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Densified SiOF Film Formation for Preventing Water Absorption

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We confirmed that the film density of fluorine-doped SiO2(SiOF) decreased with increasing atomic density of fluorine. Such a decrease in the film density had the most significant effects on the water absorption. The film density was controlled by changing O2 gas mixture ratio or by plasma-annealing after the deposition. From the TDS measurement of the water desorption and the change in dielectric constants when exposed to atmosphere, we confirmed that the densified films had low water absorptivity without sacrificing low-k characteristics.

1. INTRODUCTION

To get high-speed integrated circuits, how to reduce the wiring signal propagation delay (wiring delay) will be a key with increasing the number of interlayer dielectrics. The wiring delay depends heavily on capacitance between parallel interconnection metal lines. Insulating materials with low dielectric constants make possible to reduce the wiring delay in the interconnection layers. Recent works have indicated that the incorporation of fluorine in plasma-deposited SiO2 (hereafter denoted as "SiOF") can reduce the effective dielectric constant below 4.0[1-4]. For example, the dielectric constant of SiOF containing 6 at.% fluorine is about 3.6 which is lower than that of TEOS-SiO2 by about 10%. However, the dielectric constant of SiOF increases monotonically when exposed to atmosphere because of the high water absorptivity. A key point when integrating SiOF into actual device processes must be how to stabilize the dielectric constant of the SiOF. To prevent water absorption, TEOS-SiO2 and/or SiN capping on the SiOF was examined[4,5]. However, these methods turned out to be insufficient for reducing the wiring delay, because the structure of the capped SiOF was not effective in decreasing the total capacitance between metal lines. Our goal must be to develop SiOF films with intrinsically low water absorptivity which does not need any capping.

It has been suggested that water absorption of plasma-deposited SiO2 is attributed to some factors such as SiO2 defects, Si-OH bonds and contamination with carbon. For the water absorption of the SiOF, however, studies have not been done enough to make any comment. In the present work, therefore, we have investigated relationship between the water absorption and the film density. The results showed that the decrease in film density had the most significant effects on the water absorption. By changing O2/(TEOS+C2F6) gas mixture ratios or by plasma annealing after the deposition, we succeeded in getting dense SiOF films with low water absorptivity.

2. EXPERIMENTAL

The deposition of SiOF films was performed by adding C2F6 as a fluorine gas source to a conventional TEOS/O2 gas mixture in a parallel plate plasma chamber having a dual frequency configuration. TEOS supply was done using a He gas babbling system. The power density of low(350 kHz) and high(13.56 MHz) frequency was 0.48 and 0.43 W/cm^2, respectively. The pressure and susceptor temperature were 5 Torr and 400 ℃.

The plasma annealing was done using N2O plasma in the parallel plate plasma chamber. The high frequency power density was 1.60 W/cm^2. Low frequency was not used in this case. The flow rate of N2O was 300 sccm. The pressure and susceptor temperature were 4 Torr and 400 ℃.

We measured the film density using grazing incidence X-ray reflectivity (GIXR) method. The GIXR has been widely investigated to analyze micro structures of thermal SiO2[6,7]. The thickness, surface roughness and density of the films were estimated from reflection patterns of intensity of X-ray which was incident upon the sample at an angle less than some degrees. Every measurement was performed using synchrotron radiation at beam-line17C of photon factory, high energy physics laboratories. (PF KEK).

3. RESULTS

Figure 1 shows dielectric constants of SiOF films just after the deposition and exposed to atmosphere for a week. The dielectric constants of just as-deposited films decreased with increasing C2F6 flow rate. However, after exposed to atmosphere for a week, the dielectric constants showed a minimum at around C2F6 flow rate of 250 sccm. This indicates that the SiOF films having lower dielectric constant have higher water absorptivity.

