

High Fluidity CVD of Silicon Oxide from $\text{SiH}_4 + \text{O}_2$ Plasma

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Silicon oxide has been deposited by the glow discharge of $\text{SiH}_4 + \text{O}_2$ at substrate temperatures below -86°C where the thermal reaction on the surface is dramatically suppressed. By employing a triode reactor the ion flux onto the growth surface is also significantly reduced. The oxide deposition onto a fine patterned surface proceeds from the groove bottoms and finally the deposition surface is completely planarized. Such high fluidity CVD is inferred to occur through the formation of liquefied precursors produced by the polymerization reaction of radicals on the cooled surface.

1. INTRODUCTION

The shrinkage of ULSI devices needs an advanced CVD technology to planarize the fine patterned surfaces to conformally grow an interlayer dielectric for the multilevel metallization and to refill an insulator into the Si trench. Conventional plasma enhanced CVD of silicon oxide results in the formation of harmful voids in deep trenches and narrow grooves because the gas phase reaction basically controls the growth kinetics. The conformal step coverage of silicon oxide for high aspect ratio trenches has been achieved by using TEOS (Tetraethylorthosilicate) and ozone¹. The TEOS/ O_3 CVD with a relevant fluidity has also been developed and applied to the interlayer dielectric formation². A digital CVD technique consisting of silicon growth by the reaction between TES (Triethylsilane) and hydrogen radical and the subsequent oxidation of silicon by oxygen beam can offer the conformal step coverage in SiO_2 deposition³. A key feature for the conformality and fluidity in the CVD processes^{1~4} is the incorporation of CH_x bonds in the surface products. In contrast to this, the high fluidity CVD of silicon from an SiH_4 plasma has recently been realized by cooling the substrate down to about -100°C and suppressing the ion flux impinging onto the growth surface⁵.

In this paper, a novel plasma CVD technique to deposit silicon oxide with a very high fluidity is described.

2. EXPERIMENTAL

Silicon oxide was grown on patterned c-Si substrates by the rf glow discharge decomposition of a 3 % SiH_4 diluted in H_2 and O_2 gas mixture. The molar fraction of oxygen to silane was varied from 0 to 10. The substrates were cooled down to -110°C by liquid nitrogen. A grounded metal grid was set between the rf and the substrate electrode⁶, and the plasma was generated between the grid and the rf electrode. By applying dc bias to the substrate, the ion flux impinging onto the deposition surface was controlled. The partial pressure of SiH_4 and the rf power were maintained at 6 mTorr and 50 W, respectively.

3. RESULTS AND DISCUSSION

In silicon deposition from an SiH_4 plasma at a substrate temperature of -110°C , it is shown that the precursors are higher silanes such as Si_2H_6 and Si_3H_8 as confirmed by the mass spectrometry of reaction products emitted from the surface just after interrupting the deposition⁵. The selective silicon growth proceeds from the groove bottoms

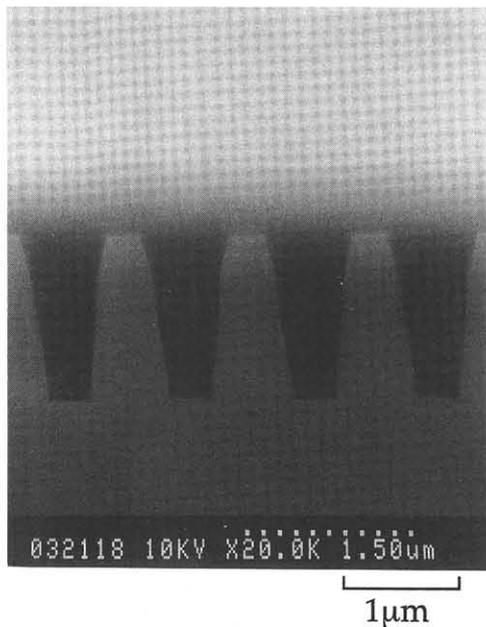


Fig. 1 Cross-sectional SEM photograph of the deposition profile of silicon in Si trenches.

so as to minimize the surface free energy and the planarization of the fine patterns is achieved as shown in Fig. 1.

