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Deposition and Characterization of Fluorine Doped SiO_2 Films Using Atmospheric Pressure Organosilane/O_3 Chemistry

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Introduction

Increased device integrity and complexity demand low dielectric constant in order to decrease the capacitance between the lines for intermetal dielectric layers. Fluorine-doped oxide is recently attracted because of its lower dielectric constant. Many plasma-CVD-based films have been investigated using SiH_4-N_2O-CF_4, Tetraethoxysilane (TEOS)-O_2-C_2F_6 or NF_3 or CF_4 chemistry by dual frequency plasma, SiH_4-SiF_4-O_2 by ECR plasma and TEOS-O_2-NF_3 or CF_4 by helicon plasma.

Fluorine is the least polarizable element and can reduce the number of polarizable Si-OH bond to change a less polarizable network. However, excess fluorine in the film formed by plasma decomposition is so unstable as to induce water absorption, resulting in the increase of dielectric constant. On the other hand, thermal CVD can introduce Si-F network with less unstable uncombined fluorine.

In this paper, we present F-doped oxide characterization by atmospheric pressure (AP) CVD using fluoro-organosilane and ozone chemistry. Excellent gap-filling with self-planarizing feature was observed. The film with low dielectric constant as low as 3.3 was obtained in combination with the plasma post-treatment.

Experimental

Fluorotriethoxysilane was used in APCVD TEOS-O_3 reactor. TEOS or triethoxysilane was used as a Si source and to stabilize the fluorine doping. Plasma post-treatment was employed using 13.56MHz and 100kHz dual frequency excitement in a parallel plate reactor. Chemical structure was examined by refractive index and FT-IR spectrum. Electrical properties were evaluated using MOS diode structure. Step coverage was observed by scanning electron microscope (SEM).

Results and discussion

Figure 1 shows the dependence of deposition rate and refractive index on deposition temperature using TEOS as an additional Si source. TEOS addition was effective to depress the hydrolysis and/or pyrolysis of highly reactive F-source which forms porous films at low temperature. Sufficient films giving high refractive index were obtained at higher than 250°C. Still lower refractive index at 350°C than that of undoped thermal oxide is considered mainly due to fluorine incorporation into the oxide structure. Figure 2 shows FT-IR spectra of F-doped oxides (SiOF). As-deposited film contained HOH and SiOH. The oxygen plasma treatment successfully reduced the absorbed moisture as shown in Fig.2. Further absorption of ambient moisture was prevented by the formation of a capping layer.

Table 1 summarizes the results of dielectric constant and leak current measurements with and without plasma post-treatment. Triethoxysilane was used as an additional Si source since its vapor pressure is close to that of F-source. The F-doped film with low dielectric constant as low as 3.3 were obtained by higher doping of fluorine followed by oxygen plasma post-treatment. The dual frequency plasma especially in oxygen was effective to remove absorbed moisture which increases dielectric constant. No significant increase of leak current was observed by fluorine doping and by plasma treatment.

Figure 3 shows the step coverage of F-doped oxide on isolated poly-Si step and sub-half-micron spaces. Flow-shape and excellent gap-fill with self-planarizing feature were observed as seen as undoped TEOS-O_3 oxide deposition.

Conclusion

i) APCVD fluorine doping was characterized using fluorotriethoxysilane as a doping source. TEOS and triethoxysilane were effectively depressed the decomposition of F-source, which made high temperature doping possible to form relatively higher density films between 250 and 350 °C.

ii) Excellent gap-fill of sub-half-micron spaces and self-planarizing coverage were obtained as seen as APCVD TEOS-O_3 undoped oxide.

iii) APCVD fluorine doping successfully reduced dielectric constant in combination with the dual frequency plasma post-treatment .

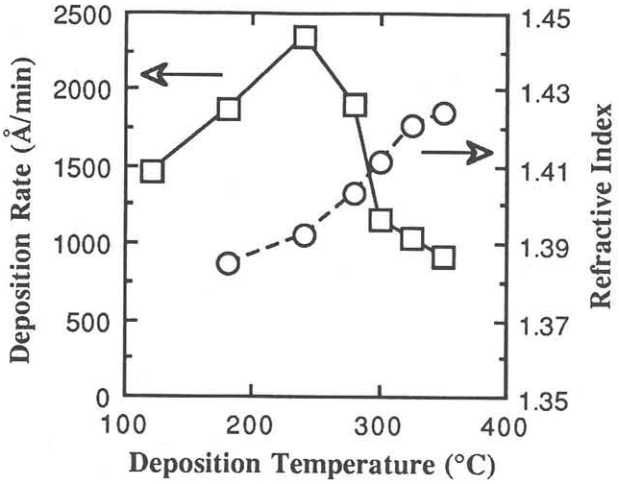

Fig. 1. Effect of deposition temperature on deposition rate and refractive index.

