Low Temperature and Atmospheric Pressure CVD Using Polysiloxane, OMCTS, and Ozone

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ABSTRACT

Silicon dioxide was deposited using an organic silicon material, OMCTS, and ozone at low temperature and atmospheric pressure. Since OMCTS in a cyclic siloxane and is thermally oxidized by ozone in this chemical vapor deposition (CVD) method, it is anticipated that high quality films will form at low temperatures. Deposition characteristics were very sensitive to base materials. However, the base material dependence on ozone concentration was less than that for the TEOS/O₃ atmospheric pressure CVD. This also suggests that the deposition reaction is rate-limited to substrate-surface; therefore, step coverage was excellent and particle generation was very low. Step coverage varied from conformal to reflowed with increasing ozone concentration. There were no voids in the films deposited between narrow Al spacings even after BHF etching. Deposition rate was a high as $0.2 \,\mu$ m/min with high film cracking durability. Film stress was settled at as low as 1×10^9 dyn/cm². Film quality, in terms of film etching rates and film shrinkage, was also studied. This newly proposed CVD technology has yielded SiO₂ films of high quality.

In very large scale integrated (VLSI) manufacturing, the trend is increasingly towards submicron dimensions, high aspect ratio, and multilevel interconnection structure. Requirements for CVD films used in VLSIs are low temperature deposition, good step coverage, low particle generation, high film quality, such as high density and low leakage current, and low film damage and stress. Silane (SiH₄)-based CVD, which has been in use for a long time (1), has limitations such as poor conformality (2), high particle generation, and film stress and damage in plasma CVD. Many investigations have been concentrated on new organosilicon sources such as TEOS (3, 4), DADBS (5), TMCTS (6), and SiOB (7) for better film characteristics. Among them, TEOS has been successfully used in thermal CVD under low pressure, and plasma-enhanced CVD at low temperature. However, the former has excellent step coverage but limited applications because of high temperature deposition, and the latter has rather poor step coverage common to the CVD and probable carbon contamination. Another TEOS CVD that uses ozone under atmospheric pressure presents excellent conformality, reflowed step coverage, and low particle generation because of surface-limited reaction, as well as high film quality (8, 9). As TEOS has four ethoxy radicals, one diethylether, or water and ethylene molecule, is formed to make one Si-O-Si bond; much diethylether or water is produced to form silicon dioxide films. To deposit SiO₂ of higher quality using ozone, we tried a new organic silicon material, a polysiloxane that includes cyclic four Si-O bonds and is saturated with CH3 radicals, octamethylcyclotetrasiloxane (OMCTS), whose chemical structure is shown in Fig. 1. Ozone lowered deposition temperature to about 400°C in the TEOS CVD, and will do the same in OMCTS CVD too. Since cyclic Si-O bonds, the units of SiO₂ structure, are included in the molecule, films of high quality are anticipated to deposit. Kinetics and characteristics of OMCTS CVD, and properties of deposited USG films were studied.

Experiment

Experimental apparatus and procedures used in this work have been described previously (9), but will be explained briefly. A Si substrate is held upside down on a susceptor/heater by a vacuum chucking, which is oscillated back and forth. OMCTS is kept at 40°C in a thermostat, and is bubbled and carried by flow-controlled nitrogen gas through both a bubbler and a dispersion head to the substrate kept mainly at 400°C. Ozone is generated up to several percent in oxygen by an ozonizer, Nippon Ozone, Model QA-2SM, and added to a OMCTS/N₂ gas mixture before the dispersion head. OMCTS piping is heated at 80°C to avoid liquefaction of OMCTS. Undoped silicon dioxide (USG) was deposited on bare silicon, thermally oxidized silicon, or patterned Al/1%Si films. The thermal oxide was formed in dry oxygen at 1000°C. Thicknesses, IR absorption, and refractive index were measured by a Nanometrics Nanospec Model 010-0180, an IR spectrometer, Nicolet ECO-8S, and a Gaertner L115B Automatic Ellipsometer, respectively. OMCTS, 99.995% purity, was refined by Asahi Electro-Chemical Co., Ltd., Tokyo, Japan.

