The Effects of Nitrogen Annealing on Etch Rates of HDPECVD and PECVD Silicon Dioxide Films

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Primary CNF Tools Used: Plasma-Therm Takachi HDP-CVD System, Oxford Plasmalab System 100 PECVD, Woollam RC2 Spectroscopic Ellipsometer, Anneal LPCVD Furnace Tube, Verteq 1800.6 Spin Rinse Dryer

Abstract:

Plasma-enhanced chemical vapor deposition (PECVD) is a reliable technique for depositing silicon dioxide (SiO_2), but these films are notably less dense than thermal oxidation. It has been proposed that as-deposited PECVD films are composed of 5% by volume of micropores [1]. Over time, this porosity becomes susceptible to humidity, affecting stress and device performance. To collapse these micropores and improve film quality, PECVD SiO_2 films are often thermally annealed after deposition. While there is an abundance of information on annealing PECVD films, little has been published about films deposited/annealed by high density plasma enhanced chemical vapor deposition (HDPECVD). Unlike the weak ionization produced by PECVD capacitive plasma systems, HDPECVD generates high density plasma with an inductively coupled plasma (ICP) source coiled around the deposition chamber. This denser plasma increases free electron/precursor interactions which gives HDPECVD the advantage of operating with lower gas flows and at lower pressures than PECVD. The ICP power combined with wafer biasing gives HDPECVD the unique capability of depositing SiO_2 at 100°C. This work will compare the effects nitrogen annealing on HDPECVD and PECVD SiO_2 films by examining changes in film thickness and wet etch rates.

The SiO2 etch reaction in pure hydrofluoric acid (HF) is the combination of the following two reactions:

- $SiO_2 + 6HF \rightarrow H_2SiF_{6(aq)} + 2H_20$
- $SiO_2 + 3HF_2^- + H^+ \rightarrow SiF_6^{2-} + 2H_20$

With concentrations of pure HF lower than 10M, the fluoride (F^-) and bifluoride (HF_2^-) ions are the dominant etch species with the bifluoride etching silicon dioxide 4.5 times faster than HF [2]. Etching silicon dioxide in pure HF is rapid and is used for completely removing the oxide or the native oxide without damaging the silicon wafer. For a more controllable silicon dioxide etch used in semiconductor processing, buffer oxide etch (BOE) is preferred. The addition of ammonium fluoride (NH_4F) with HF suppresses the difluoride resulting in the HF complex becoming the dominant etch species [3].

Summary of Research:

For this work, approximately 1000 nm of SiO_2 was deposited on single side polished N-type, 100 mm diameter, 525 μm thick, prime, <100> silicon wafers. For HDPECVD, all ten depositions were completed on a Plasma-Therm Takachi HDP-CVD System at the as-deposited temperature of 100°C with silane (SiH_4) and oxygen (O_2) precursor gases. For PECVD, an Oxford Plasmalab System 100 PECVD tool was used to deposit SiO_2 on nine wafers at an as-deposited temperature of 350°C with SiH_4 and nitrous oxide (N_2O). All wafers were MOS cleaned and nitrogen annealed from 300-1100°C for one hour. The anneal temperatures were calibrated from the combination of three separate heating elements in a low temperature chemical vapor deposition (LPCVD) furnace tube. A Woollam RC2 Spectroscopic Ellipsometer was used for all thickness measurements. The percent change in film thicknesses was calculated by the difference in as-deposited/annealed thicknesses divided by the as-deposited thickness and expressed as a percentage.

Wafers were submerged into room temperature (approximately 20°C in the temperature-controlled CNF cleanroom) 6:1 BOE at thirty-seconds intervals. After thirty seconds, the wafers were immediately submerged in deionized wafer and rinsed again using a Verteq 1800.6 spin rinse dryer. Three wafers were etched at a time and a new BOE solution was used after each three-wafer etching cycle. Wafers were etched process side up to prevent any bubbles from effecting the etch results and the position of the wafers (top, middle and bottom) was rotated in the Teflon® wafer holder after each etch. Etching measurements were done after each thirty-second etch and ended after the oxide was etched below 150 nm. Etch rates were determined by averaging the differences in thicknesses after each thirty second etch. For comparison, the etch rate for LPCVD thermally wet oxide grown at 1100°C was calculated using this same method.

