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A new surface treatment involving the spin-coating of ethanol on a substrate prior to O_3-tetraethylorthosilicate (TEOS) deposition by atmospheric pressure chemical vapor deposition (APCVD) was found to be very effective for improving the gap-filling properties and film quality. The deposited film has a flow-like surface shape, and can be used to fill trenches of 0.3 μm width and 1.2 μm depth, which could not be filled by conventional O_3-TEOS APCVD. The effects of surface treating by some other organic solvents are also reported and a possible mechanism is presented.

1 Introduction

A notable trend of LSI chips in recent years is the multiplication of metal wiring from single-layer to multi-layer, all reflecting the increasing density of transistors. And, the formation of insulating films in the multi-layered wiring calls for the following three requirements so as to reduce the irregularities of underlayer geometry: (1) excellent capability for filling deep trenches on the underlayers, (2) relaxation of gaps between the trenched portion and untrenched portion with the formation of insulating films, and (3) formation of high quality insulating films with low moisuture content to insure the corrosion resistance of wiring.

In the past the main source of insulation surface coating for LSI wires was SiO_2 film made by plasma enhancement chemical vapor deposition (P-CVD) or atmospheric pressure chemical vapor deposition (APCVD). Increased surface irregularities resulting from submicron LSIs, however, have made it increasingly difficult to fill wiring trenches completely with these films. In order to solve this problem, the application of laminated films is being considered, in which an O_3-TEOS*** film is formed first by depositing on the wiring a P-TEOS SiO_2 film with relatively good film quality and coating geometry, and then by subjecting this film to a plasma treatment.[1-3] This plasma treatment is performed to eliminate the underlayer dependency**** of the O_3-TEOS film.[4-6] When this process is applied, it becomes possible to fill wiring gaps with as aspect ratio***** of up to approximately 2.[7] Presented in this paper is O_3-TEOS film deposition using an ethanol pre-treatment as a method for filling an insulating film between wiring gaps with an aspect ratio of greater than 4 to endow devices with ever finer geometry.[8,9]

In addition to using an underlayer of P-TEOS film, the gap-filling properties and film quality of a O_3-TEOS SiO_2 film are examined for thermal SiO_2 films as well, and cases are evaluated in which ethanol solvent molecules were adsorbed to the underlayer by the ethanol treatment. Furthermore, the existence of voids (micro-

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*** TEOS (tetraethylorthosilicate, $Si(OC_2H_5)_4$): TEOS gas is resolved by plasma into SiO_2. An O_3-TEOS SiO_2 film reacts with O_3, becoming SiO_2.

**** Underlayer dependency: a phenomenon in which the deposition speed of an SiO_2 film to be grown on the underlayer is different between Al and SiO_2 films.

***** Aspect ratio: aspect ratio r is defined as $r = b/a$, where a is the trench width and b is the depth.

scopic depletion of a film) in a O_3-TEOS SiO_2 film and the resulting surface irregularities are observed.

2 Experimental

Shown in **Fig. 1** is a process sequence, in which an SiO_2 film to serve as an underlayer is deposited on a 6″ Si substrate, 3 cm^3 of an organic solvent is then dropped on to it after increasing the rotation speed to 2 000 rpm, and spin coating and spin drying (at room temperature) are performed. After spin drying, the substrate is taken out of the spin-coater for deposition of an SiO_2 film by means of O_3-TEOS CVD apparatus.

Si substrate
↓
Deposit plasma-TEOS SiO_2 film (underlayer)
or
Formed thermal SiO_2 film (underlayer)
↓
Spin coat (Spin underlayer)
↓
Pour and spread ethanol
↓
Spin dry
↓
Deposited O_3-TEOS SiO_2 film

Fig. 1 Coating process of Si substrate

2.1 Film Deposition Apparatus and Deposition Conditions

Figure 2 shows the Alcan-Tech APT-4800 O_3-TEOS CVD apparatus that was used. A particular feature of the apparatus is the dispersion head with slit gas nozzles arranged in parallel that moves transversely to improve the uniformity of deposition rate. Another feature of the apparatus is that the Si substrate is positioned facing downward to reduce the possibility of particles being adsorbed to its surface. **Table 1** shows the O_3-TEOS SiO_2 deposition conditions for the apparatus: temperature, 413°C; O_3 concentration, 120 g/Nm^3; TEOS bubbling N_2, 1.7 slm (bubbling temperature = 65°C); carrier N_2, 18 slm. Under the conditions, O_3 becomes about 5% of the O_2 generated.

