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Effect of fluorine on chemical and electrical properties of room temperature oxide films prepared by plasma enhanced chemical vapor deposition

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The effect of fluorine on SiO_2 films was investigated by comparing chemical and electrical properties of fluorinated silicon oxide (SiOF) films with those of SiO_2 films. The SiOF films were prepared at room temperature by plasma enhanced chemical vapor deposition incorporating CF_4 as the fluorine source into the deposition process of the SiO_2 films using Si_2H_6 and N_2O. The relative dielectric constant of the as-deposited SiO_2 films was reduced from 5.95 to 4.43 by the incorporation of fluorine and with postmetallization anneal. The breakdown measurements on the SiOF films showed no early failures at a field strength of ≤ 3 MV/cm, resulting in an average breakdown field strength of 7.11 MV/cm. © *1998 American Institute of Physics.* [S0003-6951(98)01710-0]

Low temperature deposition has been required for interlayer dielectric materials used in multilevel interconnection, because thermal stress degrades device characteristics and wiring reliability.[1] In all of the different low temperature dielectric materials, SiO_2 films prepared by plasma enhanced chemical vapor deposition (PECVD), where a rf discharge supplies an additional energy to promote the chemical reaction, have been preferably used. The low temperature PECVD SiO_2 films have been typically produced using silane (SiH_4) as the silicon source. However, the use of disilane (Si_2H_6) instead of silane (SiH_4) can produce PECVD SiO_2 films at lower temperature due to the high reactivity of Si_2H_6.[2] Meanwhile, the addition of fluorine into the Si–O network seems to be beneficial, in that it enhances the oxidation rate, relaxes the oxide stress, suppresses the hot-electron induced generation of interface traps, and reduces the dielectric constant with existing tool sets.[3,4]

In this letter, we have discussed the effect of fluorine on PECVD SiO_2 films by comparing chemical and electrical properties of the fluorinated silicon oxide (SiOF) films with those of SiO_2 films. The results of Fourier transform infrared (FTIR) spectroscopy, high frequency capacitance–voltage ($C-V$) measurements and ramp current–voltage ($I-V$) measurements are reported.

The deposition of the SiO_2 and SiOF films was carried out in a Plasma Therm PECVD system model VII-70 with 2.54 cm electrode and 13.56 MHz operating rf. Chemically polished, boron doped 4 in. silicon wafers with (100) orientation and resistivity of 5–15 Ω cm were used as the substrates. The wafers were cleaned as per the standard RCA cleaning procedure.[5] The substrate temperature was maintained at 30 °C. The SiOF films were deposited by flowing 20 sccm of CF_4 into the deposition process of SiO_2 films using 40 sccm of Si_2H_6 (5% in He) and 100 sccm of N_2O. The process pressure and rf power were maintained at 700 mTorr and 50 W, respectively. The thickness of the films was measured using an Applied Materials Ellipsometer Model II. Metal–oxide–semiconductor (MOS) capacitors, each with a gate area of 2.29×10^{-3} cm^2, were fabricated by a standard photolithography technique using these films. The FTIR spectra were observed using a Perkin Elmer FTIR spectrometer model 1600 with a resolution of 4 cm^{-1}. The postmetallization anneal (PMA) was carried out in a H_2 (5% in N_2) ambient at 400 °C for 30 min. The $C-V$ measurements were performed by superimposing a 25 mV ac signal at 1 MHz on a dc voltage with a sweep rate of 20 mV/s using an HP 4275A LCR meter. The $I-V$ characteristics were obtained using an HP 4140 voltage source and a Keithley 485 picoammeter. All measurements were carried out at room temperature.