Results and Discussion

Characterization of deposited films.—As shown in Table I, the molecular weight of OMCTS is higher than that of TEOS, giving it a rather low boiling point. Standard deposition conditions for both OMCTS and TEOS CVDs are given in Table II. To obtain the same deposition rate, much less vapor pressure of OMCTS was needed than that of TEOS. This is attributed to the four Si-O bonds in an OMCTS molecule compared with the one Si in a TEOS molecule. Thus, a higher deposition rate is accomplished.

Figure 2 shows IR spectra of a film deposited using only OMCTS and ozone under the standard deposition conditions, compared with those of thermally grown oxide. There are strong absorptions at 1060 and 813 cm⁻¹, both assigned to Si-O bond, and no other radicals such as Si-CH₃, which has strong absorption at 1275-1250 cm⁻¹. All the absorptions are the same as those of the thermal oxide except for the absorption at 3600 cm⁻¹, which is assigned to OH radicals, in the OMCTS spectra. The refractive index of the films was 1.451, the same as for thermal oxide. From the above two facts the deposited films prove to be SiO₂.

Deposition rate.—The relation between film thickness and deposition time for silicon oxide deposited on Si and thermal oxide is shown in Fig. 3. In the deposition where ozone concentration was 1%, film thickness increased



Fig. 1. Chemical structure of OMCTS.

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Table I. Chemical properties of OMCTS and TEOS.

Silicon source	OMCTS	TEOS
Molecular weight	296.6	208.5
Boiling point	178°C	166.8°C
Melting point	17.5°C	82.5°C
Density (* specific gravity)	0.956 g/cm ³	*0.9213
Refractive index (25°C)	1.3968	1.3830

Table II. Standard deposition conditions.

Silicon source	OMCTS	TEOS
Source temperature Vapor pressure Source carrier flow rate (N_2) Main N_2 flow rate Deposition temperature Ozone concentration Deposition rate	40°C 4.5 mm Hg 4 SLM 18 SLM 400°C 4% 0.1 μm/min	65°C 20 mm Hg 4 SLM 18 SLM 400°C 4% 0.1 μm/min

slightly at first and then steeply when deposited on Si. Deposited on thermal oxide, the film thickness increases linearly with deposition time. However, the deposition rate, slope of the curve, is much smaller than that on Si. This is much more noticeable than in the $TEOS/O_3$ CVD, which will be mentioned in the discussion of Fig. 5. The deposition is very sensitive to base materials, which means that the deposition reaction is rate-limited to substrate surface. More conformal coverage and very low particle generation are expected because the films deposit very uniformly, not only on the level surface, but also on the side walls (9). OMCTS will be hydrophobic, judging from the chemical structure where eight methyl radicals project outward, and thermal oxide is hydrophilic; contact angles, a measure of hydrophile of substrate surface, of Si and thermal oxide were 50° and 10°. Hydrophobic OMCTS may be very hard to adsorb, or to be oxidized on the hydrophilic thermal oxide. This may be the reason why the deposition rates obtained on thermal oxide are much less than those for silicon. As the deposition rate on thermal oxide is very low, the lower deposition rate at early stage of the deposition on Si can be attributed to native oxide on Si, which was hardly observed in the TEOS CVD.

Dependence of deposition rate on temperature is shown in Fig. 4. The deposition rate decreases from 300° to 350°C, then increases steeply to a maximum at 430°C. The deposition rate curve is fairly different from that of the TEOS CVD, as shown in the figure. Though the reason for the decreased rate between 300° and 350°C is not clear, slightly



Fig. 3. Relation between film thickness and deposition time, when deposited at 400°C with 1% ozone.

different films from SiO_2 may be formed in the temperature range.