Table 1. Electrical properties of AP-SiOF.*

Source Si	Source F-Si	Post plasma	Dielectric constant 1MHz	Dielectric constant 10MHz	Nf	Leak current A/cm3
1	1	No	4.86	5.41	1.441	3.0e-09
"	"	"	5.43	4.92	1.441	2.6e-09
1	1	O2, 300"	3.84	4.11	1.419	1.0e-10
"	"	"	3.86	4.14	1.420	1.3e-10
1	1	N2, 300"	3.87	4.07	1.431	1.0e-09
"	"	"	3.47	3.64	1.433	1.0e-09
1	2	O2, 300"	3.28	3.27	1.420	2.3e-09
"	"	"	3.38	3.25	1.421	8.0e-10

*Dep temp; 300°C, Si; SiH(OEt)3, F-Si; SiF(OEt)3 supply ratio, Post plasma: 370°C, 13.56MHz/100KHz dual, Nf; refractive index, Leak current; 3MV/cm.

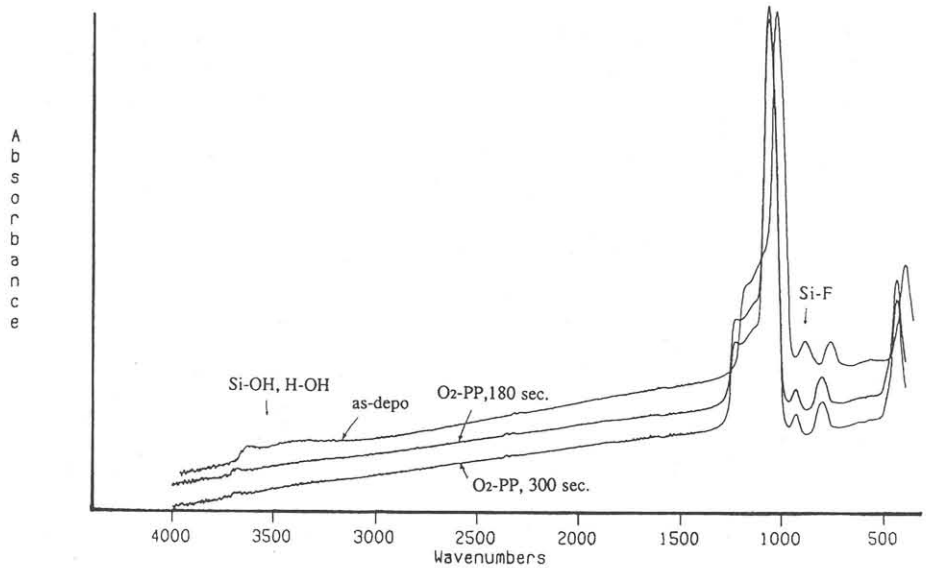

Fig. 2. Effect of O2 plasma treatment on FT-IR spectrum of AP-SiOF.

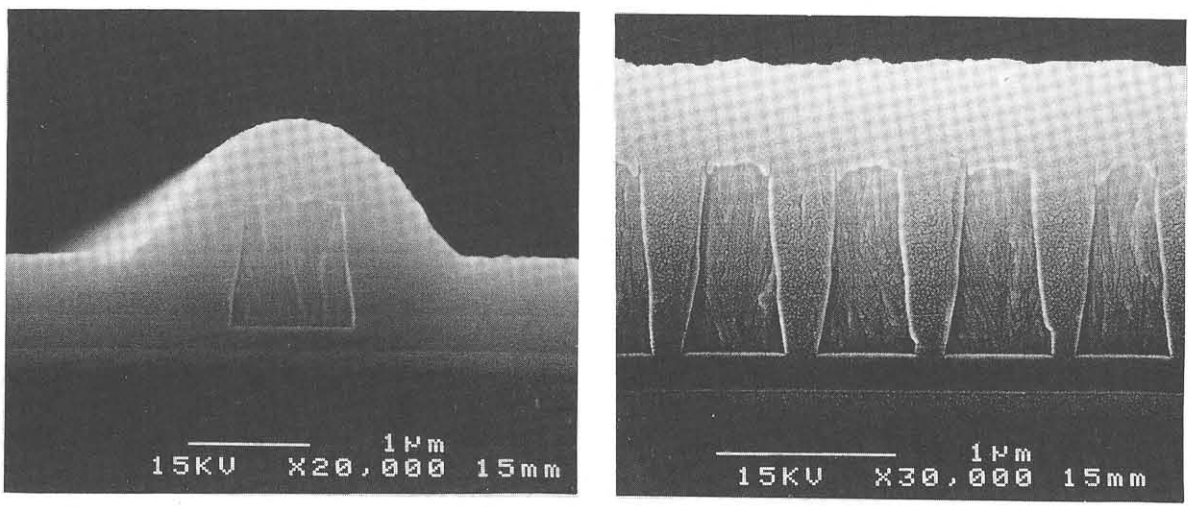

Fig. 3. Step coverage of AP-SiOF on isolated poly-Si step and sub-half-micron spaces.