2.2 Underlayers and Organic Solvents for the Underlayer Treatment

As the underlayer for an O_3-TEOS SiO_2 film, a plasma TEOS SiO_2 film and a thermal SiO_2 film were formed (thermal SiO_2, for 30 min in O_2 gas at 950°C). The plasma TEOS SiO_2 film was used as the underlayer sample to eliminate any underlayer dependency for the O_3-TEOS SiO_2 film. Three levels of plasma TEOS SiO_2 film, each having a different deposition temperature and impressed frequency, were used as shown in **Table 2**. Conditions 1, 2 and 3 were used in three independent types of apparatus. The thermal SiO_2 film was used to simulate the case of an O_3-TEOS SiO_2 film being used as the first inter-layer insulating film on an underlying thermal SiO_2 film after a transistor gate had been formed on it. As underlayer treatment reagents, such solvents as methanol, IPA, acetone, diethylether, cyclohexane, and TEOS were tested as well.

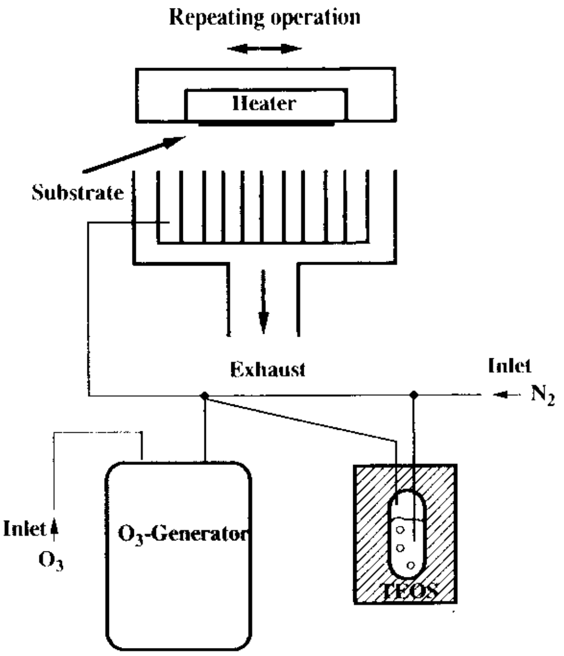


Fig. 2 O_3-TEOS CVD apparatus

Table 1 O_3-TEOS SiO_2 film deposition conditions

Temperature	(℃)	413
O_3 concentration	(g/Nm^3)	120
TEOS bubbling N_2	(cm^3/s)	28
Bubbling temperature	(℃)	65
Carrier N_2	(cm^3/s)	300

Table 2 Plasma-TEOS SiO_2 film deposition conditions

		Condition 1	Condition 2	Condition 3
Temperature	(℃)	350	400	420
TEOS flow rate	(cm^3/s)	3.0	3.8	2.3
O_2 flow rate	(cm^3/s)	67	5.8	35
Pressure	(Pa)	293	667	533