A reaction between OMCTS and ozone can be expressed as

$$(CH_3)_8Si_4O_4 + 8O_3 \rightarrow 4CH_3OCH_3 + 4SiO_2 + 8O_2$$

In the reaction formula, it is supposed that dimethylether is produced, but can be oxidized further, and just oxygen atoms decomposed from ozone are involved in the reaction. In the reaction, ozone is used as an oxidant. This is different from the TEOS/ O_3 reaction, where TEOS can produce SiO₂ by decomposition, and ozone can be a reaction catalyst (9).

Hence, deposition rate will increase with ozone concentration. Dependence of deposition rate on ozone concentration is shown in Fig. 5. The rate increases with ozone concentration at the low ozone level as anticipated above, and levels off at 1.5% or higher ozone when deposited on Si and thermal oxide. However, the films deposited on thermal oxide have much lower saturated rates than those on



Fig. 2. IR absorption of OMCTS film deposited with 4% O_3 at 400°C.



Fig. 4. Dependence of deposition rate on deposition temperature when deposited with 5% ozone.

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Fig. 5. Dependence of deposition rate on ozone concentration, when deposited at 400°C.

Si, and hazy surfaces were obtained independent of ozone concentration. The ratio of the deposition rate obtained on thermal oxide to that on Si is around 0.25 over the whole ozone concentration. Again, the OMCTS CVD is much more sensitive to base materials. This base material dependence may be an issue in device fabrication. It can, however, be eliminated by the double layer deposition method (10). Difference between the OMCTS and TEOS CVDs in the ozone concentration dependence of deposition rate for thermal oxide can be attributed to the chemical structure of the two silicon sources, although this is not clear as yet.

Etching rate, stress, and shrinkage of deposited films.— Figure 6 shows the dependence on deposition temperature of film etching rates by an aqueous HF solution when deposited on Si. The etching rate decreases monotonically as the temperature increases, which suggests higher density of the films deposited at the higher temperature by annealing effects. In Fig. 7, the dependence of etching rate of



Fig. 7. Dependence of etching rate on ozone concentration, when deposited at 400°C.

USG films on ozone concentration is shown, as deposited on both Si and thermal oxide. The etching rate decreases very little in both depositions as the ozone concentration increases. However, the etching rate of the films deposited on thermal oxide is higher than that for Si, which means that they are poorer in film quality. The etching rate ratio is constant throughout the ozone concentration. Films of uniform quality, good or poor, are deposited on Si and thermal oxide without dependence on ozone concentration.

Dependence of film stress on ozone concentration is shown in Fig. 8. The stress of "as-deposited" films depends little on ozone concentration, and is about 2.4×10^9 dyn/ cm², tensile. Three days after deposition, the film stress decreases to about 0.6×10^9 dyn/cm² at 0.6% ozone, and increases slightly with increase in the ozone concentration. Stress relaxation was observed a day after film deposition and varied no further. Eight days after film deposition, as



Fig. 6. Dependence of etching rate on deposition temperature, when deposited with 5.8% ozone.

Fig. 8. Dependence of film stress on ozone concentration, when deposited at 400°C.

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Fig. 9. Dependence of film shrinkage on ozone concentration, when deposited at 400°C.

IR absorption of Si-OH increases a little, independently of ozone concentration, the stress relaxation can be attributed to very slight inclusion of water in the deposited films, which is common in CVD films (11). Figure 9 shows dependence of film shrinkage on ozone concentration. The film shrinkage decreases a little at first and then levels off at 4.3%, which is higher than that of films deposited with 5.5% ozone in the TEOS CVD. Again, little dependence of the film shrinkage on ozone concentration was observed.

