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Surface Modification of Base Materials for TEOS/O_3 Atmospheric Pressure Chemical Vapor Deposition

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ABSTRACT

Atmospheric pressure tetraethyloxysilicane (TEOS)/O_3 chemically vapor deposited provides excellent step coverage for submicron device structures; however, the properties of the deposited films depend on the surface characteristics of the base materials being used. To illustrate this dependence, the deposition rate of nondoped silicon dioxide obtained on a thermal oxide surface is significantly lower than the deposition rate obtained on a bare silicon surface. A new method to eliminate this base material dependence involving plasma treatment has been investigated. The optimum treatment consists of exposing the base materials to a nitrogen plasma for 1 min while maintaining the base materials at 250°C. Films deposited on thermal oxide base materials which have first been treated by this new method were found to have the same deposition rate, aqueous HF etch rate, and surface morphology as those films deposited on untreated bare silicon. In addition to a nitrogen plasma, oxygen and argon plasmas were studied and found to produce similar results when the base material temperature was raised to 350°C. The elimination of base material dependence through the use of this new plasma treatment technique has resulted in higher integrity TEOS/O_3 oxides and has also expanded the range of applications for this unique planarizing technology for very large scale integrated device fabrication.

Tetraethoxysilane (TEOS) is increasingly being used as a silicon (oxide) source material for atmospheric pressure, low pressure, and plasma techniques of chemical vapor deposition because it provides better step coverage and meets tighter safety requirements. In particular, atmospheric pressure TEOS/O_3 CVD is a promising technology for advanced very large scale integrated (VLSI) device fabrication because it offers superior step coverage and improved safety of TEOS along with low deposition temperatures (1-3).

TEOS/O_3 atmospheric pressure chemical vapor deposition (APCVD) provides excellent step coverage due to the surface-limited nature of its reaction kinetics, but because of this surface-limited nature, the nature of the surface being deposited on represents an important factor. When a TEOS/O_3 film is deposited on polysilicon, aluminum, or borophosphosilicate glass (BPSG) using 5% ozone in oxygen a high-quality film is obtained; but when the same chemistry is used to deposit a TEOS/O_3 film on thermal oxide, the surface morphology and film quality are poor. This phenomenon has been correlated to the hydrophobic/hydrophilic nature of the substrate material (4). The thermal oxide surface is hydrophilic and has a contact angle of 10°. The bare silicon surface is hydrophobic and has a contact angle of 50°. This base material dependence phenomenon has been described previously in conjunction with another method for elimination base material dependence which uses a two-step deposition sequence (4).

A new method for eliminating base material dependence which incorporates the use of a plasma treatment is presented in this paper. Exposure time, substrate temperature, and gas ambient were optimized in an anode-coupled plasma system in order to obtain superior quality silicon dioxide films on thermal oxide base materials.

Experimental

The apparatus and procedure for TEOS/O_3 silicon dioxide deposition have been described previously (3). The TEOS/N_2 flow rate was 2 slpm. The plasma treatment system is a conventional parallel plate, anode-coupled system which contains a heater with a 200 mm diam anode capable of heating a silicon substrate to 450°C. In this paper, the process temperature during plasma treatment refers to the anode temperature which is assumed to be equal to the substrate temperature. One hundred nanometer thermal oxide films on 150 mm silicon wafers were used in this study. The thermal oxide films were formed at 1000°C in dry oxygen. The plasma treatment was applied only to the thermal oxide samples. The bare silicon substrates were used as reference wafers and did not receive a plasma treatment. Following the plasma treatment of the thermal oxide wafers, nondoped silicate glass (NSG) films were then deposited on both types of substrates. The deposition rate, aqueous HF etch rate, and surface morphology of the films deposited on the plasma-treated thermal oxide wafers were compared with those deposited on the bare silicon material.

The plasma treatment conditions are shown in Table I. The wet etching was done using a 2.4% aqueous HF solution at 24°C. As a reference, the thermal oxide etch rate under these conditions was 17.9 nm/min.

Results and Discussion

In Fig. 1, the effects of plasma exposure time on the deposition rate were studied. For this series of tests the substrate temperature was held constant at 350°C during plasma treatment. Following plasma treatment, NSG films were deposited at 400°C using 4.2% ozone. In the figure, the deposition rate ratio is defined as the ratio of the deposition rate obtained on the plasma-treated thermal oxide to that obtained on bare silicon without the plasma treatment. When no plasma treatment is applied, the ratio is very low, 0.48. When a 1 min plasma treatment was applied, the ratio increases to 0.96 and remained approximately 1.0 when longer exposure times were used.

