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Deposition of silicon dioxide films with an atmospheric-pressure plasma jet

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Abstract. A plasma jet has been developed which deposits silica films at up to 3000 Å min^{-1} at 760 Torr and 115 to 350 °C. The jet operates by feeding oxygen and helium gas between two coaxial electrodes that are driven by a 13.56 MHz radio frequency source at 40 to 500 W. Tetraethoxysilane is mixed with the effluent of the plasma jet and directed onto a substrate located 1.7 cm downstream. The properties of the silica films, as determined by infrared spectroscopy and capacitance measurements, are comparable to those of thermally grown silicon dioxide films at 900 °C.

Silicon dioxide films are used in the manufacture of integrated circuits for both interlayer dielectrics and transistor gate oxides [1–5]. These films are grown either by thermal oxidation of silicon [6], or by thermal [7, 8] or plasma-enhanced chemical vapour deposition [9, 10]. The use of plasma-enhanced chemical vapour deposition is preferred, since the deposition temperature can be considerably lower than in other methods. The conformal coverage obtained by plasma-enhanced chemical vapour deposition using tetraethoxysilane (TEOS) is superior to the coverage obtained with silane as the silicon source [9, 10]. Thus, TEOS has become the preferred reagent for plasma-enhanced chemical vapour deposition of SiO_2 in integrated circuit manufacturing [2].

We have developed a plasma source that can operate at atmospheric pressure and near room temperature. This source does not require a vacuum chamber and associated pumping system, which gives it a potential advantage over conventional low-pressure plasma sources. Moreover, we have found that the atmospheric pressure plasma jet etches thin films at a rapid rate [11]. In this paper, we report on the application of this new source for the plasma-enhanced chemical vapour deposition of silicon dioxide.

Shown in figure 1 is a cross-sectional view of the plasma jet. It consists of two concentric electrodes made of stainless steel. Radio frequency power at 13.56 MHz is applied to the inner electrode. Unlike an atmospheric pressure glow discharge [12], or a microbeam plasma generator [13, 14], the atmospheric pressure plasma jet does not require a dielectric material between the electrodes to create a stable plasma. Oxygen and helium gases are mixed together and fed into the annular space between the two electrodes. Helium is also passed through a bubbler containing tetraethoxysilane at 17 °C. This mixture combines with the plasma inside a nozzle placed on the end of the jet, and then is directed onto an Si(100) substrate, where the deposition of SiO_2 occurs. Outside the nozzle, the plasma is at ambient pressure, and there is no significant pressure drop across the nozzle. Unless otherwise noted, the standard process conditions are: 757.2 Torr of helium, 2.8 Torr of oxygen, 7.1 mTorr of TEOS, 49.4 l min^{-1} total flow rate (at 25 °C and 760 Torr), 115 °C substrate temperature (on the back surface), 1.7 cm from the nozzle to the sample and 280 W RF power. At the standard operating conditions, it takes 0.6 ms for the gas to exit the nozzle and strike the sample.

With the current design, the plasma jet can be sustained from approximately 40 to 500 W. Higher power leads to arcing. Cooling water is used to keep the jet from overheating (see figure 1). With the cooling jacket, the effluent temperature of the jet varies from 100 to 150 °C, depending on the RF power. This demonstrates the non-thermal nature of the atmospheric pressure plasma jet.

The effect of the RF power on the deposition rate is shown in figure 2. The rates are calculated by dividing the film thickness, measured with an ellipsometer, by the deposition time. The deposition rate increases with the power from 180 to 500 W, and the slope of the line given by the log–log plot is 1.4. Since the growth rate does not level off with increasing power, the process must be limited by the flux of reactive species in the plasma. The highest recorded deposition rate is 3020 ± 250 Å min^{-1}, obtained at a TEOS partial pressure of 0.2 Torr and an RF power of 400 W.

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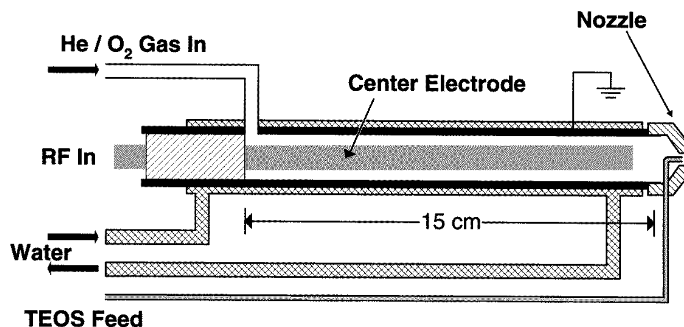

Figure 1. Cross-sectional view of the atmospheric pressure plasma jet. Drawing approximately to scale.

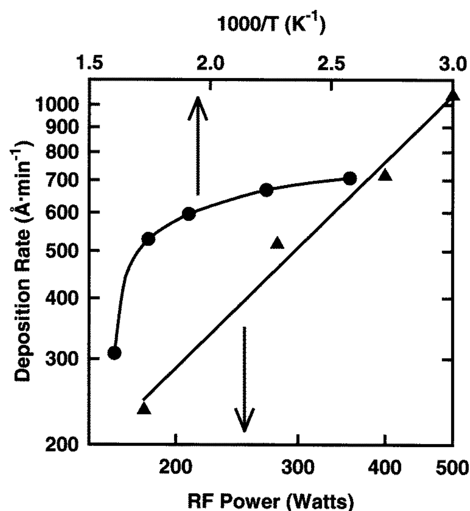

Figure 2. The dependence of the deposition rate on RF power and substrate temperature (except as noted $T_{substrate}$ = 115 °C and RF power = 280 W).

