Low-Pressure Chemical Vapor Deposition of Silicon Dioxide Using Diethylsilane

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In this study, diethylsilane (DES) has been used as a precursor to produce silicon dioxide films by low-pressure chemical vapor deposition. These films were synthesized in the temperature range 350–475 °C with the growth kinetics observed to follow an Arrhenius behavior with an apparent activation energy of 10 kcal/mol. The growth rate was seen to increase with higher pressure and to vary as a function of the square root of the O_2 flow rate and O_2/DES ratio. In both the pressure and the O_2/DES ratio studies conducted at 400 °C, film deposition ceased abruptly for conditions where total pressure was less than 0.35 Torr and where the O_2/DES ratio was higher than 2.35. The density and index of refraction of the films were close to 2.25 g/cm^3 and 1.45, respectively, independent of deposition conditions. The etch rate of the films in a 25 °C P-etch solution decreased with higher deposition or annealing temperatures, reflecting densification of the material. For aspect ratios close to 1.3, the films exhibited a step coverage better than 55%.

Introduction

Low-pressure chemical vapor deposition (LPCVD) of silicon dioxide is generally based on the reaction of SiH_4 and oxygen.[1,2] The feasibility of using organic liquid sources such as tetraethylorthosilicate (TEOS),[3–5] ethyltriethoxysilane (ETOS),[6–9] diacetoxydi-*tert*-butoxysilane (DADBS),[10,11] and tetramethylcyclotetrasiloxane (TMCTS)[12] to form silicon dioxide for microelectronic applications has been demonstrated by several researchers. Such liquid precursors offer numerous advantages over the use of silane including superior step coverage and increased safety.

Diethylsilane (DES) is a precursor capable of producing oxide films at temperatures as low as 350 °C, thus allowing its use as a dielectric between aluminum metallization levels or as a top layer passivation coating. Using conventional hot-wall LPCVD reactors, preliminary results[13–15] have shown films produced from DES to have several performance advantages over silane including superior conformality, low particulate formation, low stress, and high crack resistance. Such films also have good thickness uniformity and promising electrical characteristics. DES with a chemical formula of $(C_2H_5)_2SiH_2$ is a colorless liquid with a boiling point of 56 °C and freezing point of less than −76 °C at atmospheric pressure. It exhibits a vapor pressure of 207 Torr at 20 °C and is commercially available from Schumacher and Olin Chemicals with a 99+% chemical purity.

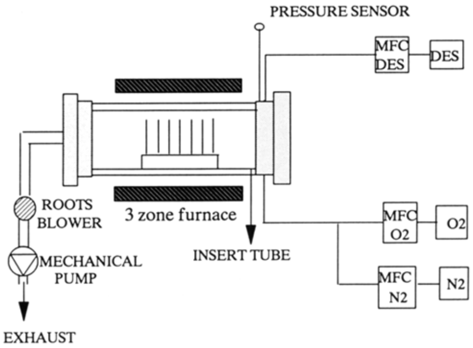

Figure 1. Schematic of LPCVD reactor.

In this study, the growth kinetics of films produced from DES were investigated as a function of process parameters and the properties of resulting films characterized. The suitability of using this precursor for low-temperature deposition of SiO_2 films is considered in context with potential microelectronic applications.

Experimental Procedures

The synthesis of the SiO_2 films was carried out in a horizontal LPCVD reactor (Figure 1) consisting of a fused quartz insert tube 13.5 cm in diameter and 150 cm in length placed within another quartz tube 19.3 cm in diameter and 155 cm in length. Such a configuration was established to improve the film thickness uniformity across the 10-cm-diameter wafers used in this study. A five-zone Lindberg furnace and control systen Model 55997-S/59744-A-2B-S provided a uniform temperature profile across the reaction chamber. The back end of the reactor was connected to an Edwards vacuum station consisting of both a mechanical pump (Model E2M80) and a Roots blower (Model EH500). The reactor pressure was monitored with an MKS baratron gauge and controlled with an MKS exhaust valve. The reactor temperature profile was measured with an Omega type K thermocouple. The DES and O_2 gases were introduced separately

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into the reaction chamber and allowed to mix downstream. Gas flows were regulated by Applied Materials model AFC 550 automatic N_2 mass flow controllers which were calibrated for DES and O_2. A standard 20–1000 sccm N_2 mass flow controller (MFC) was used to measure and control the flow rate of DES. The N_2 calibration of the MFC was checked by delivering a fixed volume of that gas (product of metered flow rate and time) into the known reaction chamber volume. The resulting pressure increase was used to calculate the volume of the gas corrected to STP. This process was repeated with DES, and the correction factor was found to have a constant value of 0.19 at flow rates above 60 sccm. Below that value, the correction factor was observed to increase rapidly achieving a value of 0.36 at the lowest investigated flow rate of 10 sccm.