3 Gap-Filling Properties and Film Quality of an O_3-TEOS SiO_2 Film Using an Ethanol Pre-treatment

3.1 Cases in a Plasma TEOS SiO_2 Film Used as the Underlayer

3.1.1 Gap filling properties and film quality

The SEM photographs in **Photo 1** show the gap-filling geometry of an O_3-TEOS SiO_2 film in cases of a plasma TEOS SiO_2 film being used on the wiring pattern as an underlayer. The photographs show that the ethanol pre-treated O_3-TEOS SiO_2 film had superior gap-filling properties, providing a film with a smooth top surface. Photo 1 (a) shows an underlayer before the formation of O_3-TEOS; this underlayer consists of a 0.3 μm plasma TEOS SiO_2 film deposited on a wiring pattern having a trench of 1.0 μm in depth, 0.5 μm in width, and 1.0 μm in pitch, which provides an aspect ratio as large as 4 for the trench before the O_3-TEOS SiO_2 film is formed. (b), (e) and (d) show the gap-filling characteristics of an O_3-TEOS SiO_2 film without the ethanol pre-treatment. (b) and (c) showing the gap-filling progress indicate that an O_3-TEOS SiO_2 film was deposited with uniform thickness on the underlayer, resulting in poor gap filling and a film with considerable surface roughness and coarseness. (d) showing the surface after gap filling indicates the formation of voids, a sign of low film quality and imperfect filling of wiring gaps. (e), (f) and (g) show the gap-filling characteristics of an ethanol pre-treated O_3-TEOS SiO_2 film. (e) and (f) showing the gap-filling progress indicate that the O_3-TEOS SiO_2 film has a smoothly flowing surface. It is apparent from (g), showing the surface after gap filling, that there are no voids in the O_3-TEOS SiO_2 film and that the wiring gaps have been completely filled.

These results established that an ethanol treatment of a plasma TEOS SiO_2 film allows an O_3-TEOS SiO_2 film to flow evenly into wiring gaps to thus form a good, void-free insulating film.

3.1.2 Pre-treatment with different organic solvents

An evaluation of the gap-filling properties of O_3-TEOS SiO_2 films treated with solvents other than ethanol confirms that the latter was far superior to the others.

Photo 2 shows the gap-filling characteristics of O_3-

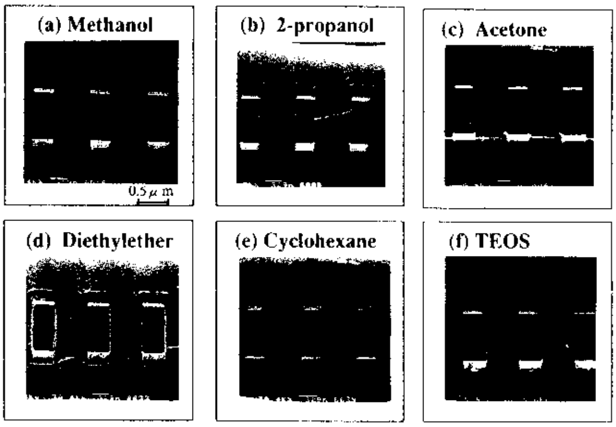


Photo 2 Cross section of O_3-TEOS films with treatment by other organic solvents (Samples were lighly etched for several seconds with 1:20 BHF)

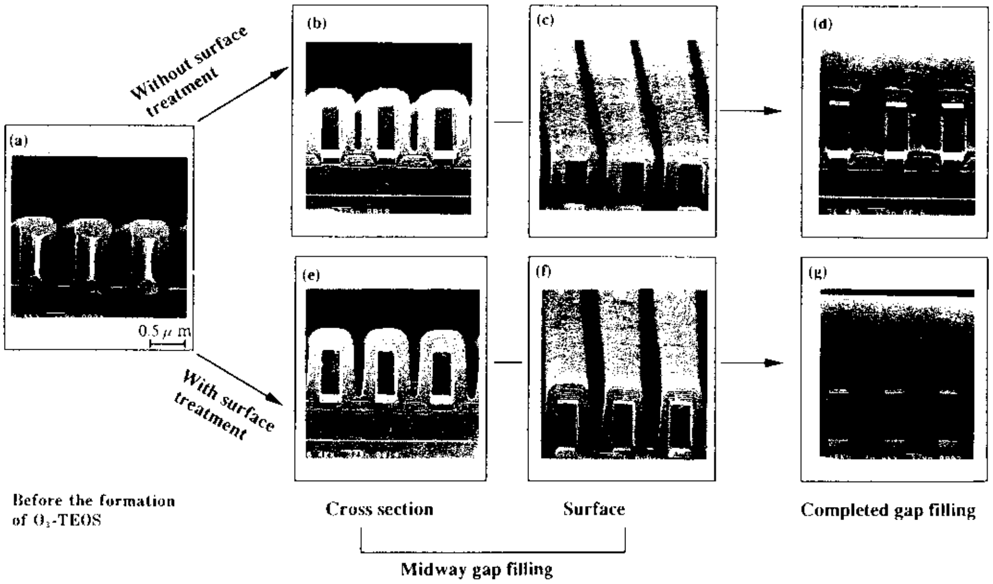


Photo 1 Cross section and surface of O_3-TEOS films with and without ethanol surface treatment (Samples were lightly etched for several seconds with 1:20 BHF)

