wave-number range from 4000 to $3000\,cm^{-1}$ with the storage time. The formation of the Si–OH bond (isolated Si–OH$=3650\,cm^{-1}$, near-neighbor Si–OH$=2800-3750\,cm^{-1}$) (Ref. 6) is not noticeable in the spectrum. It is inferred that few Si–OH bonds was generated after the water absorption. These results suggest that the water absorption caused little chemical reaction. Although all the bonds are very stable, there is a considerable change of residual stress. However, most workers observed the chemical reaction between the SiOF films and water molecules. Chang *et al.* insisted that the change of residual stress arises from the formation of Si–OH bonds in the SiOF film.[5] A decrease of Si–F bonds and increase of Si–OH bonds were also found.[4] Comparing the previous studies with the above results, the change of the residual stress and chemical bonding structure are not related with each other for our films. It is thought that there is another reason that changes the residual stress when the films absorb water.

One possible mechanism is a physical adsorption of water molecules on the SiOF film. Yang and Lucovsky explained that the hydrogen bonds are generated between the Si–F bond and H_2O molecule before the formation of the Si–OH bond.[10] If the water molecules are absorbed by physical adsorption, they will be removed by drying the films. In order to remove the absorbed water molecules, the sample was exposed to dry air (25% RH air). The residual stress was measured every 24 h. Figure 4 shows the variation of residual stress as a function of drying time. The compressive residual stress increases rapidly with an exposure to room air

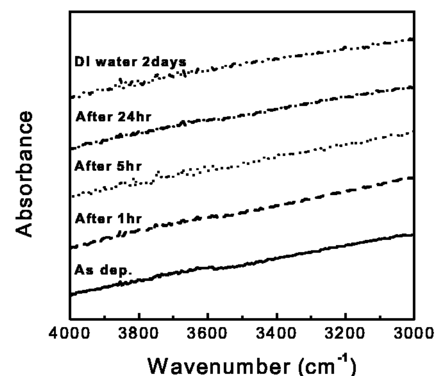

FIG. 3. Variation of FTIR spectra in the range where the Si–OH band peak is observed, $4000-3000\,cm^{-1}$, with storage time in 45% RH air for films deposited at $SiF_4=5$ sccm.

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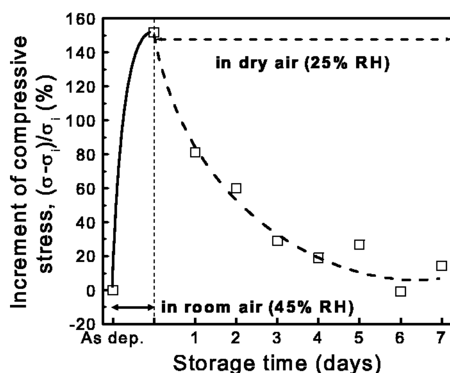

FIG. 4. Change of residual stress with H_2O adsorption in 45% RH air and desorption in 25% RH air for films deposited at $SiF_4 = 5$ sccm.

and decreases gradually with storage time in dry air. It finally returns to the initial stress value. It clearly indicates that the water absorption occurs in our study entirely by physical adsorption in SiOF films deposited by ECR PECVD. Note that the backward reaction proceeds very slowly. It means that the physical adsorption considerably lowers the total energy of the film. According to Yang and Lucovsky,[10] the energy of the hydrogen bond between 2Si–F and H_2O is about 0.45 eV. It is also supposed that the physical adsorption probably results from the hydrogen bond between fluorine and hydrogen atoms.

In summary, SiOF films deposited by ECR PECVD show an increase in compressive stress as the film absorbs water without changing the chemical bonding structure. The residual stress returns to the initial value when it is dried. It is suggested that water absorption occurs in our work entirely by physical adsorption, which probably results from the hydrogen bond between the Si–F bond and H_2O molecule.

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