For silicon oxide deposition, oxygen is added to SiH_4 . The deposition profile for the molar fraction of $[\text{O}_2]/[\text{SiH}_4]=3$ is similar to silicon deposition as shown in Fig. 2. The oxide growth starts from the groove bottoms, while the growth rate on the top surface is significantly slow, and finally the trench is selectively refilled. In order to get an insight on the growth mechanism the deposition rate in the grooves is measured as a function of the molar fraction of O_2 to SiH_4 by

changing the window ratio a/b as shown in Fig. 3. The growth rate increases with increasing the window ratio, indicating that the deposition precursors migrate from the top surface into the trenches with a very high fluidity. The surface products are inferred to be silanols and siloxanes which have a high fluidity and could be produced through polymerization reactions among higher silane and activated oxygen on the cooled surface. The smooth migration of precursors enables us to refill the extremely fine pattern with a width of $0.2 \mu\text{m}$ and an aspect ratio of 4 without any voids as displayed in Fig. 4.

The film structure has been evaluated by the infrared absorption spectra. As shown in Fig. 5, a number of bonded hydrogen are incorporated in the as-deposited film and most of hydrogen atoms desorb from the film by annealing at 400°C for 60 min in an oxygen atmosphere. The spectrum of the annealed samples is 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 probably due to the bending mode of an H-SiO₃ configuration⁷. This hydrogen bond could be eliminated by in situ O_2 plasma annealing. The refractive index of the silicon oxide after 400°C annealing is 1.42 that is close to the thermal oxide value (1.46). 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 $5 \times 10^6 \text{ V/cm}$.

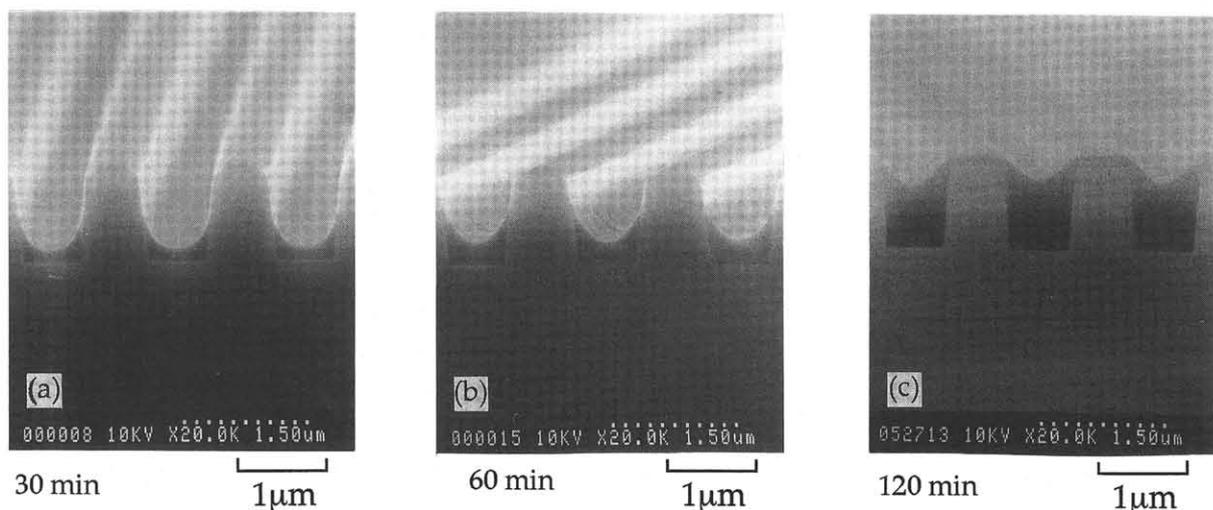


Fig. 2 Cross-sectional SEM photographs of the deposition profiles of silicon oxide grown at different deposition times: (a) 30 min, (b) 60 min, and (c) 120 min.

