Improvement in Dielectric Properties of Low Temperature PECVD Silicon Dioxide by Reaction with Hydrazine

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The dielectric properties of plasma-enhanced chemical vapor deposition (PECVD) SiO_2 deposited at 150°C were improved by reaction with anhydrous hydrazine vapor at 150–350˚C. The permittivity and loss decreased ~32% and ~86%, respectively, after reaction with hydrazine at 150°C. The decrease in permittivity and loss correlated with a decrease in the dipole concentration (silanol + water). During exposure to humid conditions, water uptake in the SiO_2 films degraded the dielectric properties. A nitrogen anneal at 350°C did not improve the dielectric properties of the PECVD SiO_2. Although water was removed from the films, silanol remained. When the PECVD SiO_2 deposited at 150°C was reacted with hydrazine vapor at 150°C, both silanol and water were removed from the films. The dielectric properties and resistance to water absorption improved.

Key words: Anhydrous hydrazine, dielectric properties, plasma-enhanced chemical vapor deposition (PECVD) SiO_2

INTRODUCTION

Plasma-enhanced chemical vapor deposition of silicon dioxide (PECVD $Si0_2$) is commonly used to form an insulating layer in integrated circuits and multichip modules Several investigations have emphasized lowering the temperature of PECVD SiO_2 in order to avoid undesirable diffusion and degradation of metals and polymers on microelectronic devices.[1-3] Recently, PECVD SiO_2 films have been deposited at 100–340°C, but films deposited below 200°C exhibited poor step coverage high porosity, and inferior dielectric properties.[2] In general, manipulation of other deposition parameters (radio frequency [rf] power, reactor pressure, residence time, and gas composition provided only limited improvement in the dielectric properties of the films deposited at low temperatures. Poor dielectric properties were primarily attributed to water and silanol impurities. The permittivity is a measure of dipole orientation, and loss is a measure of bulk conduction and time dependent polarization.[4] The permittivity is proportional to the concentration of polar molecules like silanol and water in the oxide films. Loss results when polar groups, like -OH on silanol, bend, move, and polarize.

Anhydrous hydrazine (N_2H_4) is a reactive compound which has two active nucleophilic nitrogens.[5] It has an endothermic heat of formation (50.6 kJ/mol) and a high heat of combustion (–622.1 kJ/mol). Free radicals are generated during thermal decomposition. Since its basicity is slightly weaker than ammonia, it is used to form many useful salts. It is a strong reducing agent, often used in corrosion control, metal plating, and reducing noble-metal catalysts. Under

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suitable conditions, it can also act as an oxidizing agent.

In this paper, we investigate the use of hydrazine in the improvement of the dielectric properties of low temperature (150–350°C) PECVD SiO_2 films. The dielectric properties and film composition were measured as functions of reaction time and temperature. The effect of humid environments on the dielectric constant was also investigated.

EXPERIMENTAL

Four inch diameter, double polished, n-type (100) silicon substrates with a resistivity of 1–l0 Ω-cm were used in this study. Prior to use, the silicon was cleaned with a ~5% (vol.) hydroflouric acid (HF) solution, rinsed in deionized water, dried with filtered nitrogen, and oxidized in air at 850°C for six hours. The thickness of the thermal oxide film was 300–400Å. To measure dielectric properties, parallel plate capacitors were fabricated by partially masking the samples with glass slides and depositing 20Å Ti, 1400Å Au, 20ÅTi using a CVC Products, Inc. (Rochester, NY) DC sputtering system. The parallel plate capacitors had a gold ground plane and sputtered gold top plate. Low temperature PECVD $Si0_2$ (2–2.5 µm) was deposited with a Plasma Therm (Kresson, NJ) 700 Series PECVD system under two deposition conditions: 150°C, 0.5 Torr, 150 watts rf power, N_2O/SiH_4 ratio of 112.5, and 75 min; 350°C, 0.25 Torr, 150 watts rf power, N_2O/SiH_4 ratio of 50, and 90 min. After PECVD SiO_2 deposition, samples were reacted in a 5% N_2H_4 in argon gas stream at 150°C–350°C for 1–3 h. The hydrazine reaction system has been described more fully elsewhere.[6]

As a control, several PECVD SiO_2 samples were annealed in dry nitrogen for 3 h at 150, 350, and 700°C. The top plate of the capacitors were constructed by depositing a second 20Å Ti/1400Å AUJ20Å Ti metal layer, patterning with photolithography and removing the extraneous metal.