All the oxide films decreased in thickness when annealed, but the percentage change in thickness after annealing was significantly higher for HDPECVD films (Figure 1). As annealing temperatures increase above 400°C for PECVD oxide, remaining hydrogen from the silane precursor breaks down leaving extra micropores. Higher temperatures will collapse free hydrogen and as-deposited micropores and above 600°C, Si-O bonds will relax and become more ordered [4]. The relaxation of the PECVD oxide is apparent above 700°C, but the HDPECVD densification curve is different due to the lower temperature, gas flows and operating pressure required for the deposition. Denser films and reduced porosity resulted in lower 6:1 BOE etch rates as annealing temperatures increase (Figure 2). When annealed at 1100°C, both films had comparable etch rates to thermal oxide grown at 1100°C (Table 1). From both graphs, trends in annealing temperature densifications correlate with etch rate non-linearities. Future work should examine changes in the absorbance spectra of annealed Si-O networks from both deposition methods.

References:

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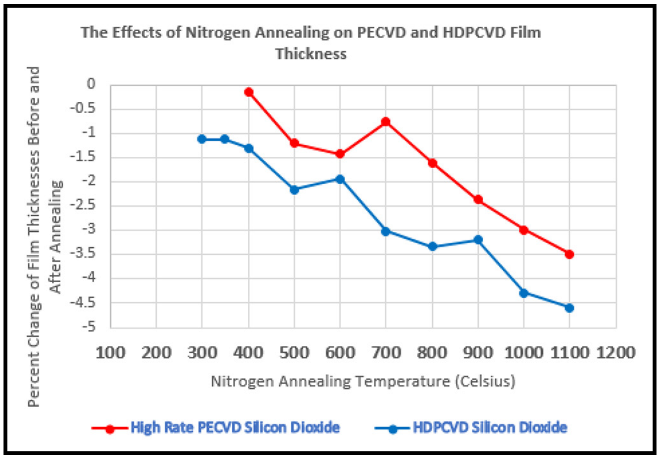

Figure 1: Changes in SiO_2 thicknesses as nitrogen annealing temperatures increase for PECVD and HDPECVD films.

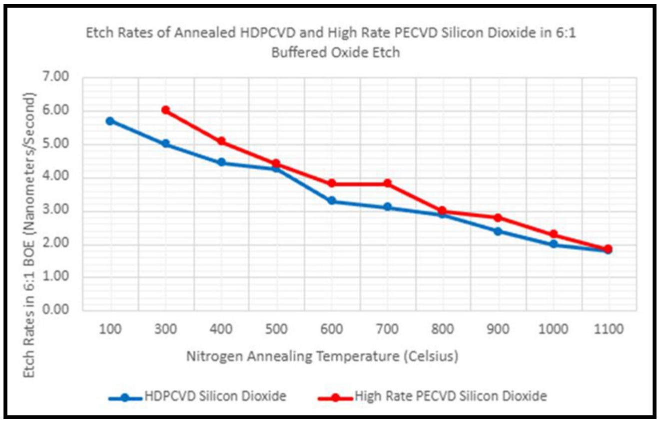

Figure 2: Changes in SiO_2 etch rates as nitrogen annealing temperatures increase for PECVD and HDPECVD films.

SiO_2 Films	Etch Rate (nm/min)
High Rate PECVD Annealed @ 1100°C	1.86
HDPCVD Annealed @ 1100°C	1.85
Wet Thermal Oxidation @ 1100°C	1.76

Table 1: Etch rates for SiO_2 deposited or grown films @ 1100°C.