TEOS SiO_2 films after pre-treating with organic solvents other than ethanol a plasma TEOS SiO_2 film deposited as an underlayer on the wiring pattern. Photo 2 (a), the cross-section of a methanol pre-treated O_3-TEOS SiO_2 film, shows that voids in the film were not eliminated, and that filling between the wiring gaps was worse than in the case of an untreated film. (b), (c), (d), (e) and (f) respectively showing the case when IPA, acetone, diethylether, cyclohexane, and TEOS was used, show that voids were formed in the O_3-TEOS SiO_2 film and that filling between the wiring gaps was also imperfect.

3.1.3 Effect of plasma TEOS SiO_2 film quality

Photo 3 shows the gap-filling properties and film quality of O_3-TEOS SiO_2 films in the cases of the underlying plasma TEOS SiO_2 film being formed under three different conditions of deposition temperature and frquency of the impressed voltages. Photo 3 (a) and (d) represent the cases for which the O_3-TEOS SiO_2 film was formed under condition 1 in Table 2, (b) and (e) under condition 2, and (c), (f) and (g) under condition 3. In these cases, (a), (b) and (f) show an untreated underlying plasma TEOS SiO_2 film, (d), (e) and (f) show one with an ethanol pre-treatment, and (g) shows the one with the plasma NH_3 treatment. These photographs confirm that, irrespective of the deposition conditions of the underlying TEOS SiO_2 film, the untreated underlayer tended to result in a poor O_3-TEOS SiO_2 film, including voids in the film, and that the gap-filling properties were not improved either. On the other hand, it can be seen from the photographs that the film quality and gap filling of the O_3-TEOS SiO_2 film was improved irrespective of the deposition conditions for the underlying plasma TEOS SiO_2 film. While the plasma NH_3 treatment of the underlying plasma TEOS SiO_2 film improved the quality of the O_3-TEOS SiO_2 film, no appreciable improvement is apparent in the gap-filling properties. From these result, it was confirmed that, when a plasma TEOS SiO_2 film is being used as an underlayer, quite a wide processing margin is provided by the ethanol treatment, and that an effective tretment can be obtained even with a TEOS SiO_2 film deposited under different conditions.

3.2 Case in a Thermal SiO_2 Film Used as the Underlayer

Photo 4 shows the gap-filling capability of an O_3-TEOS SiO_2 film with a thermal SiO_2 underlayer on a poly-Si wiring pattern. The underlayer consist of a 250-Å-thick thermal SiO_2 film deposited on a trench pattern of 0.5 μm in depth, 0.3 μm in width, and 0.6 μm in pitch. The aspect ratio between the wiring gaps before the O_3-TEOS SiO_2 film was formed is quite high at about 2. Photo 4 (a) shows the case of the underlying thermal SiO_2 film being untreated; however, as in the case shown in Photo 1 (c), it was found that the surface of the O_3-TEOS SiO_2 film was extremely irregular. Photo 4 (b), the result obtained after an ethanol pre-treatment of the underlying thermal SiO_2 film, confirms that the quality of the O_3-TEOS SiO_2 film was substantially better. It was also confirmed that the gap-filling properties were substantially better although minor key holes remain between the wiring gaps. Photo 4 (c), showing the appearance of (b) after 30 minutes' annealing at about 700°C, indicates that quite a smooth surface could be achieved.

When a thermal SiO_2 film is used as an underlayer, it is assumed that an O_3-TEOS SiO_2 film is applied as the first inter-layer insulator near the transistor gate. Since, in this case, it is difficult to apply a plasma treatment to