Film thicknesses and refractive indices of the SiO_2 films were measured with a Metricon (Pennington, NJ) Model 2010 Prism Coupler. Each measurement was the average of three positions. The dielectric properties were calculated from the capacitance and conductance measured with a Keithley (Cleveland, OH) 590 CV Analyzer at a frequency of 1 MHz. For the PECVD films, the electrical properties were measured with parallel plate capacitors. For thermally grown oxides, metal~insulator-semiconductor (MIS) diodes were biased into accumulation. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used for elemental analysis of the thin films. Auger electron spectroscopy was performed with a Physical Electronics (Eden Prairie, MN) Model 600 scanning Auger multi-probe. The base pressure inside the chamber was $\sim 2.0 \times 10^{-9}$ Torr. A 3 keV, 1 mA electron beam was used for excitation. A 2 keV, 40 µA/cm^2 Ar^+ ion beam was used for ion etching. The argon pressure was $\sim 1.0 \times 10^{-8}$ Torr. The Surface Science (Mountain View, CA) SSX-100 XPS was equipped with an aluminum Kα x-ray source and a crystalline x-ray monochromator. The operating pressure in the sample chamber was $\sim 4 \times 10^{-9}$ Torr. The XPS system was also equipped with a 4 keV argon ion gun which was used to lightly clean the surface. The argon pressure was 3.7×10^{-7} Torr during ion etching. The peak positions were referenced to Au $4f_{7/2}$ at 84.0 eV and C 1s at 284.6 eV. Fourier transform infrared (FTIR) spectroscopy with a Perkin Elmer (Norwalk, CT) 1600 FTIR spectrometer was also used for chemical analysis of the films. Thermal oxide and wafer

Table I. Refractive Index, Dielectric Property, and Impurity Concentration Results for PECVD $Si0_2$ Films Deposited at 150 and 350°C

PECVD SiO Deposited at 150°C	Refractive Index	Dielectric Constant	Permittivity	Loss	Silanol (wt.%)	Water (wt.%)	Silanol + Water (wt.%)
As Deposited	1.445	9.9	9.7	2.1	5.7	4.5	10.2
3 h in nitrigen, 150°C	1.450	9.7	9.5	1.7	5.9	4.4	10.3
3 h in nitrogen, 350°C	1.449	11.1	10.5	3.5	5.5	2.1	7.6
3 h in nitrogen, 700°C	1.430	—	—	—	1.9	0.9	2.8
3 h in N_2O plasma, 350°C	1.445	—	—	—	5.5	2.1	7.6
3 h in NH_3 plasma, 350°C	1.450	—	—	—	5.4	2.1	7.5
1 h in hydrazine, 150°C	1.447	6.6	6.6	0.3	3.6	3.3	6.9
3 h in hydrazine, 150°C	1.447	6.2	6.2	0.2	3.9	3.3	7.2
1 h in hydrazine, 350°C	1.445	7.1	7.1	0.3	3.7	2.3	6.0
3 h in hydrazine, 350°C	1.448	6.9	6.9	0.5	3.4	2.7	6.1
PECYD SiO Deposited at 350°C							
As Deposited	1.473	4.2	4.2	0.04	1.7	0.4	2.1
3 h in nitrogen, 150°C	1.468	4.3	4.3	0.03	1.7	0.6	2.3
3 h in nitrogen, 350°C	1.466	4.2	4.2	0.03	1.6	0.4	2.0
1 h in hydrazine, 150°C	1.471	4.4	4.4	0.09	1.9	1.0	2.9
3 h in hydrazine, 150°C	1.471	4.3	4.3	0.06	1.1	1.3	2.4
1 h in hydrazine, 350°C	1.472	4.3	4.3	0.07	1.6	0.6	2.2
3 h in hydrazine, 350°C	1.472	4.2	4.2	0.05	1.8	0.3	2.1

contributions were removed by scanning the wafers before oxide deposition.

