Fabrication of Low Dielectric Constant Materials for ULSI Multilevel Interconnection by Plasma Ion Implantation

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Abstract— **High dose-rate plasma ion implantation (PII) has been utilized to produce low dielectric constant (k) SiO_2 films for high quality interlayer dielectrics. The SiO_2 films are fluorine-doped/carbon-doped by PII with CF_4 plasma in an inductively-coupled plasma (ICP) reactor. It is found that the use of CF_4 doping results in exceptional dielectric properties which differ significantly from fluorinated SiO_2. The dielectric constant of the SiO_2 film is reduced from 4.1 to 3.5 after 5 minute PII. Other electrical parameters such as bulk resistivity and dielectric breakdown strength are also improved.**

I. INTRODUCTION

MULTILEVEL interconnects are widely used in ultra-large-scale integrated circuits (ULSI). However, to minimize the crosstalk and RC time delay, it is necessary to keep the interlayer dielectric capacitance low. This can be implemented through the introduction of low-dielectric constant inter-layer films. The properties and fabrication techniques of the interlayer dielectrics have to meet the following requirements: (1) low dielectric constant, (2) high bulk resistivity and breakdown field strength, (3) good mechanical and chemical properties, (4) high planarization and narrow gap filling capability, and (5) low process temperature. So far, existing techniques [1]–[4] cannot satisfy all of the above requirements due to the limitations of the physical mechanisms. Most low k processes involving organic materials, which usually have some drawbacks on their mechanical and chemical properties, require a relatively high temperature for the chemical decomposition and reaction. Silicon dioxide is a most commonly used interlayer dielectric because of its good properties and compatibility to semiconductor processing. It is known that doping silicon dioxide with fluorine can reduce its dielectric constant [1]–[4]. However, present processing technologies are not able to deliver high quality films of SiOF for low k interlayer dielectrics. The CVD processes are limited by thermodynamics constraints, and consequently, the reduction in dielectric constant is relatively small [1], [2]. The electrical and mechanical properties of the SiOF dielectric films such like bulk resistivity and breakdown field strength are usually degraded by conventional low k material processes. Also, there are remaining problems concerning the addition of fluorine, which are caused by hydrolysis and will degrade interconnect and device reliability [5]. Fluorine species in SiOF films are not stable and easy to absorb H_2O to form OH and HF. The existing OH will increase the dielectric constant of the films, and both HF and OH can corrode dielectrics and metal layers.

Plasma ion implantation (PII) is a niche doping technology and has been applied to the semiconductor processing [6]–[14]. The primary features of PII are: very high dose rate up to $10^{16}/\text{cm}^2$ s, independent of the implantation area, minimum charging effect, very low cost, and capable of very low energy implant. PII technique is thus well suited to low k dielectric application. The dielectric constant of the films can be flexibly reduced by PII incorporating F or C or any other appropriate dopants into the films by using fluorine/carbon containing gases without thermodynamics constraints.

In this letter, the preparation of a low k material for ULSI applications by PII doping technique is presented. The SiO_2 films are fluorine-doped/carbon-doped by PII with CF_4 plasma in an ICP plasma reactor. Good properties including lower dielectric constant and higher bulk resistivity and breakdown field strength have been achieved.

II. APARATUS AND EXPERIMENTS

An inductively-coupled plasma (ICP) system, which was described elsewhere [12], was used to conduct the PII experiments. The typical equilibrium CF_4 plasma parameters for this experiment were: plasma density $n_i \approx 10^{11}/\text{cm}^3$, electron temperature $T_e \approx 4$ eV, and plasma potential $V_p \approx 30$ V.

P-type $\langle 100 \rangle$ Si wafers with resistivity of 2–20 Ω-cm were used as the starting material. A 2500-Å-thick SiO_2 film was grown on the Si surface by routine thermal oxidation. In order to minimize the etching [15] and charging effects [16], the working pressure was kept low with short pulse width and low pulse potential. The typical PII parameters are: base pressure $<10^{-6}$ torr, working pressure $= 0.2$ mtorr, gas flow rate $\sim$12 sccm, RF power $=$ 700 W, pulse voltage $= -2$ kV. The sample was cooled to room temperature during PII. After PII, a 2000-Å-thick Al layer was deposited on the surface by sputtering and the capacitor structure was patterned by lithography. Afterwards, a post-implant annealing

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Manuscript received August 5, 1997; revised July 14, 1998.

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Publisher Item Identifier S 0741-3106(98)08416-X.

TABLE I

SUMMARY OF MAJOR PROPERTIES OF SiO_2 FILMS AFTER PII WHEN WORKING PRESSURE IS 0.2 mtorr. (CF_4 PLASMA, PRESSURE: 0.2 mtorr, ICP RF power: 700 W, PULSE: −2 kV, t_p 2 μs, prf 10 kHz, ANNEALING: 20 MIN, 385 °C, N_2)

	Before treatment	1 min	2 min	3 min	4 min	5 min
ε_r	4.10	4.01	3.89	3.86	3.78	3.50
ρ (10^{14} Ω cm)	0.68	0.75	1.00	1.18	1.52	2.24
E_{Break} (10^6 V/cm)	7.02	8.32	8.52	13.09	8.81	17.12
Thickness (Å)	2564	2343	1907	1700	1591	882
Refractive Index	1.460	1.441	1.466	1.464	1.465	1.461
Etching Rate (Å/min)	N/A	222	329	288	243	336

process was performed in N_2 gas at 385 °C for 20 min. The thickness and refractive index of SiO_2 films were measured by an ellipsometer (GAERTNER-L117) and a Dektak profilometer (Veeco-Sloan 8000). The dielectric constant of the films was calculated from the maximum capacitance values in the capacitance–voltage (C–V) measurement at 1 MHz using Al/SiO_2/p-Si structure. The circular capacitors with an area of 1.782×10^{-3} cm^2 were measured with a HP 4277A LCZ meter. The bulk resistivity (based on the bulk leakage current) and breakdown field strength of the SiO_2 films were measured with a HP 5155A semiconductor parameter analyzer and a curve tracer. SIMS depth profiles were acuqired using Cs ion bombardment and quantification was based on reference implant materials.