P-type ⟨100⟩ silicon wafers 10 cm in diameter were placed vertically in a fused silica boat and spaced 0.9 cm apart. Typically, six wafers were loaded in each run. A Perkin-Elmer Model 580 IR spectrophotometer was used to monitor the vibrational modes of the deposits. Film stress was determined by measuring changes in the radius of curvature of a wafer resulting from deposition on a single side. The distance between two points generated by light from two fixed and paralled He–Ne lasers was determined by reflection from the surface of a wafer before and after deposition. An angled mirror was used to project the reflection of the two points onto a wall where their separation could be accurately measured. The stress was calculated using Stoney's equation:[16]

$$\sigma = Et_s^2/6(1-\nu)Rt$$

where E is Young's modulus for the substrate, ν is Poisson's ratio, t_s is the substrate thickness, t is the film thickness, and the net radius of curvature is

$$R = 1/(1/R_2 - 1/R_1)$$

where R_1 and R_2 are the radii of curvature of the wafer before and after deposition respectively. For Si⟨100⟩ wafers, $E = 1.8 \times 10^{11}$ Pa and $t_s = 525\ \mu$m. This simple and inexpensive apparatus yielded stress values which were within 5% of those obtained from the Flexus Model 2-300 system. The hardness and Young's modulus of the films were determined using a Nano Instruments indenter. The system consists of a diamond tip, with the same area to depth ratio as the traditional Vickers pyramid, mounted on a loading column that is suspended on thin leaf springs. At the top of the loading column is a coil and magnet assembly that provides a controlled loading force with a resolution of about 0.5 μN. The position of the indenter is determined by a capacitance displacement gauge which detects displacement changes of 0.2–0.3 nm.

The Rutherford backscattering spectroscopy (RBS) measurements were taken using a High Voltage Engineering AK accelerator with He^+ ions at an energy of 1.8 MeV. Energy recoil detection (ERD) was used to confirm the presence of hydrogen in select samples.

Results and Discussion

Growth Kinetics. In the kinetics study, the process variables investigated were temperature, pressure, O_2 flow rate, and O_2/DES ratio. The deposition rate of the oxide films was determined as a function of temperature between 350 and 475 °C while maintaining a constant pressure of 0.5 Torr, a DES flow rate of 50 sccm, and an O_2/DES of 2/1. As seen in Figure 2, a semilog plot of the average deposition rate versus 1000/T follows an Arrhenius behavior between 375 and 450 °C which yields an apparent activation energy of 10 kcal/mol. Although low, this value is similar to that observed for the reaction of silane and oxygen,[17] which suggests a rate mechanism controlled by gas-phase diffusion or one that is complex. However, the poor uniformity (~±20%) observed across the wafers is indicative of a diffusion-limited process.

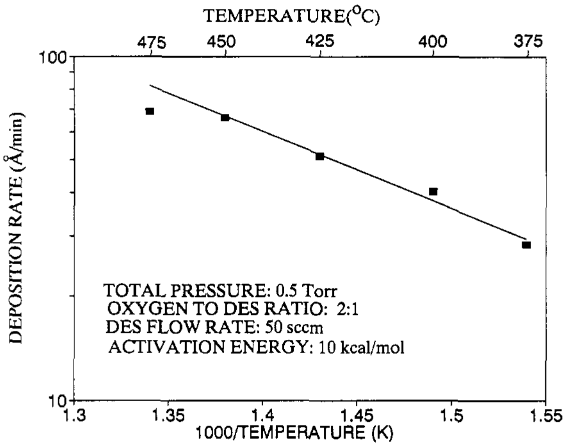

Figure 2. Variation of deposition rate as a function of inverse temperature at a constant total pressure, DES flow rate, and O_2/DES ratio.