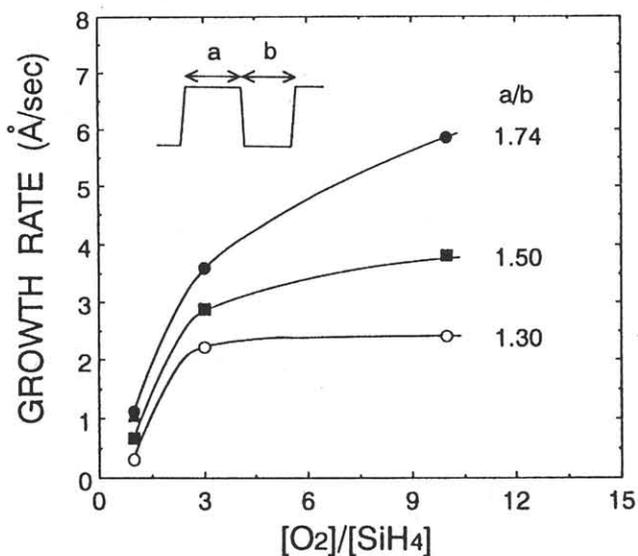


Fig. 3 Growth rate of oxide deposited in trenches with various window ratios a/b plotted as a function of $[O_2]/[SiH_4]$ ratio.

In conclusion, the deposition precursors of silicon oxide in the high-fluidity plasma CVD could be silanols and siloxanes. This new mode of deposition offers a process technology to refill or planarize the extremely fine patterned surfaces. The film properties of the silicon oxide have a potential to be used as a dielectric material for ULSI.

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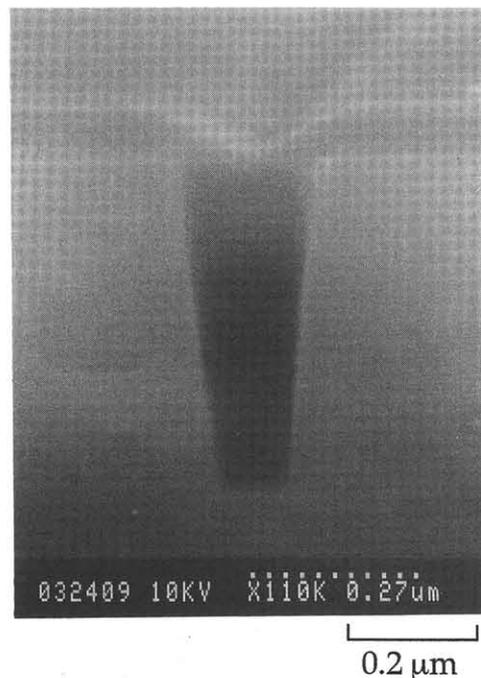


Fig. 4 Cross-sectional SEM photograph of the deposition profile of silicon oxide in a very narrow Si trench.

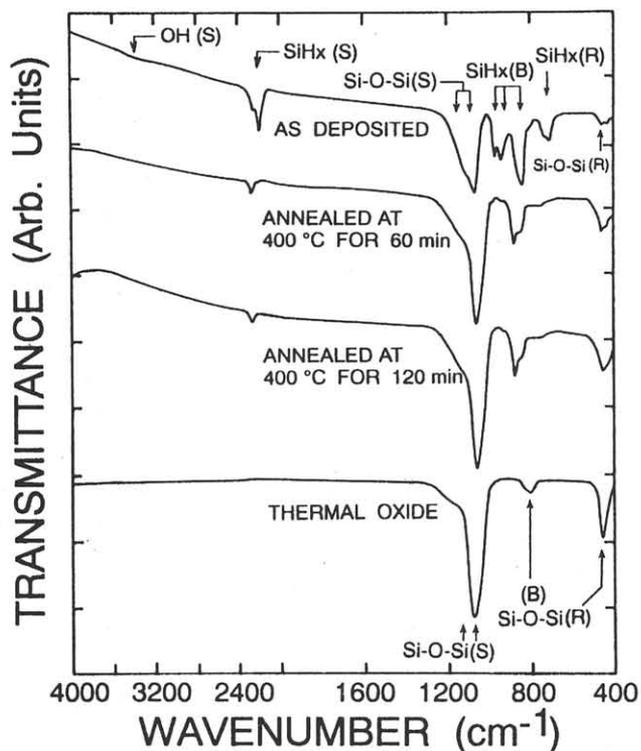


Fig. 5 Infrared absorption spectra of as-deposited and annealed oxides. The symbols (S), (B) and (R) refer the vibrational modes of stretching, bending and rocking, respectively.