III. RESULTS AND DISCUSSION

Fig. 1 shows the evolution of the dielectric constant of SiO_2 films versus PII process time for different working pressures. The dielectric constant, ε_r, monotonously decreases from 4.10 to 3.50 when the pressure is 0.2 mtorr and the process time is 5 min. This dielectric constant value is the lowest so far comparing to that of conventional fluorinated SiO_2 films. Reduction of ε_r with the implant time is caused by higher concentrations of F and C in the SiO_2 film, either by higher accumulated doses or etching effect during process. The dielectric constants are also reduced when the pressure are 0.5 and 0.7 mtorr. Table I summarizes the major properties of the SiO_2 films after CF_4 PII when the working pressure is 0.2 mtorr. Besides the significant reduction of the dielectric constant, PII also improves bulk resistivity and breakdown field strength in contrast to other conventional low k processes. As the dielectric constant reaches the lowest value of 3.50, the corresponding bulk resistivity increases from 0.68×10^{14} to 2.24×10^{14} Ω·cm. The breakdown field strength increases from 7.02 to 17.12 MV/cm. Another interesting feature is that unlike other conventional low k processes there is no obvious reduction of the refractive index of the SiO_2 film [2]. It remains fairly between 1.44 and 1.46, and this unique characteristic may be caused by the addition of carbon.

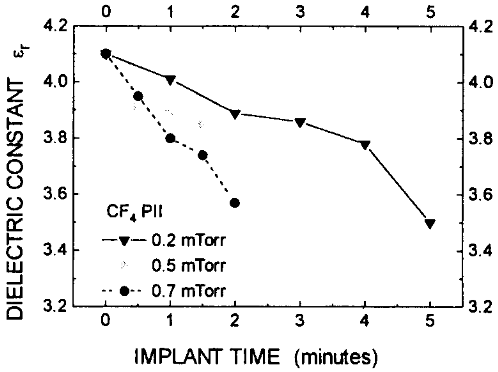

Fig. 1. The dielectric constant of SiO_2 films versus the PII process time for the different working pressure.

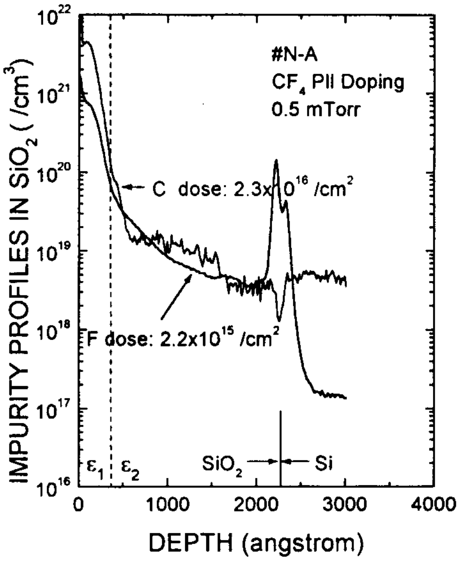

Fig. 2. SIMS profiles of F and C in SiO_2 film after a 0.5 mtorr CF_4 PII.

The etching data during CF_4 PII are also shown in Table I. CF_4 is often used as an etchant gas for both Si and SiO_2 in semiconductor fabrication. Etching will change the structure and cause reduced and saturated retained doses during PII [16]. However, a positive effect is that it may be beneficial to planarization and gap filling of dielectric interlayers [17].

The addition of carbon in SiO_2 films by CF_4 PII and its correlation with fluorine may play an important role in reducing the dielectric constant and improving the electrical properties. The hydrolysis reaction of fluorinated SiO_2 dielectrics is believed to be the major concern affecting dielectric stability and device reliability [1]–[4]. The additional use of carbon doping to achieve both a lower dielectric constant and improved film stability has been reported [3], but the mechanism still needs further investigation. The carbon can form C–F and C–O bonds and eliminate unstable Si–F or O–F bonds. Because C–F and C–O bonds have higher chemical bond strengths than Si–F and O–F bonds [18], the fluorine-doped/carbon-doped SiO_2 films by PII can retard hydrolysis reaction and therefore improve film stability and device reliability.

Fig. 2 displays the SIMS profiles of F and C in the SiO_2 films after CF_4 PII. The results show that the processed SiO_2 has nonuniform in-depth distributions of F and C. An analysis of a double layer model indicates that the 882 Å F/C doped SiO_2 film ($\varepsilon_r = 3.5$) consists of a 300 Å layer 1 ($\varepsilon_r = 2.8$) and a 582 Å layer 2 ($\varepsilon_r = 4.0$). Therefore, it appears to be possible to achieve a high quality dielectric with a dielectric constant lower than 3.0 by an optimized PII process.

IV. CONCLUSION

Plasma ion implantation (PII) has been demonstrated to be an efficient and low cost process to prepare high quality low-dielectric constant (low k) SiO_2 films for ULSI. The dielectric constant of the SiO_2 films prepared by CF_4 PII is reduced from 4.10 to 3.50 and the bulk resistivity and dielectric breakdown field strength are also improved.

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