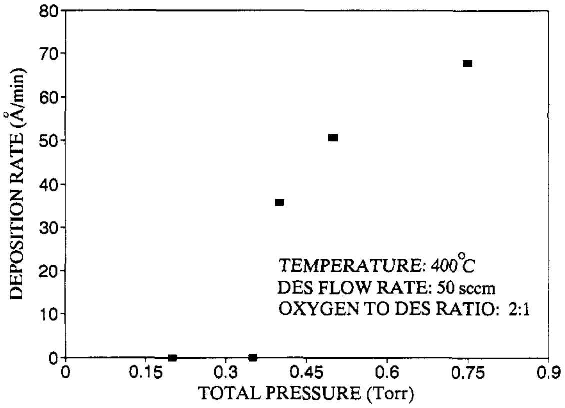

Figure 3. Variation of deposition rate as a function of total pressure at constant temperature, DES flow rate, and O_2/DES ratio.

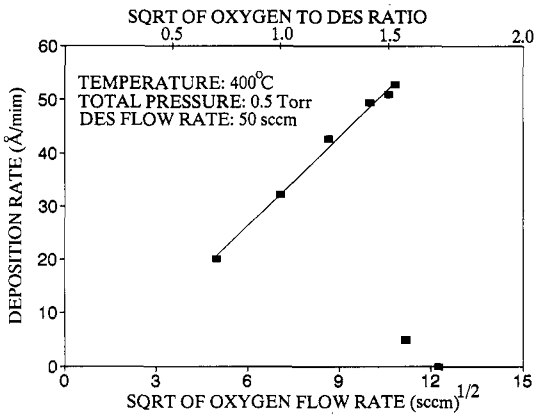

Figure 4. Variation of deposition rate versus square root of O_2 flow rate for constant temperature, DES flow rate, and total pressure.

The variation of the oxide deposition rate with chamber pressure is shown in Figure 3 for constant conditions of temperature (400 °C), DES flow rate (50 sccm), and O_2/DES ratio (2/1). The deposition rate is observed to decrease monotonically from 0.75 to 0.35 Torr, where deposition ceases abruptly. A plot of deposition rate versus square root of O_2 flow rate is shown in Figure 4 for constant conditions of temperature (400 °C), DES flow rate (50 sccm), and pressure (0.5 Torr). In the O_2 flow rate range

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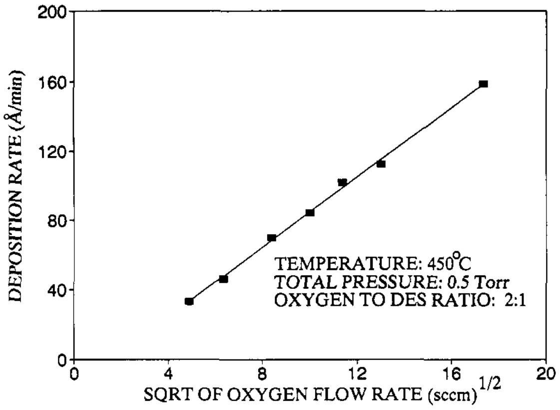

Figure 5. Variation of deposition rate versus square root of O_2 flow rate for constant temperature, total pressure, and O_2/DES ratio.

25–117 sccm, a linear dependence is observed, indicating that the reaction rate is controlled by the amount of O_2 reaching the SiO_2 surface. These data also shown as a function of O_2/DES ratio indicate an increase in deposition rate in the ratio range of 0.5–2.35 followed by a reproducible abrupt cessation in deposition at an O_2/DES ratio of 2.5. Similar observations have been reported by O'Neal and co-workers.[18] In both the pressure and flow rate studies in which film deposition ceased, the residence time of the reactant gases within the reaction chamber is short (<2 s). It is thus possible that insufficient heat is transferred to raise the temperature of these input gases high enough for deposition to occur within the reaction chamber. In their study, Huo et al.[14] preheated the DES gas and did not report such cessation in SiO_2 deposition. At the higher deposition temperature of 450 °C, this effect was no longer observed. A plot of deposition rate versus square root of O_2 flow rate with the O_2/DES ratio at 2/1, the temperature at 450 °C, and pressure at 0.5 Torr yields a linear dependence for the investigated flow rate range 12–150 sccm DES (Figure 5). Such behavior is consistent with a mechanism in which oxygen diffusion to the surface is the rate-limiting step[19] and oxide deposition depends on the square root of the O_2 flow rate. For an O_2 flow rate of 300 sccm, the deposition rate is close to 160 Å/min, making this process attractive for high throughput semiconductor manufacturing.