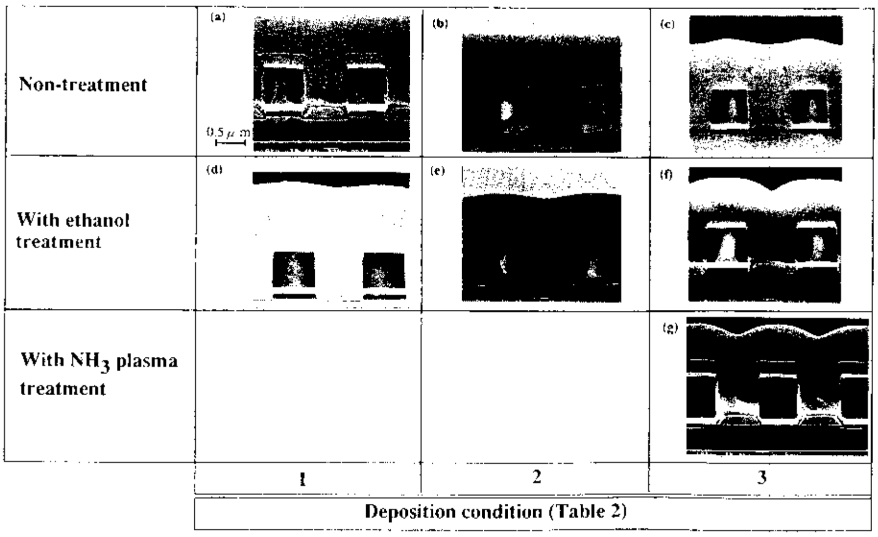
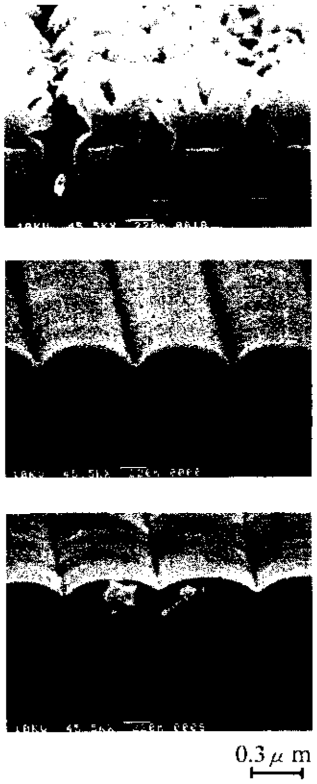


Photo 3 Dependence of the gap-filling properties and film quality of an O_3-TEOS SiO_2 films on the plasma-TEOS-SiO_2 film deposited under different conditions


(a) Non-treatment

(b) With ethanol treatment

(c) After annealing of (b)

Photo 4 O_3-TEOS SiO_2 film deposited on thermal SiO_2

the underlying SiO_2 film without causing electrical damage, the application of the non-damaging ethanol treatment to the underlayer is quite effective.

4 Mechanism for Improvement of the Gap-Filling Properties of O_3-TEOS SiO_2 Films Using an Ethanol Pre-treatment

4.1 Analysis of the Ethanol-Treated Underlayer Surface by High-Sensitivity Reflection FTIR (RAS)

Ethanol treatment improved the gap-filling properties and quality of O_3-TEOS SiO_2 films. In order to clarify the mechanism for this, the surfaces of ethanol-treated substrates were examined by means of high-sensitivity reflection FTIR (RAS).

Figure 3 shows the differential spectrum obtained after subtracting the high-sensitivity reflection FTIR spectrum of an ethanol-treated plasma TEOS SiO_2 underlayer from that of an untreated one. C-H bond-stretching vibration peaks are apparent at 3 020 cm^{-1}, 2 930 cm^{-1} and 2 860 cm^{-1}.

These results lead us to believe that the ethanol treatment caused ethoxyl and the like to be chemically adsorbed to adsorption sites on the surface of the underlying plasma TEOS SiO_2 film.

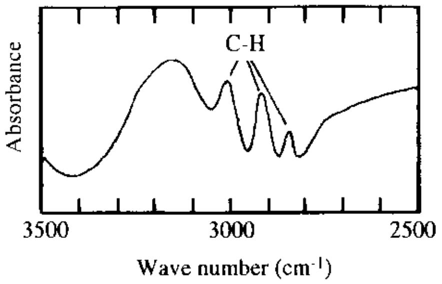


Fig. 3 High-sensitivity reflection FTIR spectrum of an ethanol-spin-coated substrate subtracted from that of an untreated substrate

Accordingly, we consider that the quality of an O_3-TEOS SiO_2 film was improved and the wiring gap-filling properties enhanced mainly because treating the underlayer with ethanol or methanol caused these solvent molecules to be adsorbed to the underlayer surface. Based on this assumption, a mechanism will next be considered.