It was observed that the deposition rates of the SiO_2 and SiOF films were 12.1 and 12.7 nm/min, respectively, with a thickness uniformity $\leq \pm 3\%$ on 4-in. wafers. It is supposed that the slight increase in the deposition rate for the SiOF films is due to the additional flow of CF_4, whereas the etching effect of CF_4 plasma was considered to be insignificant in this experiment. Meanwhile, the higher etch rate of the as-deposited SiOF films (15.2 nm/s, which was four times higher compared with that of the as-deposited SiO_2 films) in P-etch solution [HF(48%):HNO_3(70%):H_2O=3:2:60] indicated a decrease in the film density and an increase of bond strain due to the incorporation of fluorine. The higher etch rate also resulted from the increased concentration of HF at the film surface due to the fluorine dissolved from the film.[1]

Figure 1 displays typical FTIR spectra of the SiO_2 and SiOF films with and without postdeposition anneal (in N_2 ambient at 400 °C for 30 min), respectively. The absorption peaks corresponding to Si–O stretching and bending vibration modes[6] were observed for all films at around 1065 and 808 cm^{-1}, respectively. With postdeposition anneal, the absorption peak at 929 cm^{-1} corresponding to hydroxyl-containing (Si–OH) vibration modes[7] for the as-deposited SiO_2 films disappeared; meanwhile, a weak absorption peak at 940 cm^{-1} corresponding to Si–F stretching vibration

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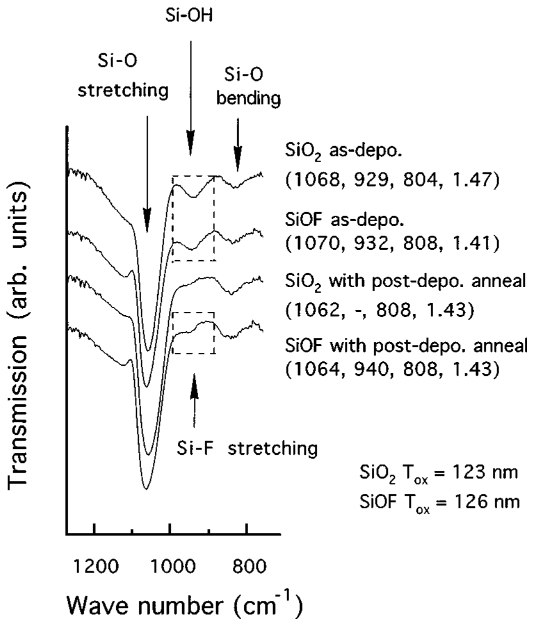

FIG. 1. FTIR spectra of the SiO_2 and SiOF films deposited at room temperature. The numbers in parentheses for the as-deposited SiO_2 and SiOF films indicate the absorption peak positions corresponding to Si–O stretching, Si–OH, and Si–O bending vibration modes, respectively, followed by refractive index. With postdeposition anneal (in N2 ambient at 400 °C for 30 min), the absorption peak corresponding to Si–OH vibration modes for the as-deposited SiO_2 films disappeared; meanwhile, a weak absorption peak corresponding to Si–F stretching vibration modes remained for the as-deposited SiOF films. T_{ox} indicates an oxide thickness.

modes[7,8] remained for the as-deposited SiOF films. The larger Si–O stretching frequency of the SiOF films compared with that of the SiO_2 films is related to the larger Si–O bond angle and is accompanied by a smaller refractive index and is also associated to a decrease in the film density,[6] which is consistent to the higher etch rate.

Table I shows the relative dielectric constant (ϵ_r) and effective oxide charge density (Q_o) of the SiO_2 and SiOF films. The relative dielectric constant was calculated from the relation $\epsilon_r = T_{ox}C_{ox}/\epsilon_o$ (where T_{ox}=oxide thickness, C_{ox}=oxide capacitance per unit area, and ϵ_o=permittivity of vacuum).[9] The relative dielectric constant of the as-deposited SiO_2 films was reduced from 5.95 to 4.43 by the incorporation of fluorine and with PMA. Being the most electronegative and least polarizable on the periodic table, fluorine reduces the number of polarizable Si–OH bonds and also causes changes in the Si–O network to a less polarizable geometry. These changes resulted in lowering the polarizability of the SiOF films, thus lowering the dielectric constant.[4,7] The dielectric constant was further decreased with PMA which contributed to reduce the number of polarizable Si–OH bonds. Table I also shows that an effective oxide charge density, which was calculated from the relation $Q_o = -C_{ox}\Delta V_{FB}/q$ (where ΔV_{FB}=flat band voltage shift, and q=magnitude of the electronic charge), was effectively decreased with the incorporation of fluorine. This fact is attributed to the replacement of hydrogen or defect-related bonds by fluorine in the Si–O network. In particular, the PMA decreased the effective oxide charge density by more than one order of magnitude with the incorporation of fluorine.