Oxide Film Properties. The stoichiometric composition as well as the optical, chemical, and mechanical properties of the oxide deposits were determined. The RBS data indicated that the composition of all deposits was close to $SiO_{2.1}$ and the incorporated carbon was less than the detection limit of the technique (a few percent). Energy recoil detection measurements taken on oxide films deposited at 375 and 400 °C revealed the presence of hydrogen in the deposits in agreement with the IR results discussed below. Hydrogen was not detected by either technique in a thermal oxide control sample.

Figure 6 illustrates an IR spectrum in the range 4000–390 cm^{-1} for an oxide deposited at 375 °C. Besides the Si–O stretching, bending, and rocking modes identified at 1060, 800, and 440 cm^{-1}, respectively, the presence of a SiOH peak at 3650 cm^{-1} and a broad absorbed water peak at around 3400 cm^{-1} were readily detected. A small peak at 880 cm^{-1} was also observed and identified as an HSi–O_3 moiety.[20] The associated H–Si stretching mode appeared as a weak peak near 2250 cm^{-1}. The 880-cm^{-1} peak normalized with respect to the 1060 cm^{-1} decreased with higher temperatures (Figure 7), lower DES flow rates (Figure 8), and lower pressures (Figure 9). In view of the presence of hydrogen in that moiety, these results provide processing guidelines for avoiding incorporation of that type of hydrogen in the films.

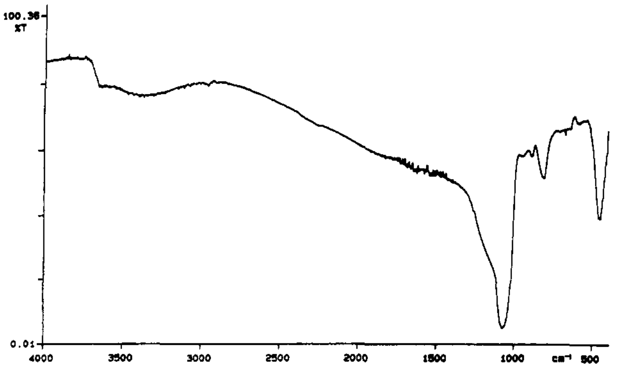

Figure 6. IR spectrum of an oxide film deposited at 375 °C, 0.5 Torr, DES flow rate of 50 sccm, and oxygen flow rate of 100 sccm.

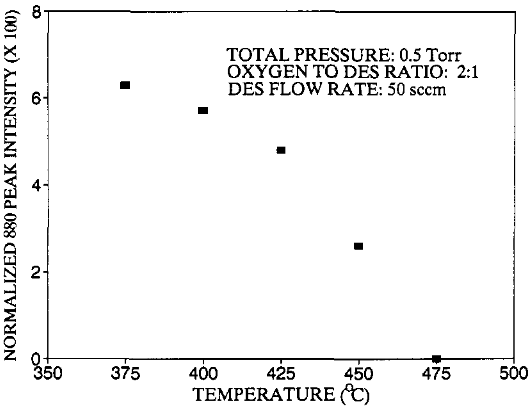

Figure 7. Normalized 880-cm^{-1} peak as a function of deposition temperature.

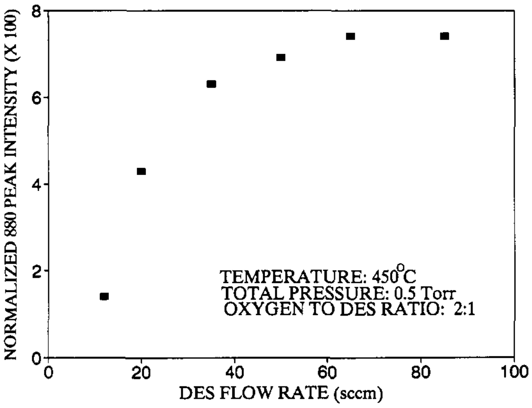

Figure 8. Normalized 880-cm^{-1} peak as a function of DES flow rate.