RESULTS

Dielectric Properties

The permittivity and loss of the PECVD SiO_2 deposited at 150°C were 9.7 and 2.1, respectively, as shown in Table I. The films deposited at 150°C were annealed in nitrogen and reacted in hydrazine in an attempt to improve the dielectric properties. Annealing the films in nitrogen for 3 h at 150 and 350°C had no beneficial effect on the permittivity and loss. In contrast, reacting the films in hydrazine improved the dielectric properties. When reacted for 1 h at 150°C, permittivity and loss of the oxide decreased 32 and 86%, respectively. After a 3 h reaction at 150°C, the permittivity of the oxide decreased 36%, and the loss decreased 89%. Reacting the PECVD SiO_2 deposited at 150°C in hydrazine at 350°C had a similar effect. The permittivity decreased 27% after reacting for 1 h and 29% after 3 h. Likewise, the loss decreased 84% after reacting for 1 h and 79% after 3 h.

The dielectric properties of the as-deposited 350°C PECVD oxide, 4.2 (permittivity) and 0.04 (loss), were lower than those of the PECVD SiO_2 deposited at 150°C. These low values were the result of the higher deposition temperature. Annealing these films in nitrogen and hydrazine did not change their dielectric properties appreciably.

Several oxide samples were exposed to humid environments to measure the effect ofwater absorption on the dielectric constant. As shown in Fig. 1, the dielectric constant of the PECVD SiO_2 deposited at 150°C increased 15% after a 72 h exposure to air with 50% relative humidity and increased 41% when immersed in boiling water for 100 min. When the PECVD SiO_2 deposited at 150°C and reacted with N_2H_4 at 150°C was exposed to similar humid conditions, the dielectric constant increased only 2% after a 72 h exposure to air with 50% relative humidity and 12% after immersion in boiling water for 100 min. This compares well with the small increases in the dielectric constant found after a ~500Å thermal oxide grown at 800°C was exposed to the similar humid environments (6% increase after 72 h in 50% relative humidity air and 11% increase after 100 min in boiling water). Thus, water absorption caused large increases in the dielectric constant of the as-deposited 150°C film. Reaction with hydrazine improved the resistance to water absorption. The modest increase in dielectric constant after exposure to humid environments was similar to that found for a thermal oxide grown at 800°C.

CHEMICAL ANALYSIS

FTIR

The chemical composition ofthe PECVD oxide films was investigated with FTIR. The wavelength was scanned from 450–4000 cm^{-1}. The Si-O absorptions occurred at 1075 cm^{-1}, 800 cm^{-1}, and 465 cm^{-1}.[1,7] The silanol absorptions were observed at 3650 cm^{-1} and 935 cm^{-1}.[3]. The O-H absorption for water was identified at 3330 cm^{-1}.[3] Si-N absorptions at 833 cm^{-1},[8] were not observed. No Si-H stretch was found at either 2270 or 885 cm^{-1}.[9] Within the sensitivity of FTIR, the PECVD films were composed of SiO_2, silanol, and water. No silicon nitride was identified. Oxidation of $Si-H_x$ was not involved in the improvement of dielectric properties after reaction with hydrazine.

Silanol and water concentrations (weight percent) were calculated from the IR spectra using the correlations described by Pliskin.[3] The estimated relative error for these measurements was 5–10%. As shown in Table I, the PECVD oxide deposited at 150°C had a silanol concentration of 6% and a water concentration of 4%. Annealing the film in dry nitrogen at 150°C for 3 h did not decrease the silanol and water concentrations. After a 3 h anneal in nitrogen at 350°C, the water content of the oxide decreased 53%, but the silanol concentration was unchanged. Higher temperatures were needed to decrease the silanol content of the films. When annealed at 700°C in nitrogen for 3 h, the silanol and the water concentrations both decreased ~80%.

When the PECVD films deposited at 150°C were annealed in hydrazine instead of nitrogen, silanol and water removal occurred at lower temperatures. After reaction in N_2H_4 at 150°C for 1 h, the silanol concentration decreased 37%, and the water concentration decreased 27%. Similarly, reaction in N_2H_4 at 350°C for 1 h decreased the silanol concentration 35% and water concentration 49%. Reaction times longer than 1 h did not reduce the impurity concentration further. After reaction in N_2H_4 at 150°C for 3 h, the silanol concentration decreased 32%, and the water decreased 27%. At 350°C for 3 h, the silanol and water content decreased 40 and 18%, respectively.