Film crack durability.--Dependence of the film crack limit on ozone concentration is shown in Fig. 10. The film crack limit is defined as maximum film thickness without cracking. In the OMCTS CVD method the film crack limit does not depend on the ozone concentration, and is 1.6 µm when deposited at 400°C; whereas in the TEOS CVD it depended conspicuously on ozone concentration and its maximum is 1.8 µm at 5% ozone, which is higher than that of the OMCTS films at the same ozone concentration. Figure 11 shows dependence of film crack limit on deposition rate. The film crack limit decreases slightly with the deposition rate. The limit is 1.4 µm at a 0.19 µm/min deposition rate, and is very high compared with that in the TEOS CVD, 0.8 μ m at 0.2 μ m/min, for which the film crack limit decreases steeply as the deposition rate increases. This can be explained as follows. In the TEOS CVD the crack limit is low at the low ozone, 1% ozone for example, as shown in Fig. 10. To increase the deposition rate, the flow rate of TEOS/N₂ was increased, keeping the ozone concentration constant, so the ozone content in the total gas flow becomes relatively low. That is why the crack limit at the high deposition rate, around $0.2\,\mu\text{m/min}$, is very low in the TEOS CVD. On the other hand, the dependence of the crack limit on ozone concentration is slight, hence the crack limit depends less on the deposition rate in the OMCTS CVD. The less dependence of the deposition characteristics on ozone concentration is one of main features of the OMCTS/O3 CVD. In the OMCTS CVD, high throughput can be obtained without film cracking; this is another advantage of the OMCTS deposition.

Surface morphology and step coverage.—Figure 12 shows surface morphology and profiles of films deposited at 430°C with 2.4% ozone on aluminum lines. The film surface is very smooth (a, left), and the step coverage is conformal (b, right). Figure 13 shows surface morphology and profiles of films deposited at 430°C with 5.8% ozone on aluminum lines. The film surface is also very smooth, even on aluminum (a, top left), and the film step coverage is more reflowed (b, top right), than that obtained at the lower ozone concentration, 2.4%, Fig. 12. So the higher ozone concentration gives a more reflowed profile as seen in the



Fig. 10. Dependence of film crack limit on ozone concentration, when deposited at 400°C.

TEOS/O₃ atmospheric pressure CVD. Whereas the profile of aluminum lines has a negatively tapered outline in Fig. 13 (c, left), the deposited film has no voids, even after etching by a buffered HF solution. This means that the film keeps high quality even at substrate steps. The films deposited with OMCTS and ozone have excellent step coverage and high quality throughout because of the CVD reactions being rate-limited to the substrate surface.

Conclusion

Films of high quality were deposited at low temperatures, around 400°C, under atmospheric pressure using a new organic silicon source, OMCTS, and ozone. This was possible because of the chemical or thermal reaction, at atmospheric pressure, in contrast to plasma CVD.



Fig. 11. Dependence of film crack limit on deposition rate, when deposited at 400°C with 4% ozone.



Fig. 12. Surface of film deposited on Al steps (a, left) and film step coverage on Al step (b, right), when deposited at 430°C with 2.4% ozone.

Deposition rate was as high as 0.2 μ m/min with high film cracking durability, 1.5 μ m thick without cracks, because of four Si-O bonds in an OMCTS molecule. Film stress was low, 2.5 \times 10⁹ dyn/cm² just after deposition and 1 \times 10⁹

dyn/cm² after stress relaxation. Film surface was very smooth, even on aluminum lines, and film quality and step coverage were excellent; the deposited films had no voids between aluminum lines or even at aluminum steps which







Fig. 13. Surface of film deposited on Al steps (a, top left) and film step coverage on Al steps (b, top right), (c, left), when deposited at 430°C with 5.8% ozone.

were etched negatively tapered. Film deposition was very sensitive to base materials; namely, deposition rates obtained on thermal oxide were much lower and film surface was hazy independent of ozone concentration. On the other hand, this phenomenon leads to excellent step coverage, which changes from conformal to reflowed with increases in the ozone concentration, and low particle generation. High film cracking durability and less dependence of deposition characteristics on ozone concentration are rather superior to the TEOS CVD. By using OMCTS, a cyclic siloxane, films of the same or higher quality were obtained compared with those by TEOS, a silicon alcoxide. These high film qualities must be supported by electrical tests such as I-V characteristics and life tests of devices.

