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High-fluidity chemical vapor deposition of silicon dioxide

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Silicon dioxide has been deposited by the glow discharge decomposition of SiH_4 and O_2 at substrate temperatures below -80 °C, where the thermal reaction on the surface was basically suppressed. Ion flux onto the growth surface was significantly reduced by employing a triode reactor. Oxide deposition onto surfaces with narrow features proceeds from the bottom of a trench or groove and results in planarization of the topography. Such high-fluidity chemical vapor deposition is inferred to occur through the formation of liquified precursors on the cooled surface.

The shrinkage of ultra large-scale integrated circuits (ULSIs) needs a novel chemical vapor deposition (CVD) technique to deposit an insulator into narrow grooves or deep trenches for planarizing topography created by narrow features. Conventional plasma-enhanced CVD of SiO₂ results in the formation of harmful voids in the grooves or trenches because the gas phase products basically control the growth kinetics. The conformal step coverage of silicon dioxide for high aspect ratio trenches has been achieved by using tetraethylorthosilicate (TEOS) and O₃.¹ The TEOS/ O3 atmospheric-pressure CVD (APCVD) with a moderate fluidity has also been developed and applied to the interlayer dielectric formation for the multilevel metallization.² A digital CVD technique consisting of repetitive cycles of silicon growth by the reaction of triethylsilane (TES) with hydrogen radicals and the subsequent oxidation of the silicon layers by an excited oxygen beam can offer the conformal step coverage of SiO₂.³ Very high-fluidity CVD of silicon dioxide has been realized on a cooled substrate (< -20 °C) by using tetramethylsilane (TMS) and excited oxygen.⁴ A key feature to achieve the conformality or high fluidity in such CVD processes 1-4 is considered to be a high surface migration capability of deposition precursors which contain CH_x bonds. In contrast to this, the highfluidity silicon deposition from an SiH₄ plasma has recently been realized by cooling the substrate down to about -100 °C and suppressing the ion bombardment on the growth surface.⁵ In this letter, we describe a novel plasma CVD technique of silicon dioxide with a very high fluidity. The structural and dielectric properties of as-grown and annealed oxide are also shown.

Silicon oxide was grown on patterned c-Si substrates using an rf glow discharge decomposition of 3% SiH₄ diluted with H₂ and O₂ gas mixture in a capacitively coupled reactor. It has two different features compared to a conventional plasma CVD reactor. One is the substrate electrode which is cooled down to less than -100 °C by liquid nitrogen. The thermal reaction on the growth surface is basically suppressed. The other is the use of a grounded metal grid (no. 30 mesh) which is set between the rf and the substrate electrode and located at 1.5 cm away from the sample surface.⁶ Hence, the rf plasma is generated between the grid and the power electrode with a distance of \sim 5.5 cm. A dc bias of +30 V that is a little higher than the plasma potential was applied to the substrate electrode for significantly reducing the ion flux incident onto the growth surface. The molar fraction of oxygen to silane was varied from 1 to 10 by changing oxygen flow rate. The partial pressure of SiH₄ and the rf power density were maintained at 6 mTorr and 0.44 W/cm², respectively.

In silicon deposition from a SiH₄ plasma by using a conventional diode-type reactor at a substrate temperature of -110 °C, it is shown that the film formation is promoted by higher silanes which are produced on the surface and have a high migration capability.⁵ This has been confirmed by the mass spectrometry of reaction products emitted from the growth surface just after interrupting the deposition.⁵ In this case, the conformal step coverage of silicon has been achieved for the 1 μ m patterns with an aspect ratio of about 1. However, the step coverage for the finer patterns with a higher aspect ratio has become worse. This is because the ion flux impinging onto the surface decomposes the polymerized precursors to enhance the network formation, which interrupts the surface migration. For reducing the ion flux incident to the growth surface, a grounded metal grid and a positive substrate bias have been employed. Consequently, the selective silicon growth from the groove bottoms has been achieved so as to minimize the surface free energy of the deposit, and finally, the fine patterned surface has been planarized as shown in Fig. 1.⁷