Figure 2 shows the dependence of etch rate on plasma exposure time using the same conditions used to generate

Table I. Standard conditions of plasma treatment.

RF frequency	13.56 MHz
Power	200 W
Pressure	1 Torr
Gas and Flow Rate	Nitrogen, 400 sccm
Duration	1 min

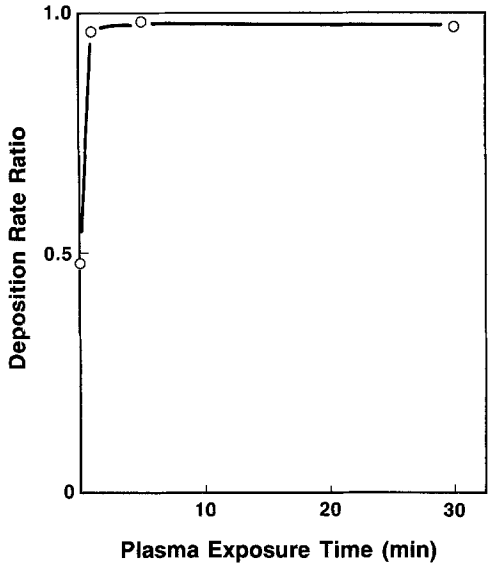

Fig. 1. Dependence of NSG deposition rate ratio on plasma exposure time, when plasma-treated at 350°C in N_2 deposited at 400°C with 4.2% ozone.

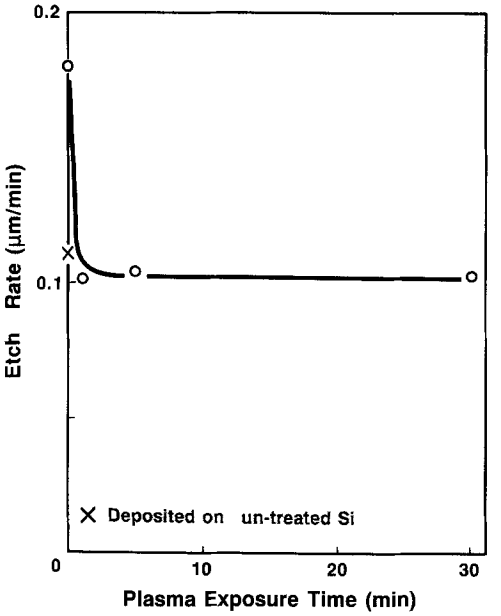

Fig. 2. Dependence of etch rate of films deposited at 400°C with 4.2% ozone on time of plasma treatment made at 350°C in N_2.

Fig. 1. Without plasma treatment, a high etch rate of 180 nm/min was observed, but when a 1 min plasma treatment preceded deposition, the etch rate was reduced to 100 nm/min. This is slightly lower than the 105 nm/min etch rate observed for films deposited on bare silicon. As above, the etch rate remains constant at 100 nm/min when longer treatments are used. Based on Fig. 1 and 2, the addi-