TABLE I. Summary of the relative dielectric constant (ϵ_r) and effective oxide charge density (Q_o) of the SiO_2 and SiOF films.

	As-deposited		With PMA	
	ϵ_r	Q_o (cm^{-2})	ϵ_r	Q_o (cm^{-2})
SiO_2	5.95	1.07×10^{12}	5.90	5.83×10^{11}
SiOF	5.20	7.42×10^{11}	4.43	5.82×10^{10}

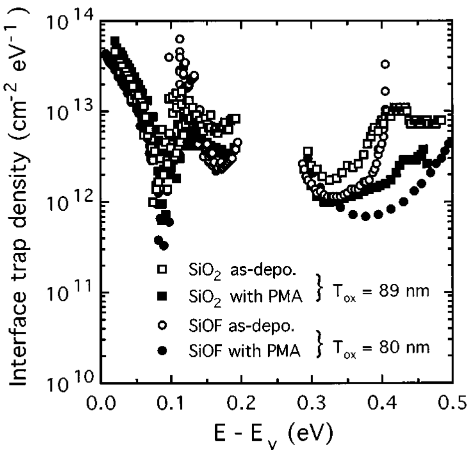

FIG. 2. Interface trap density of the SiO_2 and SiOF films as a function of the energy location from the valence band edge.

The interface trap density (D_{it}) was determined by the high frequency Terman method.[10] From the experimental measurement of the gate voltage (V_G) and the corresponding semiconductor surface potential (Φ_s), the interface trap density was calculated by[11]

$$D_{it}(\Phi_s) = \frac{C_{ox}}{q}\left(\frac{dV_G}{d\Phi_s} - 1\right) - \frac{C_s(\Phi_s)}{q},$$

where $C_s(\Phi_s)$ is the semiconductor capacitance per unit area. The interface trap density of the SiOF films as a function of the energy location from the valence band edge (E_v) is compared with our previous result for the SiO_2 films[12] in Fig. 2. It was observed that the interface trap density of the SiOF films also followed W shape having two minimum values. Two minimum values of the interface trap density for the SiOF films with PMA were 3.30×10^{11} and 6.92×10^{11} $cm^{-2}\,eV^{-1}$ at 0.09 and 0.38 eV above E_v, respec-

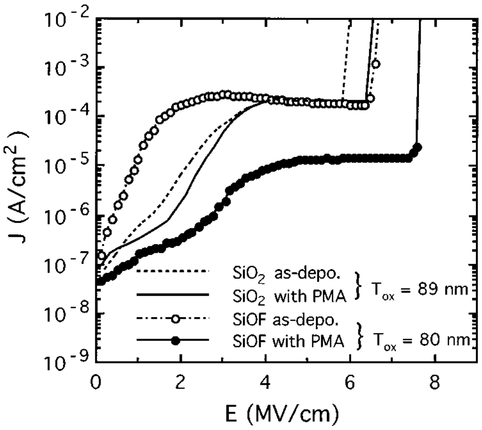

FIG. 3. J–E characteristic of the SiO_2 and SiOF films. The negative bias at a ramp rate of 1 V/s, which causes electron injection, was applied to the gate.