The refractive index data, obtained by standard ellipsometry at the He–Ne laser wavelength of 632.8 nm, revealed values in the narrow range 1.453–1.456, independent of deposition conditions. These results are close to those reported by Patterson and Ozturk[15] for LPCVD

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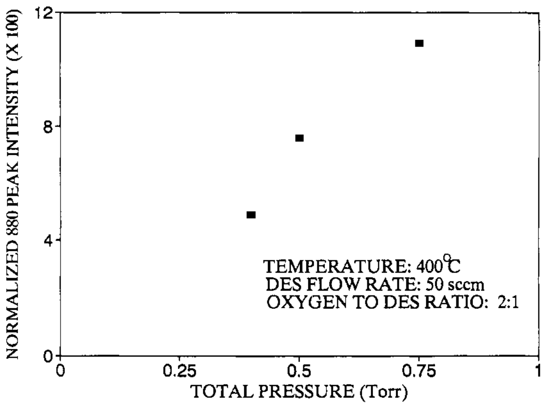

Figure 9. Normalized 880-cm^{-1} peak as a function of total pressure.

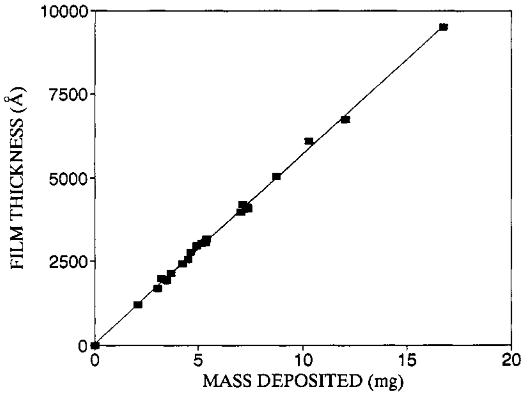

Figure 10. Variation of film thickness as a function of the mass deposited.

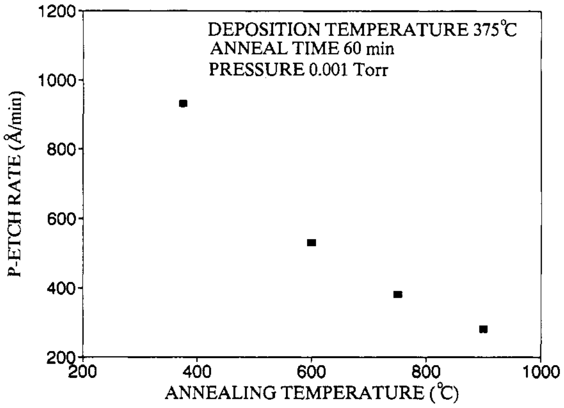

Figure 11. P-etch rate as a function of annealing temperature.

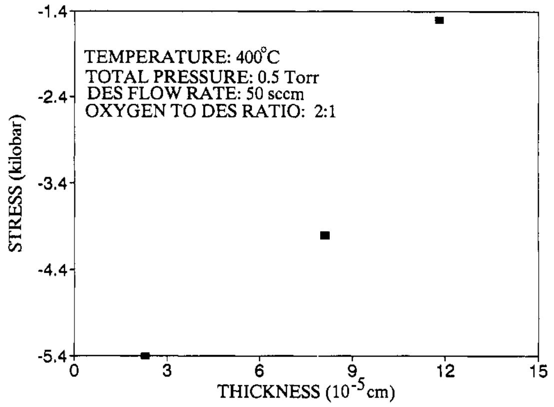

Figure 12. Variation in film stress as a function of film thickness.

oxides grown from DES and approach the value of 1.459 for thermal oxide.[21]

The density of the deposited films was measured as a function of process parameters. A plot representing average film thickness as a function of mass for all process parameters is shown in Figure 10. The minimal deviation of the data from the linear least-squares fit indicates little dependence of density on process variables. From the slope of the curve and the known area of the wafer, the density was calculated to be 2.25 g/cm^3, which is close to the value of 2.27 g/cm^3 for thermal oxide.[21]