The PECVD oxides deposited at 350°C had much lower as-deposited impurity concentrations (1.7% silanol and 0.4% water) than the oxide deposited at

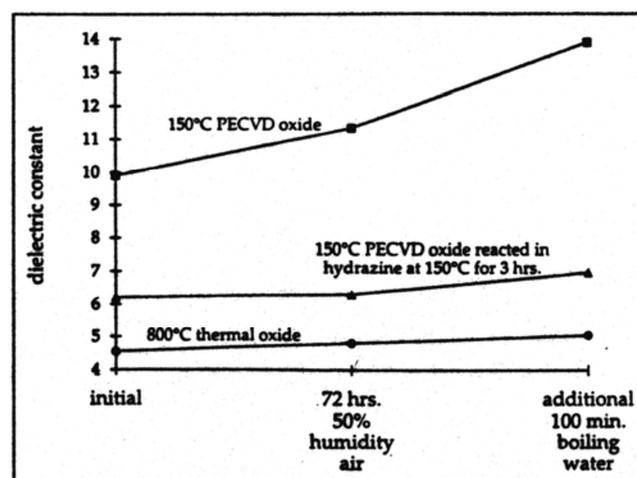


Fig. 1. Dielectric constant for the PECVD oxide deposited at 15O°C and a thermal oxide grown at 800°C as a function of time exposed to a humid environment.

150°C. The higher deposition temperature decreased the impurity content in the oxide. Annealing the films at 150 or 350°C in nitrogen or hydrazine did not decrease the silanol and water content of the film further because the Si-O-Si bonding is more complete at 350°C.

The PECVD oxide deposited at 150°C was also exposed to N_2O and NH_3 plasmas at 350°C and a power of 100 W for 3 h to investigate their effect on the silanol and water concentrations. The intention was to expose the silanol to reactive ions and radicals in an effort to induce a chemical reaction. As shown in Table I, neither plasma decreased the silanol concentration, but the water concentration in both cases decreased 53%, which was similar to the decrease found after a 350°C anneal in nitrogen. Thus, it is concluded that the plasma treatment only dries out the films. The ions and radicals in the plasma do not affect the samples.

XPS and AES

X-ray photoelectron spectroscopy was used to analyze the oxidation state of Si in the PECVD SiO_2 deposited at 150°C. First, the binding energies for the Si 2p spectra were calibrated using thermally oxidized silicon (300Å) and HF cleaned silicon, a hydride surface.[10–3] For thermally oxidized silicon, a narrow Si 2p peak was centered at 103.7 eV, which corresponds to silicon dioxide as discussed previously by He et al.[14] For HF cleaned silicon, the silicon 2p peak was positioned at 99.8 eV. After 10 s of ion etching to remove the hydride, the XPS peak shifted to a lower binding energy and was centered at 99.4 eV, previously reported for elemental silicon (99.2–99.4 eV).[15] When the PECVD SiO_2 deposited at 150°C was analyzed, the Si 2p peak was centered at 103.8 eV, similar to that of the thermally oxidized silicon. This suggests that silicon in the i50°C PECVD oxide film has a +4 oxidation state. No evidence of lower oxidation states, such as +3 to 0, was found indicating that the silicon was only oxygen bonded.

Elemental depth profiles of the hydrazine-treated PECVD oxide films were collected by alternatively argon ion etching and analyzing with AES (~100 nm steps). The silicon LMM, carbon KLL, and oxygen KLL peaks were identified at 103, 294, and 533 eV, respectively. No nitrogen (nitrogen KLL peak = 360–390 eV) was found for any of the hydrazine-treated PECVD SiO_2 samples. Silanol and SiO_2 in the PECVD films did not react with hydrazine to form silicon nitride or oxynitride.