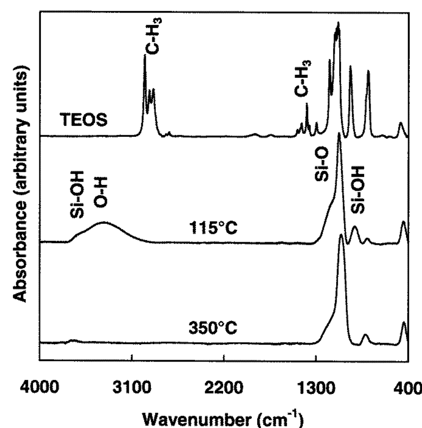

Figure 3. Transmission infrared absorption spectra of TEOS and two films deposited at 115 and 350 °C.

Also shown in figure 2 is a plot of the logarithm of the deposition rate as a function of inverse temperature. The silicon dioxide growth rate decreases with increasing sample temperature. This trend is not linear, indicating a departure from the Arrhenius relationship. The dependence on temperature shown in figure 2 is similar to that seen in low-pressure plasma-enhanced chemical vapour deposition [15]. However, in an atmospheric-pressure glow discharge, the opposite trend is observed in which the growth rate rises with sample temperature [16].

In figure 3, infrared spectra are presented of tetraethoxysilane and of silicon dioxide films grown at 115 and 350 °C. The precursor exhibits a series of infrared bands at 478, 795, 967, 1000–1100, 1170, 1370–1390, 1444, 2890, 2930 and 2977 cm^{-1} which are due to Si–O, O–C and C–H rocking, deformation and stretching modes [17]. The SiO_2 film deposited at 115 °C exhibits infrared peaks at 450, 800 and 1080 cm^{-1} that are due to the rocking, bending and stretching modes of siloxane linkages. In addition, infrared bands are seen at 930 and 3400 cm^{-1} that may be assigned to the bending and stretching vibrations of hydroxyl groups [17, 18]. The latter band is very broad, which can be attributed to hydrogen bonding between neighbouring hydroxyl and oxide groups. This broad feature is indicative of the dissociative adsorption of water onto the SiO_2 surface. By contrast, the hydroxyl bands are completely absent from the infrared spectrum of the silicon dioxide film grown at 350 °C. In fact, this latter spectrum is indistinguishable from the infrared spectrum of SiO_2 produced by the thermal oxidation of a silicon wafer at 900 °C.

The refractive index measured by ellipsometry ranges from 1.43 to 1.47 for the SiO_2 films. As a more thorough measure of film quality, the dielectric constant was calculated from capacitance data of several samples, each deposited at a different temperature. In the limit of zero hydroxyl ion concentration in the SiO_2, the dielectric constant approaches 3.8073 [19]. The dielectric constants ranged from 5.0 ± 0.2 for films grown below 150 °C to 3.81 ± 0.03 for films grown at 350 °C. The latter value indicates that excellent dielectric properties are attained for films grown at higher temperatures.

In the preceding paper [11], we examined the nature of the reactive gases in the plasma jet. Optical emission spectra reveal that between the electrodes there are electronically excited ions, atoms and metastable species, whereas in the jet effluent only metastable oxygen molecules ($b^1\Sigma_g^+$) are detected. This latter result can be explained by the lack of an excitation source in the effluent and by the long lifetime of metastable oxygen molecules [20]. Langmuir probe measurements indicate that there are charged particles in the effluent as well.

However, the flux of these charged particles reaches a maximum of approximately 10^{14} cm^{-2} s^{-1}, which is too low to have a significant impact on the rates of the etching and deposition processes. For example, assuming all the charged species strike adsorbed TEOS molecules on the substrate and convert them into SiO_2 units, then the average deposition rate would be 15 Å s^{-1}. This rate is nearly fifty times lower than the observed value.

Metastable oxygen molecules might be involved in the deposition reaction. It has been found that singlet metastable oxygen molecules ($a^1\Delta_g$ and $b^1\Sigma_g^+$) are capable of oxidizing some organic compounds [21, 22]. Infrared emission of the delta state is detected in the jet at a wavelength of 1.27 μm using a germanium detector. The signal persists for more than 10 cm downstream of the nozzle, which is consistent with the lifetime of $a^1\Delta_g$ O_2 of 100 ms [20]. Nevertheless, we do not have an estimate of the metastable oxygen concentration in the atmospheric pressure plasma jet, and cannot make any conclusions regarding its role in the deposition process.

We have also detected ozone in the jet effluent at concentrations ranging from 0 to 200 ppm [11]. Ozone and tetraethoxysilane have been used for the chemical vapour deposition of silicon dioxide [3, 23]. However, in these studies, much higher O_3 concentrations (>1.0 vol.%) were required to achieve appreciable growth rates. We also observe different dependencies of the O_3 concentration and the growth rate on the process variables, suggesting that the ozone is not responsible for decomposing TEOS into silicon dioxide. On the other hand, the ozone is produced by the reaction of O atoms with O_2 molecules. We estimate that the O atom concentration is approximately 30 to 40 ppm [11]. This concentration at 1 atm and 100 °C produces a collision rate with the substrate of 2.4×10^{18} cm^{-2} s^{-1}. Assuming the reaction probability for O atoms with TEOS is greater than 10^{-3}, this flux is sufficient to account for the observed deposition rate [11]. Nevertheless, further studies are under way to determine the chemical species that are responsible for the deposition of the silicon dioxide films.

In conclusion, we have demonstrated that an atmospheric-pressure plasma jet may be used for the plasma-enhanced chemical vapour deposition of SiO_2 at 115 to 350 °C. Deposition rates in excess of 1000 Å min^{-1} are achieved, and the properties of the films deposited at 350 °C are comparable to those of thermally grown silicon dioxide.

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