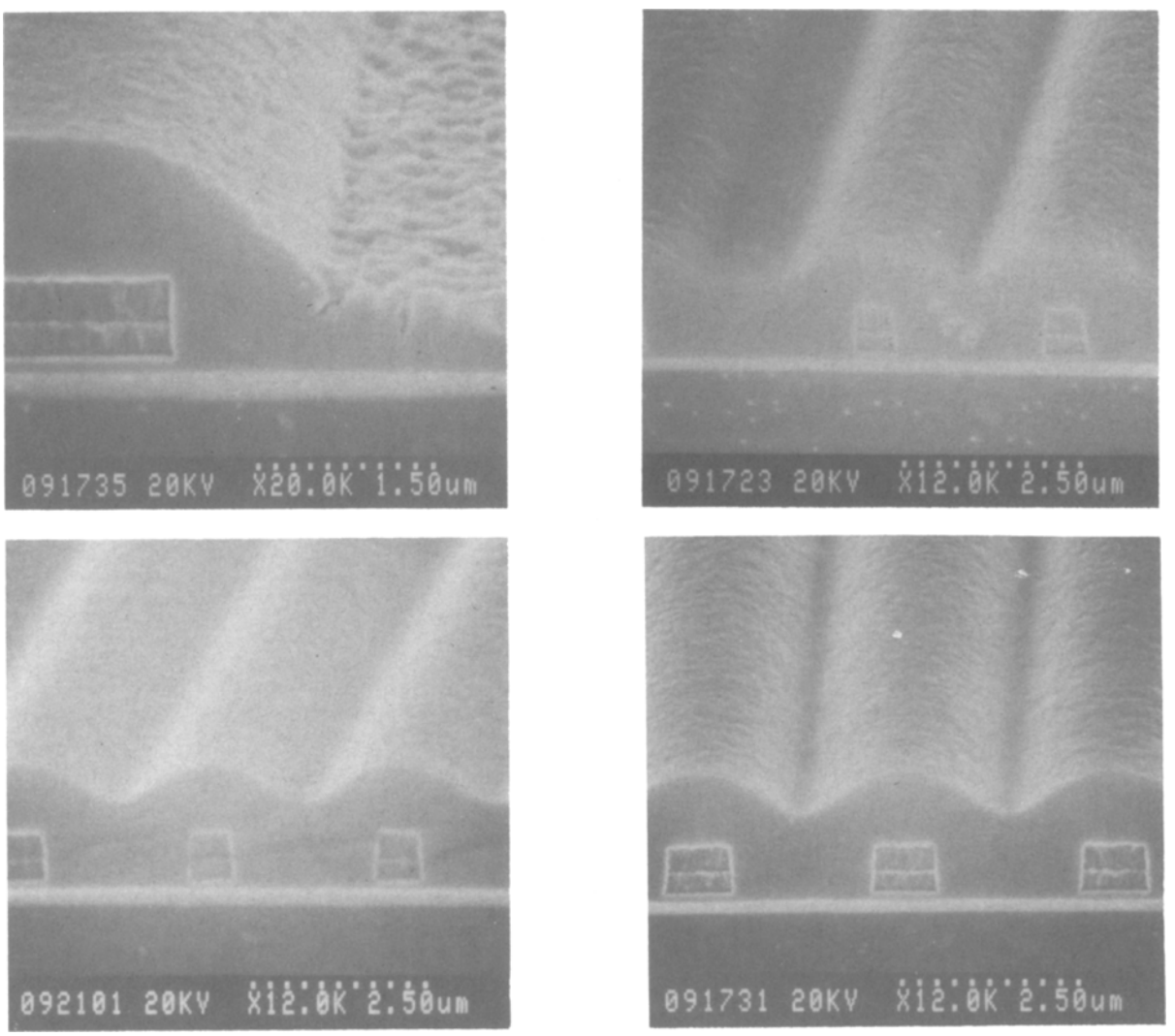

Fig. 3. Surface morphology and step coverage of films plasma-treated at 350°C in N_2 for 0 min (a, top left), 1 min (b, top right), 10 min (c, bottom left), and 30 min (d, bottom right), and deposited on polysilicon lines on thermal oxide at 400°C with 5% ozone.

tion of a plasma treatment of 1 min or longer prior to deposition on thermal oxide produced films of equivalent quality to those produced on bare silicon.

The micrographs in Fig. 3 show the surface morphology of an NSG film deposited over polysilicon lines on thermal oxide using the same plasma treatment and deposition conditions that were used in Fig. 1, except that the ozone concentration was increased from 4.2 to 5%. Figure 3a shows an NSG deposition sample without plasma treatment. The film deposited just on the thermal oxide is porous, and the film quality is poor. Figures 3b, c, and d illustrate how the film quality is improved when plasma treatments of 1, 10, or 30 min, respectively, are performed prior to depositon. These results show that a 1 min plasma treatment at 350°C is sufficient to modify the thermal oxide surface and obtain a smooth, conformal NSG film. Shorter times and lower temperatures will be explored in future experiments.

Figure 4 compares NSG deposition rate ratios at different substrate temperatures. All materials underwent a 1 min plasma treatment prior to NSG deposition at 400°C with 4.2% ozone in oxygen. For a room temperature plasma treatment, the rate ratio is approximately 0.6. The ratio increases to 0.7 for a substrate temperature of 150°C. Plasma treatments performed at 250°C or higher achieve ratios approaching 1.0 indicating the elimination of the base material dependence. In Fig. 4, the ratio decreases slightly as the temperature increases from 250 to 400°C, but it is not known whether this decrease is significant or simply data scattering. During the study, it was found that a rate ratio of 1.0 could be achieved at a lower minimum temperature if the plasma exposure times were increased.

