

Effect of Post Plasma Treatment on Water Absorption
and Dielectric Properties of Fluorine Doped SiO₂ Films
Formed by ECRCVD with SiF₄ and O₂

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The effect of post plasma treatment on water absorption and dielectric properties of fluorine doped silicon oxide (SiOF) films for intermetal dielectrics (IMD) in multilevel interconnections of ultralarge-scale integrated circuits (ULSIs) with various gases such as N₂, O₂ and N₂O are investigated. The SiOF films were deposited on Si substrates by using electron cyclotron resonance chemical vapor deposition (ECRCVD : AsTeX model AX4505) with SiF₄ and O₂ as source gases in order to avoid incorporation of impurities such as C and H. The SiOF films were deposited as a function of the SiF₄/O₂ gas flow ratio. The post plasma treatment of SiOF films were carried out N₂, O₂ and N₂O plasmas in-situ after the deposition. The deposition condition is shown in Table 1 and the plasma treatment condition is shown in Table 2.

Table 1. Deposition condition of SiOF films.

Gas flow rate (sccm)			Substrate temperature (°C)	Process pressure (mTorr)	Microwave power (W)
SiF ₄	O ₂	Ar			
1~5	5	10	300	3	700

Table 2. Post-treatment condition

Post-treatment	Gas	Microwave power (W)	Flow rate (sccm)	Temperature (°C)	Process pressure (mTorr)
O ₂ -plasma treatment	O ₂	700	20	400	3
N ₂ -plasma treatment	N ₂	700	20	400	3
N ₂ O-plasma treatment	N ₂ O	700	20	400	3

We studied changes in water absorption and dielectric properties of SiOF films as a function of exposure time in atmosphere to learn the effect of post plasma treatment using N₂, O₂ and N₂O gases. Relative dielectric constant was determined from capacitance-voltage (C-V) measurements at 1MHz using a MIS (Ag/SiOF/p-Si) structure. The wet etching rates were measured by dissolving films in a buffered HF solution (50%HF : 40%NH₄F = 1 : 6) step by step and by measuring the thickness at each step. Fourier transform infrared (FTIR) spectra were examined in order to investigate differences in the chemical properties of SiOF films before and after the plasma treatments. X-ray photoelectron spectra (XPS) were taken to investigate changes in surface chemical composition and depth profiles of SiOF films before and after the plasma treatment with N₂, O₂ and N₂O plasmas. chemical bonding structures in the SiOF films were determined by using FTIR

spectrometer. FTIR measurement was carried out in vacuum in order to avoid data interference due to appearance of Si-OF and/or H-OH peaks originated from atmosphere.

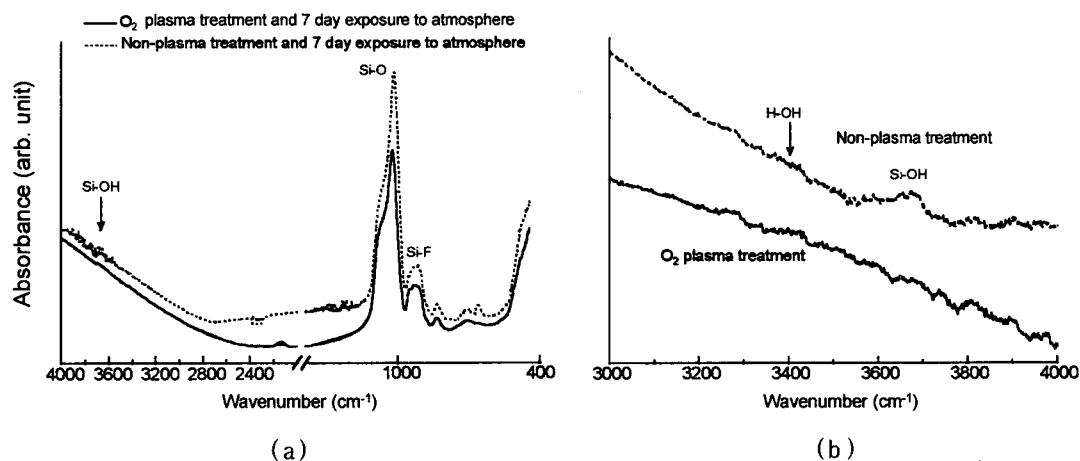


Fig. 1 FTIR spectra of SiOF films exposed to the atmosphere for 7 days before and after the O₂ plasma treatment (a) in the range from 400 to 4000cm⁻¹ and (b) in the range from 3000 to 4000cm⁻¹.

Fig. 1 (a) shows FTIR spectra of SiOF films (deposited with gas flow ratio of 1.0) exposed to the atmosphere for 7 days before and after O₂-plasma treatment and fig. 1 (b) is the spectra in the range from 3000cm⁻¹ and 4000cm⁻¹. After O₂-plasma treatment, no appreciable peak directly related to water absorbance is detected. However, the film which exposed to atmosphere without any plasma treatment beforehand appears to have H-OH and Si-OH peaks appearing at around 3400cm⁻¹ and 3650cm⁻¹. This results clearly shows that the O₂-plasma treated SiOF film has lower moisture absorptivity than non-plasma treatment SiOF films. It is regarded that the O₂ plasma treated SiOF film is more dense than non-plasma treatment SiOF films because of ion bombardment effect of O₂ plasma. And it is also thought that some of fluorine atoms in the very top layers of the SiOF film are replaced by oxygen atoms by O₂ plasma treatment. Generally speaking, SiOF films with fluorine content much higher than a certain amount tend to have high moisture absorptivity when exposed to moisture atmosphere. Therefore, it is proposed that the surface oxidation and densification due to O₂ plasma treatment make SiOF films a very attractive material for ULSI's IMD.

In this presentation, we reports studied on changes in dielectric constant as a function of time to atmosphere, effects of plasma treatment using N₂, and N₂O besides O₂, and changes in surface chemical composition and molecular structure of SiOF films due to plasma treatment.

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