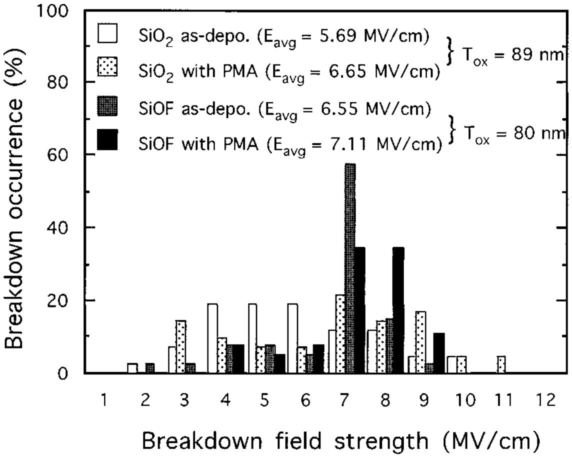

FIG. 4. Histogram of dielectric breakdown occurrences as a function of the applied field strength for the SiO_2 and SiOF films. In each case, forty MOS capacitors, each with a gate area of 2.29×10^{-3} cm^2, were stressed to breakdown by applying a negative bias at a ramp rate of 1 V/s to the gate. E_{avg} indicates an average dielectric breakdown field strength.

tively. These two minimum values are smaller by 48% and 31%, respectively, compared with those of the SiO_2 films with PMA.

A ramp $J-E$ characteristic of the MOS capacitors fabricated using the SiOF films in Fig. 3 was measured by applying negative bias at a ramp rate of 1 V/s to the gate with respect to the substrate and was compared with our previous result for the SiO_2 films.[12] As a result of PMA on the as-deposited SiOF films, premature electron injection at low electric field was reduced significantly, and also the initial leakage current was decreased to the same order of PECVD SiO_2 films deposited at 350 °C using SiH_4 as the silicon source.[13] As electrons are injected from the gate, some electrons are trapped into bulk traps creating a space charge. At a suitably high current, the increase in the internal field of the trapped electron space charge buildup cancels the increase due to the voltage ramp,[13] thereby causing the ''trapping ledge'' and eventually resulting in destructive dielectric breakdown.

Figure 4 shows a histogram of such dielectric breakdown occurrences for the MOS capacitors fabricated using the SiOF films and our previous result for the SiO_2 films[12] is also compared. In each case, forty MOS capacitors, each with a film thickness of 80 nm and a gate area of 2.29×10^{-3} cm^2, were stressed to breakdown by applying negative bias at a ramp rate of 1 V/s to the gate. The average breakdown field strength for the MOS capacitors fabricated using the as-deposited SiOF films was 6.55 MV/cm, which is 13% higher than that for the as-deposited SiO_2 films. Moreover, the average breakdown field strength was increased to 7.11 MV/cm with PMA. In particular, the MOS capacitors fabricated using the SiOF films with PMA showed no early failures at a field strength of $\leqslant 3$ MV/cm and 79% of the MOS capacitors had a breakdown field strength of 7 MV/cm or higher resulting in an overall shift of the breakdown field distribution to higher value. This is attributed to the fact that the bulk traps which are related to hydrogen incorporation were reduced by the incorporation of fluorine.

In summary, the effect of fluorine on the chemical and electrical properties of the room temperature PECVD SiO_2 and SiOF films were discussed. It has been shown that the effective oxide charge density and interface trap density were effectively reduced by the incorporation of fluorine and with PMA. In particular, the relative dielectric constant of the as-deposited SiO_2 films was reduced from 5.95 to 4.43 due to the change of the Si–O network to a less polarizable geometry. In addition, the breakdown measurements on the MOS capacitors fabricated using the SiOF films with PMA showed an increase of an average breakdown field strength with no early failures at a field strength of $\leqslant 3$ MV/cm. The significant decrease of the dielectric constant and the increase of the breakdown field strength are two of the main effects of fluorine on SiO_2 films, promising the potential capability for interlayer dielectrics and passivating materials in multilevel interconnection.

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