The dependence of the aqueous HF etch rate on the temperature of the plasma treatment is shown in Fig. 5. The etch rates for room temperature and 150°C treatments are higher. This relation correlates to the lower deposition rate ratios shown for the same treatment temperatures in Fig. 4. At treatment temperatures of 250°C or higher, the etch rate is equivalent to the etch rate for NSG depositions on untreated bare silicon.

Surface morphology and step coverage were also studied for films deposited under the conditions described above. Slightly rough surfaces resulted for treatments performed at room temperature, but for those treated at 150°C for above smooth surfaces were obtained. This trend correlates with the deposition rate ratio and etch rate trends.

In addition to nitrogen, oxygen and argon plasmas were also explored for their ability to eliminate the base material dependence. One minute exposure time at 350°C produced results which were similar to those observed for nitrogen indicating that all three gases would be suitable for minimizing surface effects.

Thermal oxide surfaces, which produce NSG films with low deposition rates and poor film quality, proved to be

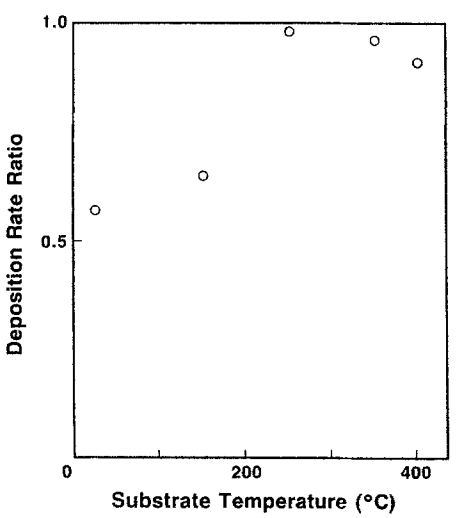

Fig. 4. Dependence of deposition rate ratio on temperature of 1 min plasma treatment in N_2, when deposited at 400°C with 4.2% ozone.

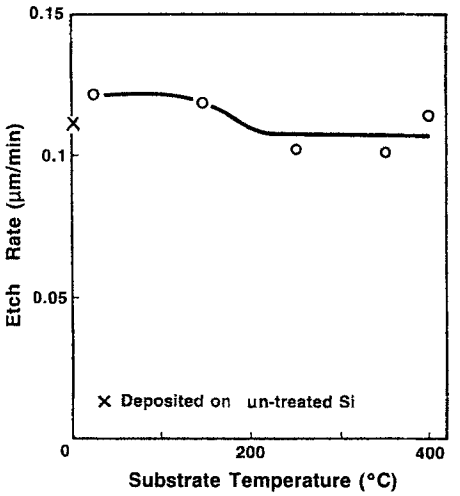

Fig. 5. Dependence of etch rate of deposited films on temperature of 1 min plasma treatment in N_2, when deposited at 400°C with 4.2% ozone.

hydrophilic (4). In comparison, bare silicon surfaces, a source of high quality NSG films, were found to be hydrophobic. When thermal oxide surfaces are treated with a plasma they can become hydrophobic. Oxidation or nitridation of the surface of the thermal oxide by the oxygen or nitrogen plasma is one possible explanation; however, this is not very probable because the argon plasma resulted in similar film properties. Since there can be OH (hydroxyl) or H radicals on the hydrophilic thermal oxide, a more feasible explanation of the effect of the plasma treatment would be that it eliminates all of these OH or H radicals through ion bombardment.

Conclusion

The effect of plasma exposure time and substrate temperature on deposition rate, aqueous HF etch rate, and surface morphology, as well as the effect of different plasma gases on the surface morphology were studied to eliminate the thermal oxide base material dependence.

A plasma treatment in an anode-coupled plasma system was very effective for modifying thermal oxide surfaces and enabling the deposition of NSG films with an equivalent quality to those deposited on bare silicon surfaces. A minimum plasma treatment of 1 min in nitrogen with a substrate temperature of 250°C was required to duplicate the deposition rate, HF etch rate, and surface morphology of a comparable film deposited on bare silicon. When oxygen and argon plasma were used at 350°C, the surface morphology was comparable to that obtained when nitrogen was used.

Silicon dioxide films that are deposited using atmospheric pressure TEOS/O_3 CVD can now be used for an increased variety of VLSI applications as a result of the elimination of base material dependence through plasma treatment.

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