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Liquid Phase Oxidation Employing O Atoms Produced by Microwave Discharge and $Si(CH_3)_4$

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Silicon oxide CVD at lower temperature than 0°C has been studied employing reaction of oxygen atoms generated by the separate microwave discharge with $Si(CH_3)_4$. The deep Si grooves are filled and finally planalized with the oxide film at liquefaction temperature of $Si(CH_3)_4$. Partially oxidized TMS, which may condense first in the narrowest groove bottom, is oxidized completely, then the groove is fully buried. Although the film involves C-H bonds, it shows similar etch rate with BHF solution to usual CVD SiO_2 film.

1. Introduction

Continuous shrinkage of VLSI device dimension requires high aspect ratio process such as the trench capacitor and the multi-layer metalization. However, most of film deposition techniques produce overhang step coverage causing a void in the deep trench or the space between lines. Planarization of substrate topography also becomes necessary for both multi level metalization and multi level resist process in submicron optical lithography. The nonconformable step coverage in the current CVD (e.g. LPCVD, plasma), which utilize diffusion limit process, results from the large solid angle for deposition species incoming to the corner of the step[1]. This problem is not substantially prevented as long as the deposition was performed mainly by the use of gas phase reactive species. In response to these problems, a photochemical CVD, in which step coverage is expected to be improved due to higher surface migration rate of deposition species[2], attracts considerable attention recently.

For these requirements, in the course of studying the CVD technology employing reaction of O atoms generated by the separate microwave discharge[3] with $Si(CH_3)_4$ (Tetramethylsilane ; TMS), it was found that the high aspect ratio Si groove was successfully filled and finally planalized with glass film at substrate temperature which was kept at liquefaction condition of TMS.

This paper reports the deposition characteristics, and discusses a possible deposition mechanism.

2. Experimental

Figure 1 shows the schematic diagram of experimental apparatus. Oxygen (O) atoms, which are generated by a 2.45 GHz microwave discharge, were transported to a reaction chamber through a quartz tube. Simultaneously, TMS was introduced into the reaction chamber. The substrate cooling was controlled by N_2 gas through a SUS tube immersed in liquid nitrogen. All experiments were carried out after the reaction chamber had been exhausted to a

pressure below 10^{-5} Torr. The total pressure was kept at 2 Torr, and the partial pressure of TMS was 0.3 Torr.

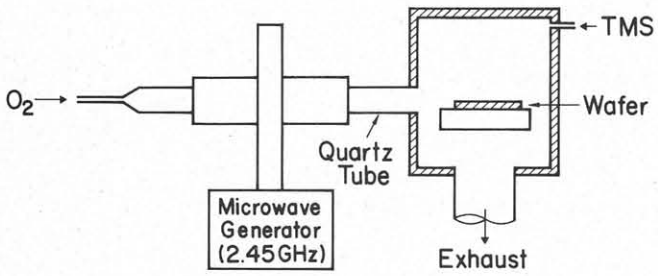

Fig. 1. Schematic diagram of experimetal apparatus

3. Result and Discussion

3.1 Deposition Profile

The film deposition rate increases with decreasing substrate temperature, as shown in the left hand side of Fig.2, while the overhang feature due to low surface migration rate of adsorbate was observed. This result suggests that decrease in substrate temperature leads to enhancing the adsorption rate of deposition species. In anticipation of higher deposition rate, the substrate temperature was reduced further up to liquefaction temperature of adsorbates. As a result, as if the liquid materials flow into the groove just like water. The groove was fully refilled with the deposited film, as shown in the right hand side Fig.2.

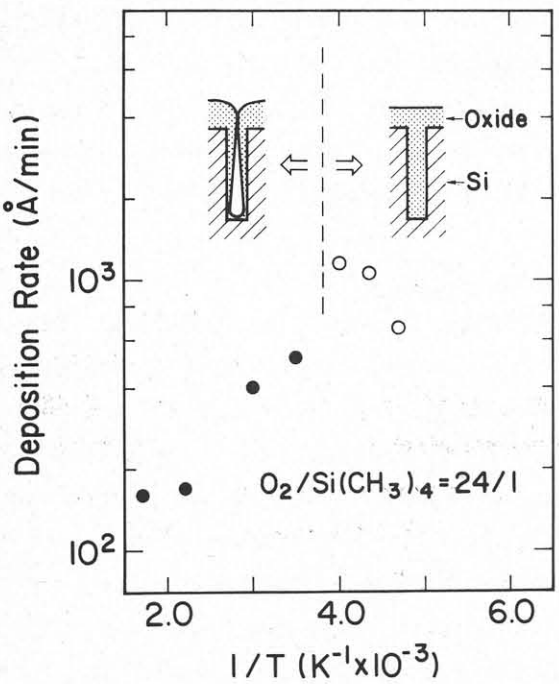

Fig. 2. Deposition rate vs. Substrate temperature

Figure 3 shows the deposition profile for various opening sizes as a function of deposition time. First of all, the film was buried in the groove with narrowest opening size (Fig.3(a)). However, as the deposition time increases, the groove with large opening size was filled with the deposited film as if the liquid overflowed into the neighboring groove. Eventually, perfect planarization was achieved independent of the opening size (Fig.3(b)).

