PLASMA DEPOSITION CHEMISTRY OF FLUORINATED SILICON OXIDE FILMS.

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ABSTRACT

Silane-based fluorinated silicon oxide dielectric films were deposited on silicon substrate in a single-wafer, single-frequency (13.6) MHz rf plasma chemical vapor deposition system using diluted SiH_4(2% in Argon)/SiF_4/N_2O as precursors. The properties of the film were studied using various analytical methods such as Ellipsometry, Fourier Transform Infrared (FTIR), Auger, and Secondary Ion Mass Spectroscopies (SIMS). Stable fluorinated silicon oxide films with up to 10 atomic percent fluorine can be deposited with this deposition chemistry. Parametric studies of film's deposition rate, refractive index, fluorine incorporation and Si-F & Si-O bonding variations with deposition parameters show that the amount of fluorine incorporation in the film is controlled mostly by SiF_4/SiH_4 ratio, while the film stability is strongly influenced by both ion bombardment and plasma dissociation chemistry.

INTRODUCTION

The incorporation of fluorine in silicon oxide to improve film properties for wave guide application (1), and radiation and hot electron damage resistance for gate oxide have been investigated (2-3). To enhance switching performance in ultra large scale integration (ULSI) silicon devices, fluorinated silicon dioxide films have also been studied (4-14) as potential low dielectric constant (d.c.) insulator to reduce the wiring capacitance between interlevel metals. For these new dielectrics to be utilized in advanced integrated circuits, they must be stable under exposure to high humidity and temperature ambient. Our recent studies (8-9) showed that both C_2F_6 and SiF_4 can be used as fluorination sources for plasma CVD silicon oxide films deposited with an organosilicon (Tetraethoxysilane, TEOS) precursor. Furthermore, incorporation of fluorine by direct Si-F bonding precursors using PECVD process produces fluorinated oxide films with improved stability as compared to other fluorine precursors (8-9, 14). In this paper, we present the plasma deposition and characterization of fluorinated silicon oxide films using diluted SiH_4(2% in Argon)/SiF_4/N_2O as precursors.

EXPERIMENTAL

Fluorinated silicon oxide films were deposited on 200 mm p-type silicon

substrates in a single-wafer, single-frequency (13.6) MHz rf plasma chemical vapor deposition system using diluted SiH_4(2% in Argon)/SiF_4/N_2O as precursors as shown in Figure 1. The details of the plasma CVD system have been described in a recent publication (15) and will not be presented here. The properties of the film were studied using various analytical methods such as Ellipsometry, FTIR, Auger, and SIMS Spectroscopies. A Perkin Elmer 1725X FTIR system was used to analyze the films as described in our recent publication (9). Auger analysis was performed on a Perkin Elmer Model 650 Scanning Auger Microscope with a beam voltage of 5 kV and an approximate current of 100 nA (100 micron spot size). The typical deposition conditions and film properties are presented in Table I. Parametric studies of film deposition rate, refractive index, film composition and bonding, fluorine incorporation and film stability were analyzed to understand the plasma deposition chemistry.

RESULTS and DISCUSSION

Parametric studies of deposition rate, refractive index, fluorine incorporation and Si-F & Si-O bonding variations with deposition parameters (SiF_4 flow (i.e. SiF_4/SiH_4 ratio), rf power density) reveal interesting results. Both SiF_4 flow and rf power parameters have the strongest influence on F-oxide film properties. Futhermore without the SiH_4 source, the fluorinated oxide films have very low deposition rates and absorb water more readily when deposited under conventional plasma CVD conditions. Using a $SiF_4/SiH_4/N_2O$ precursor chemistry, relatively higher fluorine concentrations (up to 10 atomic percent) can be incorporated into the silicon oxide bonding network while still maintaining film stability. An FTIR spectra of a stable F-oxide film shows the presence of Si-F (930 cm^{-1}) and Si-O (450, 820 and 1130 cm^{-1}) bonds without any water absorption (Figure 2). Auger analysis shows uniform fluorine incorporation with depth (Figure 3). The SIMS analysis results confirm the amount of 9 atomic % fluorine incorporation, and also show no carbon contamination in the film. This stable fluorine incorporation is due to the direct insertion of Si-F bonding units, forming from SiF_4 dissociation, into the Si-O bonding network. Excess fluorine from SiF_4 dissociation is also effectively removed by excess hydrogen from SiH_4 dissociation. During this plasma CVD process, there are simultaneous deposition and etching mechanisms occurring on the substrate surface. The deposition species are formed from reactions between reactive species of SiH_4(2% in Argon)/SiF_4/N_2O generated in the plasma. Fluorine etching species are produced from SiF_4 dissociation. Although the F etching yield of deposited oxide films is much smaller than those of CF_x as in when C_2F_6 and/or TEOS are used as deposition precursors (8), the etching component is still quite high under high rf power and/or large SiF_4 flow. More ion bombardment and fluorine dissociation will enhance the etching component, and thus effectively reduce the deposition rate and the amount of fluorine incorporation at high rf power or/and large SiF_4 flows (Figures 4 & 5 and Tables II & III). Figure 4 shows the typical variation of F-oxide film refractive index and deposition rate with SiF_4 flow; It can be seen that the film deposition rate first decreases due to the etching effect of the fluorine etching species. As the SiF_4 flow increases, the insertion of Si-F (or

