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Structural properties of low temperature plasma enhanced chemical vapor deposited silicon oxide films using disilane and nitrous oxide

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The structural properties of low temperature plasma enhanced chemical vapor deposited SiO_2 films using Si_2H_6 and N_2O have been studied. It is observed that the degree of compaction of as-deposited SiO_2 films, upon subsequent annealing, increases up to 4%. The shift of Si-O-Si stretching peak wave number of the as-deposited SiO_2 films ($\Delta\omega=-20$ cm^{-1}) compared to the undensified SiO_2 films is attributed to 9.4% increase in the film density, resulting in smaller Si-O-Si bridging bond angle of 138°. It is also believed that the high temperature annealing results in the reduction of hydroxyl containing species in the film and in turn drives the dielectric constant towards that of thermal SiO_2 films. © *1995 American Institute of Physics.*

A great deal of research on the low temperature deposition of silicon oxide (SiO_2) films has been reported for applications toward primary insulator layers in the microelectronic industry. One of the more preferred low temperature deposition techniques is plasma enhanced chemical vapor deposition (PECVD), where the plasma dissociation of the reactant gas molecules enables the deposition temperature to be further decreased compared to other thermal CVD techniques. Silane (SiH_4) as the silicon source and nitrous oxide (N_2O) as the oxidant source are typically used in the PECVD process.[1–4] Recently, low temperature SiO_2 deposition process with disilane (Si_2H_6) instead of SiH_4 as the silicon source has been reported,[5,6] indicating that the SiO_2 films can be deposited even at room temperature due to the high reactivity of Si_2H_6. In this letter, we present the dependence of the structural properties of SiO_2 films prepared by low temperature PECVD using Si_2H_6 and N_2O on the postdeposition annealing process.

Chemically polished, 4 in. diameter boron doped silicon wafers with (100) orientation and 5–15 Ω cm resistivity were used as the substrates. Deposition of 100 nm thick SiO_2 films was made in Plasma Therm VII-70 PECVD reactor with 2.54 cm electrode spacing and 13.56 MHz operating rf frequency. The deposition process parameters were maintained the same throughout this study. The substrate temperature was set at 120 °C while the top electrode temperature was 60 °C. A 140 sccm gas mixture of 4.8% Si_2H_6 in He and pure N_2O was introduced into the process chamber while the gas flow ratio of N_2O to Si_2H_6 was fixed at 50 in order to ensure the stoichiometry of the SiO_2 films. The process pressure and rf power were 700 mTorr and 50 W, respectively. These conditions gave a deposition rate of 12.5 nm/min and thickness uniformity of within ±3% across 4 in. wafers. The conventional RCA cleaning followed by 100:1 parts by volume of DI water-HF (48%) dipping was used as predeposition cleaning procedure. The thickness of the deposited SiO_2 films was measured using an Applied Materials Ellipsometer II. The postdeposition annealing processes were carried out in conventional tube furnace flowing N_2 at different temperatures for 30 min. The vibrational properties in the 400–4000 cm^{-1} wave number range were observed using a Perkin Elmer Model 1600 Fourier transform infrared spectrophotometer with a resolution of 4 cm^{-1}. A bare silicon wafer was used for background subtraction purposes. Al gate MOS capacitors with predefined area of 2.6×10^{-3} cm^2 were fabricated using a standard photolithography technique to investigate the dielectric constant of the SiO_2 films annealed at different temperatures. Forming gas anneal with 5% H_2 in N_2 ambient at 400 °C for 30 min was carried out as the postmetallization anneal (PMA) prior to capacitance-voltage ($C-V$) measurements.

In Fig. 1, degree of compaction and chemical etch rates in the P-etching solution are plotted as a function of the postdeposition annealing temperature. The degree of compaction increases with increasing the annealing temperature. The maximum compaction, as a result of high temperature annealing, obtained in this study was about 4% when the

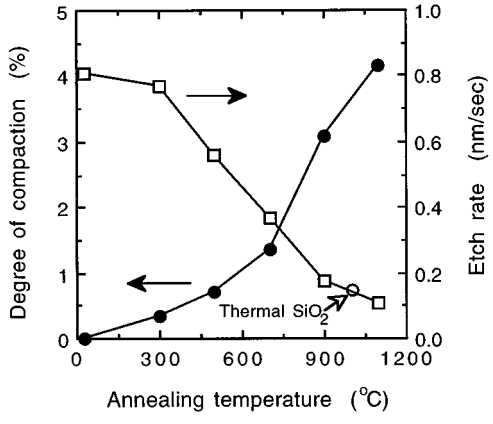

FIG. 1. Percentage degree of compaction (●) and etch rate in the P-etching solution (□) of the SiO_2 films as a function of postdeposition annealing temperature. Experimental data at 25 °C are for the as-deposited film. The circle corresponds to etch rate of the thermal SiO_2 films grown at 1000 °C, 0.15 nm/s.