The etch rates of the oxide films in a P-etch solution (15 parts hydrofluoric acid (49%), 10 parts nitric acid (70%), and 300 parts of water) were determined by measuring the change in film thickness as a function of etch time. The etch rate which was 930 Å/min at the deposition temperature of 375 °C decreased slightly down to 850 Å/min at the deposition temperature of 475 °C reflecting the gradual removal of the $HSi–O_3$ moiety and associated reduction in the breakup of the network-forming structure. The substantial decrease in etch rate observed with higher annealing temperature (Figure 11) can be attributed to the removal of the water and hydroxyl group, which in turn resulted in structural changes of the material. This was confirmed by the gradual disappearance of the 3650- and 3400-cm^{-1} peaks[22,23] and accompanying shifts to higher wavenumbers for the three remaining peaks. Those shifts are thought to result from a decrease in the Si–O–Si bond angle and the Si–Si distance. At a constant deposition temperature, the etch rate measurements were found to be independent of flow rate variation.

Film stress was measured as a function of oxide film thickness for process conditions of 400 °C, 0.5 Torr, 50 sccm DES flow rate, and 100 sccm O_2. The stress was found to be compressive and to decrease in magnitude with increasing thickness as illustrated in Figure 12. A similar behavior was observed with thermal oxide by Kobeda and Irene,[24] who attributed the effect to rapid stress relaxation caused by time-dependent oxide viscosity. The hardness and Young's modulus of the as-deposited films were observed to vary in a range 4–5 GPa and 50–70 GPa, respectively, for all deposition conditions. Although no systematic variation was noted in the case of hardness, values of Young's modulus exhibited a decreasing trend with increasing total pressure, DES flow rate, and O_2/DES ratio. Both the hardness and Young's modulus were observed to increase from 4.6 and 57 GPa to 8.4 and 74 GPa respectively when a sample deposited at 375 °C was subsequently annealed at 800 °C for 1 h at 0.001 Torr. This is a result of the structural changes reflected in the IR data discussed above.

The step coverage of a 200-nm-thick oxide film deposited at 400 °C in a via ~1 μm deep and ~1.25 μm wide yielded, as shown in Figure 13, a better than 85% conformality as determined by taking a ratio of oxide film thickness along the via wall to that on the top surface. For a higher aspect ratio exemplified in a via ~1 μm deep and ~0.75 μm wide, the conformality was better than 55%.

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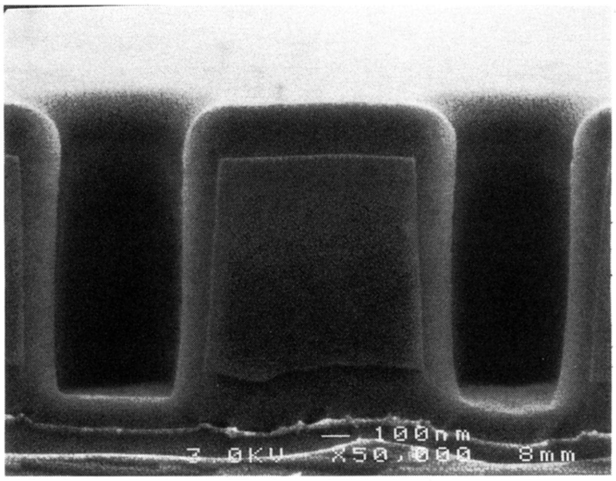

Figure 13. Step coverage of 200-nm-thick oxide film deposited at 400 °C, 0.5 Torr, 50 sccm DES, and 100 sccm O_2.

Conclusions

In this study, we have demonstrated the use of diethylsilane for synthesizing silicon oxide films by low-pressure chemical vapor deposition. The deposition rate as a function of temperature was found to follow an Arrhenius behavior yielding an apparent activation energy of 10 kcal/mol. The growth rate was observed to increase with higher pressure and to vary as a function of the square root of the DES flow rate and O_2/DES ratio. In both the pressure and the O_2/DES ratio studies, there were points at which deposition ceased abruptly. The films were determined to be essentially carbon free and slightly oxygen rich. An additional peak was detected in the IR spectrum at 880 cm^{-1} reflecting the presence of the $HSi-O_3$ moiety which may be useful in monitoring hydrogen content. The refractive index and the density were observed to be close to 1.45 and 2.25 g/cm^3, respectively, and in good agreement with corresponding values of thermal oxide. The etch rate of the films in a 25 °C P-etch solution decreased with higher deposition or annealing temperatures. For aspect ratios close to 1.3, the films were seen to exhibit a step coverage better than 55% rendering the process attractive for submicron device applications.

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