F-Si-O) species into the film becomes significant, thus resulting in higher deposition rates and more fluorine incorporation into the films up to a maximum value of 10 atomic percent (Table III). At low rf power, the dissociation of SiH_4 and SiF_4 precursors and the chemical reactions between theirs intermediates play a much larger role in the deposition process. Films deposited under lower rf power have higher deposition rates due to a lower etching component with less ion bombardment. The films also have lower density and reduced refractive indices (Figure 5 and Table II). Thus, the films deposited with lower RF power density will absorb water more readily. Higher rf power enhances film stability but does not increase deposition rate significantly. With similar deposition chemistry, more stable F-oxide film have been made using ECR plasma to increases the ion bombardment density as shown by Fukada et al. (11).

In general, plasma deposition chemistries are complex and involve many reaction steps (16), especially our plasma CVD processes that include simultaneous etching and deposition. However, ours and others results indicate two principle mechanisms control STABLE PECVD fluorinated oxide film deposition : a) the insertion of more stable and direct Si-F bonding species into the films; This can be accomplished by suitable deposition precursors with Si-F bonding (6,8,9 ,11,14), and the removal of excess fluorine generated in the plasma discharge by formation of volatile species such as H-F (9,12). b) the enhanced ion bombardment to remove or/and to densify loosely bonded species in the film which increases the oxide film stability; This can be accomplished by an increase rf power as in this study or using high density plasma processing (10).

Figure 6 shows a 0.25 micron tungsten interconnect structure with stable fluorinated silicon oxide (9 atomic % fluorine) as dielectric. The measured dielectric constant of this film is in 3.5-3.6 range. Overall, both the deposition chemistry and process conditions must be selected carefully to form stable PECVD fluorinated silicon oxide films as advanced insulators suitable for ULSI fabrication.

SUMMARY

Stable silane-based fluorinated silicon oxide films with up to 10 atomic percent fluorine were deposited on silicon substrates in a single-wafer, single-frequency (13.6) MHz rf plasma chemical vapor deposition system using diluted SiH_4(2% in Argon)/SiF_4/N_2O as precursors. Parametric studies of the film deposition rate, refractive index, fluorine incorporation and Si-F & Si-O bonding variations with deposition parameters show that the amount of fluorine incorporation in the film is controlled mostly by SiF_4/SiH_4 ratio. The film stability is strongly influenced by both plasma deposition chemistry and ion bombardment. F-oxide films formed by direct Si-F bonding insertion and greater ion bombardment density are more stable.

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Process Parameters	Values
RF power (13.6 MHz)	20-200 W
Gases	SiF_4/SiH_4(2 % in Ar)/N_2O = 5-350/500/375 sccm
Substrate Temperature	400°C
Electrode Spacing	0.76 cm
Pressure	2.8-5.0 Torr
Deposition Rate	40-120 nm/min.
Refractive Index	1.32-1.46
Uniformity	2-10 % (1 sigma)
Average Stress (0.7 um, 25°C)	(-)1.6 x 10^9 dynes/cm²

Table I- Deposition conditions for fluorinated silicon oxide

RF power	Atomic % Silicon	Atomic % Oxygen	Atomic % Fluorine
200 W Standard SiO_2	33.4	66.6	0
200 W F-Oxide	31.4	59.1	9.5
150 W F-Oxide	31.7	59.1	9.2
100 W F-Oxide	31.8	58.4	9.8
75 W F-Oxide	32.1	58.5	9.4
50 W F-Oxide	31.4	60.4	8.3
40 W F-Oxide	31.3	61.1	7.6
30 W F-Oxide	32.6	59.7	7.7
25 W F-Oxide	32.1	60.5	7.4
20 W F-Oxide	32.4	58.2	9.4

Table II - Variation of F-Oxide film composition with RF power.