The mechanistic understanding of the high-fluidity silicon CVD⁵ has been extended to silicon-dioxide deposition. The oxide deposition profiles are similar to those of silicon, as displayed in Fig. 2. The growth rate on the top surface is significantly slow compared to that on the groove bottoms. And finally, the trenches are selectively refilled with silicon dioxide. In order to get a quantitative insight in the deposition profile, the growth rate in the groove is measured as a function of the molar fraction of oxygen to silane by changing the window ratio b/a as shown in Fig. 3. The film growth rate at the trench bottom increases as the window ratio increases. This is explained by two mechanisms: One is the temperature-dependent condensation rate of gas-phase products on the surface. The temperature of the trench bottom is lowest and hence the film growth proceeds from the bottom corner. The other is the migration capability of deposition precursors from the top surface



FIG. 1. Cross-sectional scanning electron microscopy (SEM) photograph of the deposition profile of hydrogenated silicon in Si trenches.

and the side wall to the trench bottom. The surfacereaction products are inferred to be silanols and siloxanes because they have a high fluidity and could be produced through polymerization reactions among silane radicals and activated oxygen on the cooled surface. The surface migration of such deposition precursors could also be enhanced by energy transfer from neutral gas molecules whose temperature is as high as ~ 500 K.⁸ The smooth migration of precursors enables us to refill an extremely



FIG. 3. Growth rate of oxide deposited in trenches with various window ratios b/a plotted as a function of $[O_2]/[SiH_4]$ ratio.

fine pattern with a width of 0.2 μ m and an aspect ratio of 4 without any voids, as illustrated in Fig. 4. Note that the formation of gas-phase precursor is not important because of a very low silane partial pressure of 4.6–5.8 mTorr.

The film structure has been evaluated by the infrared absorption spectra. A significant amount of bonded hydrogen are incorporated in an as-deposited film and most of them are effused from the film by annealing at 400 °C for 60 min in an oxygen atmosphere as illustrated in Fig. 5. The spectra of the annealed samples are very similar to the thermally grown oxide except for a little incorporation of SiH bonds and a small absorption peak at 880 cm⁻¹ that is presumably due to the bending mode of an H-SiO₃ configuration.⁹ This kind of hydrogen bond could be eliminated by *in situ* O₂ plasma annealing by interrupting the oxide



FIG. 2. Cross-sectional SEM photographs of the deposition profiles of silicon dioxide grown at different deposition times: (a) 30 min, (b) 60 min, and (c) 120 min.



FIG. 4. Cross-sectional SEM photograph of the deposition profile of silicon dioxide in a very narrow Si trench.

growth. It should be noted that the deposition profile remains unchanged and no crack is observable before and after annealing at 400 °C in an oxygen atmosphere. This is because a little increase in the oxide volume due to oxygen incorporation by annealing is compensated for by a significant decrease in the bonded hydrogen content in the matrix. The refractive index of the silicon oxide after 400 °C annealing is 1.42, that is close to the thermal oxide value (1.46). A little lower value of the refractive index originates from the incorporated hydrogen which slightly lowers the film density. The leakage current of the silicon oxide is a little higher than that of thermally grown oxide and the breakdown field strength is higher than 5×10^6 V/cm.

In conclusion, the deposition precursors of silicon dioxide in the high-fluidity plasma-enhanced CVD could be silanols and siloxanes. This new mode of self-planarizing



FIG. 5. Infrared absorption spectra of as-deposited, annealed oxides and the thermally grown oxide. The symbols (S), (B), and (R) refer to the vibrational modes of stretching, bending and rocking, respectively.

deposition offers a process technology to refill or planarize the extremely fine patterned surfaces. The film properties of the silicon dioxide have a potential to be used as a dielectric material for future ULSI.

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