Application possibilities of the OMCTS CVD oxides to VLSI or ULSI are much greater than conventional CVD. These films will be intermetal dielectric films, or an underlayer for passivation. Doping the films will be tried for passivation and higher film cracking durability.

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Sealed Interface Local Oxidation by Rapid Thermal Nitridation

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ABSTRACT

Because of the presence of the bird's beak, local oxidation of silicon technology is no longer suitable for submicron circuits. Sealed interface local oxidation by rapid thermal nitridation is a new isolation technique which uses a rapid thermal nitride and a trilayer of nitride/oxide/nitride to limit the lateral diffusion of oxidant species under the nitride mask. Different rapid thermal nitridation conditions (surface preparation, time, temperature) are explored in order to obtain an efficient sealing nitride film. Masking-layer thicknesses are optimized in order to obtain a defect-free isolation structure with a bird's beak length shorter than 0.15 µm for a 0.7-µm-thick, as-grown field oxide. The process is then characterized on submicron complimentary metal oxide semiconductor devices.

Local oxidation of silicon (LOCOS) (1) is the dominant isolation technology for large-scale integrated circuits. This technology uses a deposited film of silicon nitride on a thin layer of buffer oxide as an oxidation mask. But this kind of selective oxidation is limited in submicron technologies by the lateral diffusion of oxidizing species under the nitride mask. The transition region from thin oxide to thick oxide, commonly known as the "bird's beak," is enhanced by the presence of the buffer oxide. With high nitride thicknesses the bird's beak length can be reduced, to the detriment of the good crystalline quality of the silicon substrate. Several new processes have been proposed to overcome the mask encroachment of the bird's beak. Among them, the sidewall masked isolation technique (2-4), which uses sidewall spacers to inhibit lateral oxygen diffusion under the active area, has been proven to suppress the bird's beak. Unfortunately, this technique is rather sensitive to dislocation generation near the vertical sidewalls. Another technique (5, 6), which consists of introducing an extra layer of polysilicon between the nitride and the buffer oxide in the LOCOS process, can provide a short bird's beak (in the range of 0.1 µm to 0.2 µm), without introducing defects in the silicon substrate, but it creates a nonisoplanar structure.

In a sealed interface local oxidation (SILO) process (7, 8), the buffer oxide is completely eliminated and the nitride film is directly sealed to the silicon surface. The sealed nitride film can be achieved by different methods: low-pressure chemical vapor deposition (LPCVD) (9), ion implantation (10, 11), or plasma-enhanced thermal nitridation (12). In our SILO process, rapid thermal nitridation (RTN) on bare silicon and a subsequent LPCVD of nitride are achieved to form an efficient sealing layer. An oxide and a second nitride are then deposited in order to achieve an efficient lateral oxidation resistance mask.

Rapid thermal nitridation is studied in detail, including nitridation kinetics for different cleaning treatments before RTN and different nitridation temperatures. The influence of respective nitride/oxide/nitride thicknesses on bird's beak length and dislocation generation is investigated. All these results give process parameters which can provide a shorter bird's beak length without induced defects in the silicon substrate. The SILO process has been implemented in complete submicron complimentary metal oxide semiconductor (CMOS) technologies. Electrical results are then discussed.

Experimental

Sample preparation.—The sealing nitridation achieved in a lamp-heated thermal annealer (ADDAX Technologies) under pure ammonia and atmospheric pressure. Three different pretreatments are explored: no cleaning before RTN step (native oxide is still at the silicon surface during nitridation); HF cleaning just before RTN (1 h delay maximum); and HF cleaning + rapid thermal oxidation (20 s at 1000°C under O2 in order to grow 35 Å of silicon dioxide). Nitridation kinetics are studied at different temperatures: 950, 1000, and 1200°C. The LPCVD tech-

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