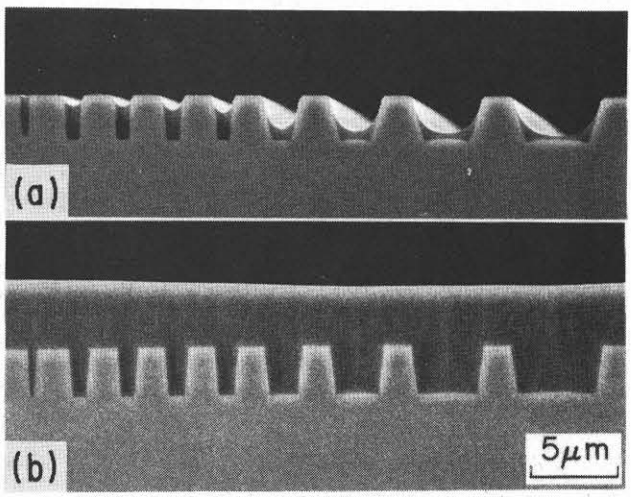

Fig. 3. Deposition profile for various opening sizes vs. deposition time

3.2 Possible deposition mechanism

At the substrate temperature below -20°C, transparent liquid-like materials were observed on the surface. This suggests that the oxidation process occurs in the liquid phase. In order to study the deposition mechanism in detail, the deposition profile was investigated as a function of deposition time. As shown in Fig.4(a), the deposition species, which exist in the vicinity of the trench bottom, condensed first at the bottom corners

because the equiblirium vapor pressure in the bottom corner is lower than that in the plane surface[4]. The deposition profile reveals that the angle of contact between the condensed materials and Si surface is small. This result implies good wetting of the condensed materials for Si surface. Consequently, the condensed materials migrate readily on the Si surface, and stay stably at the corner so as to minimize surface free energy. Thus, the film grows as keeping the initial profile (Fig.4(b,c)). Since the condensed materials selectively always flow into the lowest hollow on the whole growing film surface, finally, the perfect planarization was achieved, as shown in Fig.3(b).

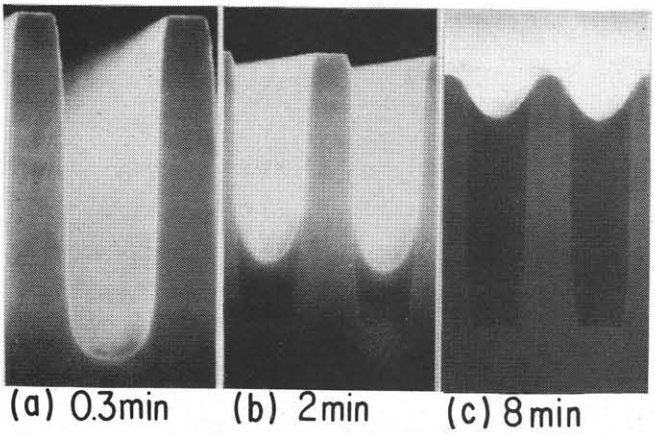

Fig. 4. Variations in deposition profile for deposition time

In order to investigate how the oxidation proceed, the following experiments were carried out. From the phase diagram, the precursors for condensation are considered to be partially oxidized species of TMS such as hexamethyldisiloxane ($(Si(CH_3)_3)_2O$;HMDS). After HMDS was condensed on the Si surface at the substrate temperature of -40°C, the residual HMDS in the gas phase, which was not condensed yet, was exhausted by vacuum pump for 5 min. Thereafter, the liquefied HMDS was exposed to O atoms for 10 min. As a result, only the upper part of the groove changed to solid film, as shown in Fig.5. HMDS which filled the groove was vaporized when the sample was taken to atmosphere for SEM observation. In other words, the condensed materials could be considered to be oxidized to change into the solid film from the bottom surface gradually.