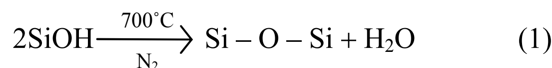
Refractive Index

The refractive index of the PECVD films is shown in Table I. The refractive index was lower for the 150°C oxide than the 350°C oxide (1.45 vs 1.47) and was not dependent upon post-deposition treatments. Using the Gladstone-Dale equation,[16] density = K (refracttive index –1), the refractive index results suggest that the density of the 150°C PECVD oxide was lower and the porosity was higher than that of the 350°C oxide. This agrees with the results of others who have found that low temperature PECVD oxides (100–200°C) have low density and high porosity.[1,3,9,17] Meanwhile, PECVD oxides deposited at higher temperature (350–550°C) have high densities and low porosities.[1,3,9,17]

DISCUSSION

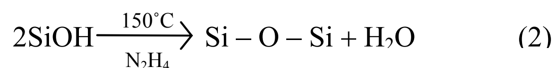
The FTIR, refractive index, and dielectric constant results all suggest that silanol was the primary impurity in the PECVD SiO_2 deposited at low temperatures(150°C). Silanol molecules provide bonding sites for the adsorption of water. Water can be removed through dehydration, but the film will re-adsorb water if silanol is present in the film. For example, when the properties of the PECVD films deposited at 150 and 350°C are compared, the films deposited at 150°C have a higher silanol content (5.7% vs 1.7%), higher water content (4.5% vs 0.4%), lower refractive index (1.45 vs 1.47), and higher dielectric constant (9.9 vs 4.2). This suggests that the dielectric properties were degraded by the large amounts of water and silanol in the oxide. Incomplete bonding in the lattice decreased the refractive index.

To improve the dielectric properties, the PECVD SiO_2 deposited at 150°C was annealed in nitrogen and hydrazine. Annealing in nitrogen at 350°C dehydrated the PECYD SiO_2. Water was removed temporarily, but the silanol concentration was not affected. Upon exposure to humid environments, water reabsorbed and associated with silanol in the oxide lattice. Annealing the PECVD SiO_2 deposited at 150°C at higher temperatures (700°C) induced a condensation reaction where silanol molecules combined, and water was released.
At the elevated temperatures, the water diffused out of the film, and the silanol and water impurity concentration decreased.



$$2SiOH \xrightarrow[N_2]{700^\circ C} Si-O-Si+H_2O \quad (1)$$

When the PECVD SiO_2 deposited at 150°C was annealed in hydazine, the condensation reaction occurred at much lower temperatures (150°C). Hydrazine readily adsorbs and can help initiate the condensation of silanol molecules.



$$2SiOH \xrightarrow[N_2H_4]{150^\circ C} Si-O-Si+H_2O \quad (2)$$

As the silanol and water concentrations decreased, the reduced number of ^-OH groups in the film increased the resistance to water absorption and improved the dielectric properties. At higher temperatures, the rate of hydrazine decomposition increases,[5] lowering the concentration of hydrazine available for catalyzing the condensation reaction. At lower temperatures (150°C), it is expected that the reaction is kinetically limited. At higher temperatures (350°C), the decomposition of hydrazine increases, and the

condensation reaction becomes limited by the concentration of the catalyst (hydrazine). Thus, as the resuits indicate, the conversion of the condensation reaction does not increase significantly at higher reaction temperatures (350°C).

CONCLUSION

The dielectric properties of PECVD SiO_2 deposited at 150°C improved after reaction in hydrazine at 150–350°C. The permittivity and loss decreased ~32 and ~86%, respectively, after reaction with hydrazine at 150°C. Fourier transform infrared and X~PS results indicated that oxidation of Si-H_x was not involved in the reaction. Auger electron spectroscopy results showed that hydrazine did not react with silanol or SiO_2 and form silicon nitride. Instead, FTIR measurements suggested that the decrease in permittivity and loss correlates with a decrease in the silanol and water concentrations. In humid conditions, water uptake into the PECVD SiO_2 films increased and degraded the dielectric properties. When the films were annealed in nitrogen at 350°C, water was removed from the films, but silanol remained, and the dielectric properties of the films did not improve. During reaction with hydrazine at 150–350°C, both silanol and water were removed from the films. The dielectric properties and resistance to water absorption improved.

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