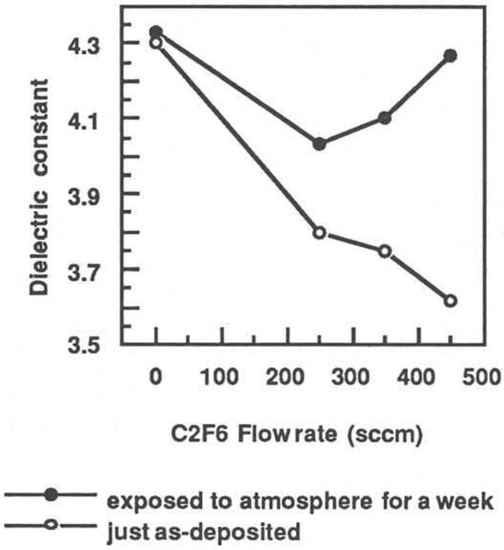

Figure 1. Dielectric constants of SiOF films as a function of C2F6 flow rate for just as-deposited and exposed to atmosphere for a week.

Figure 2 shows density of SiOF films as a function of C2F6 flow rate. The density decreased with increasing C2F6 flow rate. The density of the film with C2F6 700 sccm was 2.06 g/cm^3 which was lower than that of undoped film(TEOS-SiO2) by about 9%. As seen from the figure 1, relationship between the stability of the dielectric constants and the changing in the film density suggest that the decrease in the film density has the most significant effects on the water absorption.

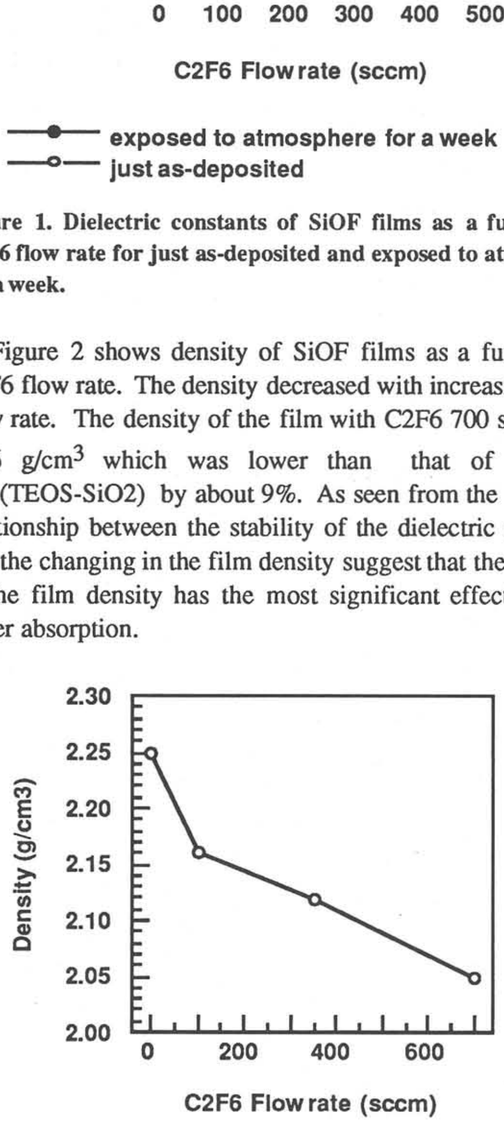

Figure 2. Density of the SiOF film as a function of C2F6 flow rate.

The density of the films was controlled by changing O2 gas mixture ratio or by plasma-annealing after the deposition. The gas mixture ratios defined by O2/(TEOS(He)+C2F6) for O2 rich and conventional conditions were 1.70 and 0.84, respectively. The SiOF film deposited under a conventional condition was annealed using N2O plasma.

Table 1 summarizes the density of SiOF and TEOS-SiO2 films. For the O2 rich condition and plasma annealing, the density was 2.26 g/cm^3 which was denser than that of a conventional condition by about 6 % and was equal to that of TEOS-SiO2.