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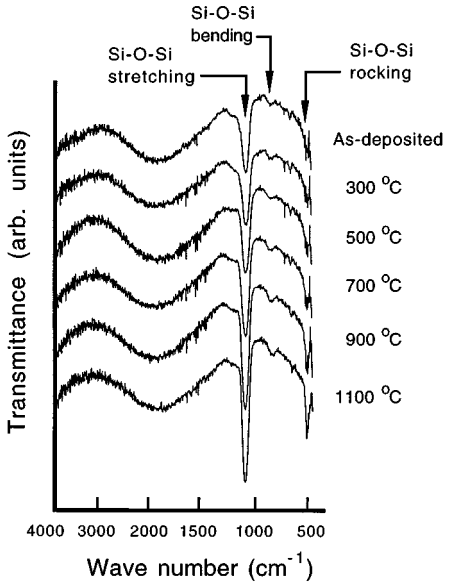

FIG. 2. Infrared transmission spectra of the SiO_2 films annealed at different temperatures. Three characteristic peaks of Si–O–Si vibrational motion are marked.

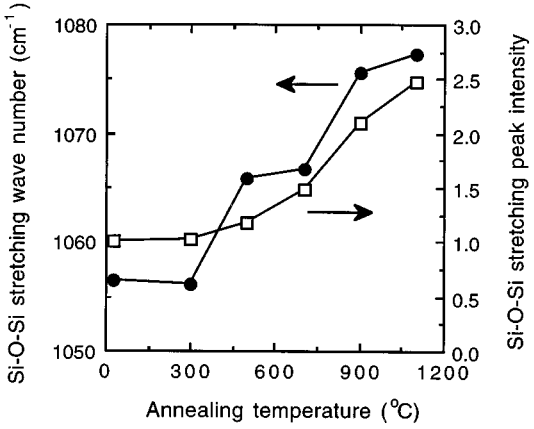

FIG. 3. Si–O–Si asymmetric stretching peak wave number (●) and its relative peak intensity with respect to the as-deposited SiO_2 films (□) as a function of postdeposition annealing temperature.

as-deposited SiO_2 films were annealed at 1100°C. This matches with the results reported for SiH_4 based PECVD SiO_2.[1,7] The chemical etch rate was obtained by dipping the films in the P-etching solution, that is, 15 HF (48%):10 HNO_3 (70%):300 DI water. The etch rate of the as-deposited SiO_2 films was found to be 0.81 nm/s. As the annealing temperature increases, the etch rate decreases. The etch rate ratio of the as-deposited to the annealed SiO_2 films at 1100 °C was 7.4. Higher etch rates obtained indicate that the as-deposited SiO_2 films may have strained bonds, micropores, and impurities in the network. The stress induced cracking which is known to occur during high temperature processing, particularly in films prepared at low temperatures, has not been observed even at 1100 °C.

Infrared transmission spectra of the SiO_2 films annealed at different temperatures are shown in Fig. 2. Three characteristic peaks located at 1075 cm^{-1}, 800 cm^{-1}, and 450 cm^{-1} corresponding to Si–O–Si asymmetric stretching, bending, and rocking motion, respectively, are evident.[8,9] Also from the figure, transmission intensities of the hydrogen containing bonds[10] such as Si–H (2270 cm^{-1}, 880 cm^{-1}), Si–OH (3620 cm^{-1}), H_2O (1620 cm^{-1}) are below the spectrophotometer's detection level. It is claimed[11] that the detection limit for a 100 nm film is five times higher than the 0.5–1 at. % limit estimated for 500 nm films.[2] This indicates less than 5 at. % of bonded hydrogen content in the films studied.

The Si–O–Si stretching vibration mode is commonly used to study the structural property of the SiO_2 films. The Si–O–Si stretching peak wave number and its relative peak intensity as a function of the annealing temperature are plotted in Fig. 3. As the annealing temperature increases, the stretching peak wave number increases: for example, from 1056 cm^{-1} for as-deposited SiO_2 films to 1077 cm^{-1} for SiO_2 films annealed at 1100 °C. Also, the relative intensity of the stretching peak increases with annealing temperature and is up to 2.5 times higher for films annealed at 1100 °C compared with as-deposited films.