SiF_4 flow	Atomic % Silicon	Atomic % Oxygen	Atomic % Fluorine
0 sccm (PECVD SiO_2)	33.5	66.5	0
5 sccm	33.8	62.9	3.3
10 sccm	32.4	62.3	5.3
20 sccm	32.4	61.1	6.5
300 sccm	31.2	59.0	9.8
375 sccm	31.4	59.1	9.5

Table III- Variation of F-Oxide composition with SiF4 flow.

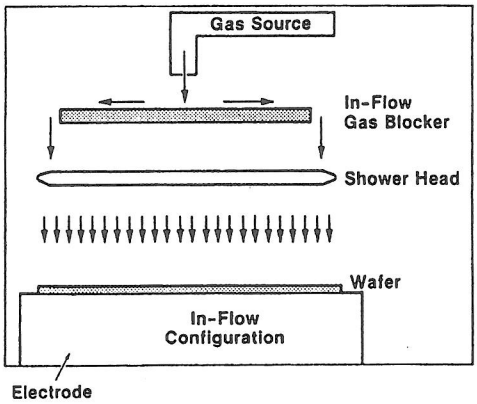

Figure 1- Schematic of 200 mm single-wafer PECVD system.

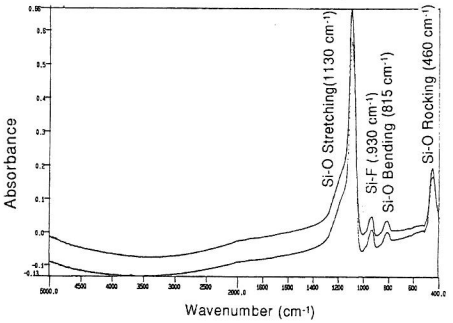

Figure 2- FTIR spectra of typical silane-based F-Oxide films (9 atomic % F).

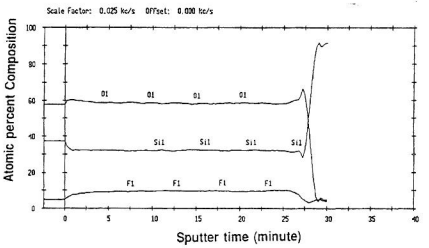

Figure 3- Typical Auger compositional depth profile analysis of F-Oxide.

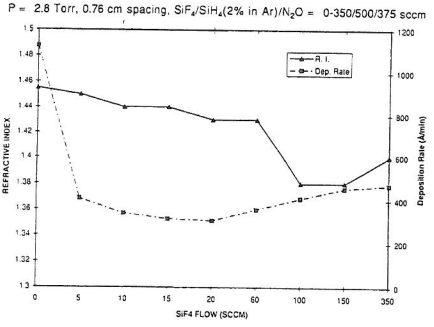

Figure 4- Variation of F-Oxide deposition rate and RI with SiF4 flow.

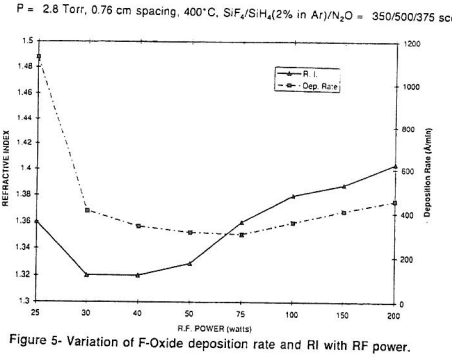

Figure 5- Variation of F-Oxide deposition rate and RI with RF power.

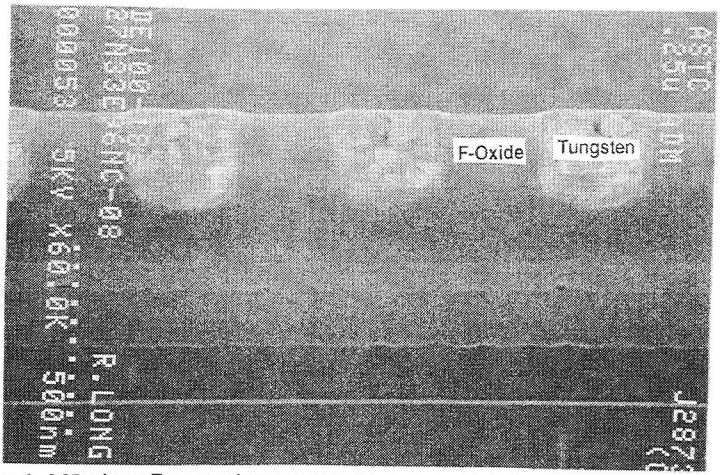

Figure 6- 0.25 micron Tungsten interconnects fabricated with F-Oxide dielectric (d.c.:3.6)