4.2 Mechanism for Gap Filling by an O_3-TEOS SiO_2 Film Using an Ethanol Pre-treatment

Figure 4 shows the mechanism by which an ethanol pre-treatment would improve the gap filling properties and quality of an O_3-TEOS SiO_2 film. A case will be considered of a thin plasma TEOS SiO_2 film being formed on an irregular wiring surface. Silanol sites (represented by A's in Fig. 4) cover most of the plasma TEOS SiO_2 film surface, leaving only a few areas without them. On the other hand, the atmospheric CVD reaction between O_3 and TEOS forms several types of O_3-TEOS SiO_2 films, of which the most highly active films with a short lifetime are rapidly adsorbed to the silanol adsorption sites. In this way, since a highly active film would form an O_3-TEOS SiO_2 film without flowing into the trenches, the film geometry conforms to the underlayer geometry, resulting in poor gap-filling properties.

The formation of voids in a film will next be considered. While the deposition speed is low in the areas where there is no silanol, it is high where there is silanol, and this difference in deposition speed causes voids to develop in a film; in other words, the difference in deposition speed is responsible for voids in the O_3-TEOS SiO_2 film. On the other hand, when the underlayer has been treated with ethanol, the underlying silanol sites are filled with ethoxyl and the like (represented by R's in Fig. 4), and the underlayer surface becomes covered with ethoxyl. This can be expected from the results of high-sensitivity reflection FTIR shown in Fig. 3. In this way, the highly active films with a short lifetime cannot be adsorbed to the underlayer, and form oligomers by a repeated dehydrated condensation reaction between the films (polymers). The oligomers, which have a long lifetime, would continue filling the

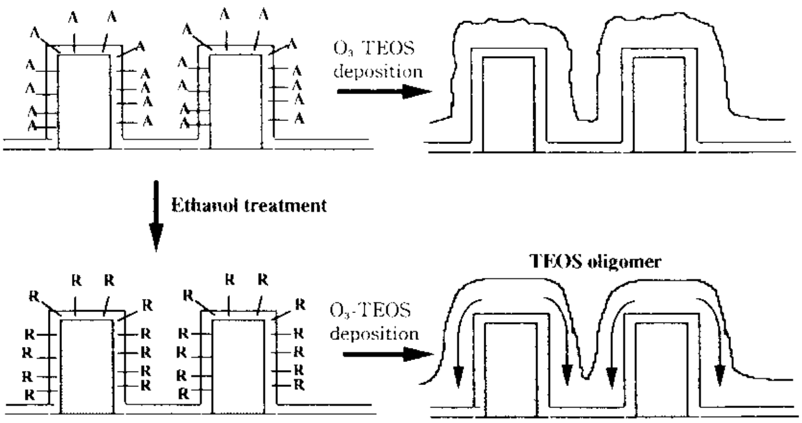


Fig. 4 Mechanism of gap filling with and without ethanol surface treatment (A, OH site; R, OC_2H_5 site)

gaps as they flow over the surface. The foregoing is the currently logical mechanism for the formation of an ethanol pre-treated O_3-TEOS SiO_2 film.

5 Conclusions

When forming an SiO_2 film by means of atmospheric O_3-TEOS CVD, the gap-filling properties and quality of the film can be improved by pre-treating the underlayer with an organic solvent. Conventional underlayer pre-treatment, which primarily uses plasma, is limited to inter-layer insulating films separated from the substrates because of possible damage by the plasma. In addition, it is known that changes inside the chamber make such a plasma treatment unstable. On the other hand, the ethanol treatment described in this report contributed to a damage-free improvement of film quality and enhanced filling of trenches with a high aspect ratio of more than 4. In addition, since the ethanol treatment does not require the use of a deposition chamber, adverse effects on the formation of the underlying plasma TEOS SiO_2 film do not have to be considered.

The authors propose that the new, inter-layer insulating film planarization method described here is one of the important future techniques for forming a highly reliable multi-layer wiring pattern in future processes involving very large-scale integration.

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