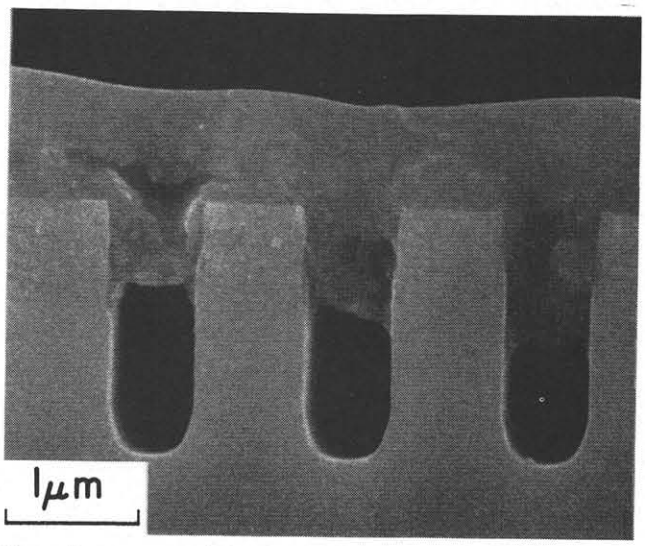

Fig. 5. Deposition profile after previously condensed HMDS was oxidized by O atoms

3.3 Film property

The film etch rate with BHF solution showed 7200 A/min for as deposited film and the etch rate decreased to 1700 A/min by O_2 annealing for 60 min at 300°C. Thus, this annealing decreased the film thickness by about 15 %.

Next, the changes in infra-red absorption spectra before and after annealing were examined. As shown in Fig.6(a), the as-deposited film consists of $Si-CH_3$(1273,849 cm^{-1}), Si-O(1064 cm^{-1}) and O-H(3400 cm^{-1}) groups. This spectrum is similar to that for polymerized film obtained by plasma CVD of HMDS[5]. In addition, unidentified peak appears in the vicinity of 880 cm^{-1}, which is considered to be Si-H deformation mode[6]. However, another specific peak at 2200 cm^{-1}, which results from Si-H streching mode, was not detectable in the present film. Therefore, unidentified peak can be assumed to be

related to Si-OH streching mode[7] or Si_2O_3[8]. After annealing, the absorption intensity due to $Si-CH_3$ group changed scarcely, as shown in Fig.6(b). On the other hand, significant change was observed in Si-O, Si-OH or Si_2O_3 groups. The decrease in Si-OH absorption intensity suggests that the OH groups were removed by dehydration with O_2, which results in the decrease in effective number of O atoms which surround Si atom. Actually, the wavenumber shift of Si-O from 1064 to 1047 cm^{-1} supports these speculations[9]. These considerations suggest that the decrease in the film etch rate is considered to be attributed to the densification.

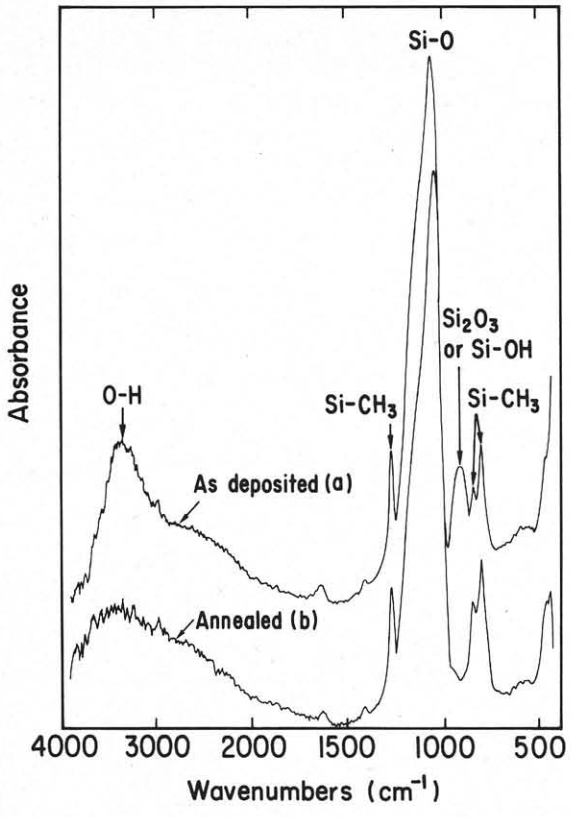

Fig. 6. Variations in infra-red spectra before and after O_2 anealing

4. Conclusion

Ultra-planarization technique has been developed employing reaction of O atoms produced by microwave discharge with $Si(CH_3)_4$. The substrate temperature was lowered to a dew point of partially oxidized species of TMS such as HMDS. The condensed materials readily migrate on the Si surface, and flow into hollow space because of good wetting for Si surface. Consequently the high aspect ratio groove was perfectly filled with oxidation film of the adsorbates. The film consisted of methyl group containing oxide film as well as plasma polymerized film from HMDS. For VLSI applications, further investigation has to be performed.

References

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