Table 1. Density of the SiOF and TEOS-SiO2 films

	Conditions	Density (g/cm3)
	Conventional	2.12
SiOF	O2 rich	2.26
	Plasma annealing	2.26
TEOS-SiO2		2.25

Table 2 summarizes atomic ratios of the various SiOF films measured by XPS. Oxygen ratios of the films densified by the O2 rich condition and plasma annealing were slightly higher than that of conventional condition. Fluorine ratios were almost equal in any conditions.

Table 2. Atomic ratios of the SiOF films

Conditions	atomic ratios(%)		
	Si	O	F
Conventional	33.5	60.3	6.2
O2 rich	31.7	62.1	6.2
Plasma annealing	30.5	63.2	6.3

To evaluate dielectrical stability, we measured change in dielectric constants of these films when exposed to atmosphere (see Figure 3). Until 7 days after the deposition, the increment of the dielectric constant of SiOF deposited under the O2 rich condition was about 1/3, comparing with a conventional condition. The increment of the plasma annealed SiOF was about 1/5 which was almost equal to that of TEOS-SiO2.

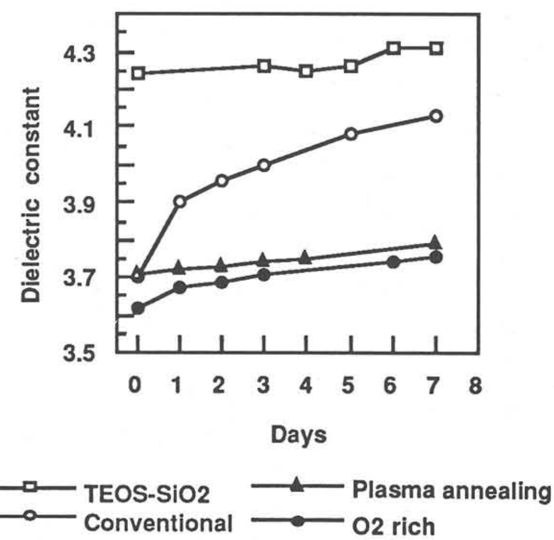

Figure 3. Change in dielectric constants of the SiOF and TEOS-SiO2 films.

Figure 4 shows TDS spectra of water absorbed SiOF films in atmosphere. The peaks at 220 and 320 ℃ are assigned to physi-adsorbed and hydrogen-bonded water, respectively[5,8]. The peak at 560 ℃ is assigned to dehydration of Si-OH bond which does not effect on increasing dielectric constant. The intensities of the TDS peaks at 220 and 320 ℃ for SiOF films densified by the O2 rich condition and plasma annealing were lower than those of a conventional condition. This indicates that the dense SiOF film has low water absorptivity.

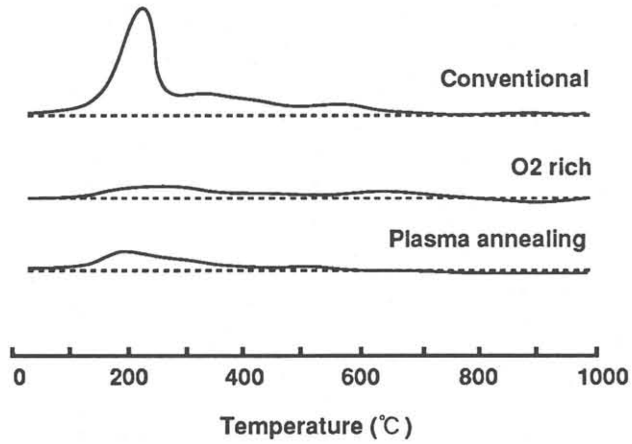

Figure 4. TDS spectra of the H2O desorbtion for the SiOF films.

4. CONCLUSIONS

Our study showed that the decrease in film density had significant effects on water absorption. We confirmed that the SiOF films densified by O2 rich conditions or plasma annealing had low water absorptivity. This makes possible to apply the SiOF to interlayer dielectrics without any capping, which decreases the capacitance between metal lines effectively.

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