Previous studies[12,13] had reported that the position of the stretching peak angular frequency (ω) is related to the film density (ρ), $d\omega/d\rho = -93\ g^{-1}\ cm^2$, and to the mean Si-O-Si bridging bond angle (θ), $d\theta/d\rho = -28\ °g^{-1}\ cm^3$. The changes in the film density ($\Delta\rho/\rho$) and θ calculated using these relationships are plotted in Fig. 4. The Si–O–Si stretching peak wave number of 100 nm thick thermal SiO_2 films grown at 1000 °C in our laboratory is located at 1076 cm^{-1} and is used as the reference wave number for the undensified SiO_2 films. Assuming that ρ and θ of the undensified amorphous SiO_2 films are 2.2 g/cm^3 and 144 °,[12,14] the film density and Si–O–Si bridging bond angle of the as-deposited SiO_2 films are calculated to be 2.4 g/cm^3 and 138 °. This results in 9.4% densification of the as-deposited SiO_2 films compared to the undensified SiO_2 films. It is believed that the high temperature annealing favors the relax-

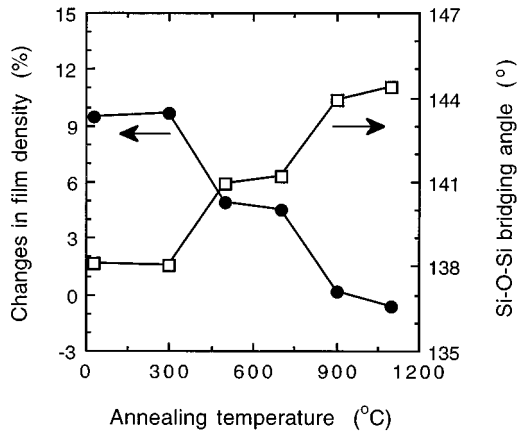

FIG. 4. Changes in the SiO_2 film density $\Delta\rho/\rho$ (●) and Si–O–Si bridging bond angle, θ (□) as a function of postdeposition annealing temperature. It is assumed that ρ and θ of the undensified amorphous SiO_2 films are 2.2 g/cm^3 and 144°, respectively.

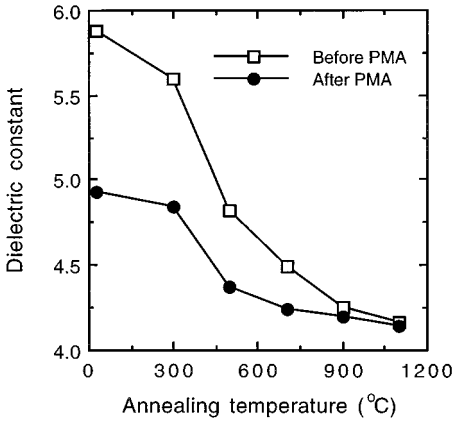

FIG. 5. Dependence of dielectric constant of SiO_2 films annealed at different temperatures on postmetallization annealing (PMA). The PMA was carried out in 5% H_2 in N_2 ambient at 400 °C for 30 min.

ation of the SiO_2 film network,[15] presumably by reduction of porosity and hydrogen-containing species.

The effect of high temperature annealing in terms of change in dielectric constant was also investigated using $C-V$ measurement and is shown in Fig. 5. The dielectric constant is calculated from the measured values of the capacitance in the accumulation region of MOS devices with SiO_2 films, annealed at different temperatures prior to Al evaporation, as dielectric layers. Increase in annealing temperature caused the reduction of dielectric constant of the SiO_2 films. For instance, the dielectric constant of the as-deposited SiO_2 films was 5.88 whereas that of the SiO_2 films annealed at 1100 °C was 4.16. Dielectric constant has been known to be proportional to the OH content in the film,[16] thereby suggesting the presence of reduced number OH bonds in the SiO_2 films annealed at higher temperature. It was also found that the PMA resulted in further reduction of the dielectric constant. This may be due to hydrogen related passivation[17] known to occur during forming gas anneal. More detailed study is in progress to understand the bearing of these results on the electrical properties of the SiO_2 films.

The results reported in this letter indicate that the structural properties of the PECVD SiO_2 films deposited at 120 °C using Si_2H_6 and N_2O are not significantly different from the conventional SiH_4 based SiO_2 films deposited at 250–350 °C. It is concluded that PECVD deposition of SiO_2 films using Si_2H_6 and N_2O can be a promising technique toward making available a low temperature process for device fabrication where such conditions might be crucial.

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