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Conformable CVD of SiO_2 into Deep Trench Using the Digital Method

H. Sakaue, M. Nakano, T. Ichihara and Y. Horiike

Department of Electrical Engineering, Hiroshima University,

Shitami, Saijo, Higashi-Hiroshima 724, Japan

The extraction reaction of hydrogen in TES with hydrogen radicals has achieved conformable CVD of a organic Si film for 60%H_2 in TES at 250 °C. The feature results from high viscosity nature of the film which includes C_xH_y groups produced by dominant surface reaction of TES/hydrogen radicals. To fill the high quality SiO_2 film into a deep trench, the digital CVD which was carried out by repeating a cycle of the conformable deposition of the Si film, then its oxidation was studied. The SiO_2 film which was deposited at 250 °C and in initial thickness per cycle of 5A at 1 sec oxygen pulse offered low concentration of organic species, thus relatively low BHF etch rate.

1. Introduction

For the multilevel metallization down to lower submicron sizes in ULSI's, high insulation resistance is required for insulators filling between metal wires on same level as well as the upper and lower level. Much efforts are made for development of the TEOS (Tetraetylorthosilicate)/O_3 reaction system to fill SiO_2 film into the high aspect trenches and holes[1]. Although the reaction mechanism of the conformable CVD using TEOS/O_3 is not understood well, oligomers of $\{Si\text{-}(OC_2H_5)_x\}_y$ are considered to be generated in the gas phase, condensing uniformly on the topological surface[2]. On the other hand, a multilayer insulator such as stacked SiO_2/Si_3N_4 is expected as a film with high integrity for insulation. TEOS which involves originally oxygen atoms can provide only the SiO_2 film. Therefore, at first TMS (Tetramethylsilane; $Si(CH_3)_4$) or TES(Trietylsilane; $SiH(C_2H_5)_3$) without oxygen bonds was investigated regarding a possibility that the reaction of these gases with oxygen radicals generates some oligomers. However, the overhang features were observed for a variety of conditions for gas composition, pressure and temperature. Hence, a TES/H_2 reaction system has been studied. In this paper, Si like film deposition is developed employing this reaction, and then the digital CVD[3] which repeats a process consisting of first this film deposition and following its oxidation is described.

2. Result and Discussion

2.1. TES/H_2 Reaction System

A possibility that hydrogen atoms in TES was extracted by a reaction with hydrogen radicals to polymerize Si based materials was investigated on the basis of high binding energy of 104.2 kcal/mol in the hydrogen bonds. TES and hydrogen radicals produced by a remote H_2 plasma were introduced simultaneously to a Si wafer set on a temperature controlled substrate in a reactor through each quartz tube see Fig. 3. Total pressure was 1.0 Torr. The deposition temperature was 250 °C. Microwave power of H_2 discharge in a quartz tube was 60W. Figure 1 shows deposition rate of films and step coverage as a function of H_2 concentration in TES. Any film was not formed with TES alone, while the deposition occurred rapidly with increasing H_2 in TES and also a value of B/A ratio of step coverage became almost unity. Here A and B expressed thickness at the plane

of the films and lateral thickness at the upper edge in the trench, respectively.

For the more H_2 addition, step coverage degraded rapidly after deposition rate reached a maximum. In the FTIR measurement of the films varying H_2 concentration in TES, $Si-C_2H_5$ (1250cm^{-1}), CH_2 (2926cm^{-1}) and CH_3 (2962, 2872cm^{-1})[4] bonds were observed at relatively lower H_2 concentration of 40 and 60%, while these organic species were not observed at 80% H_2 concentration.

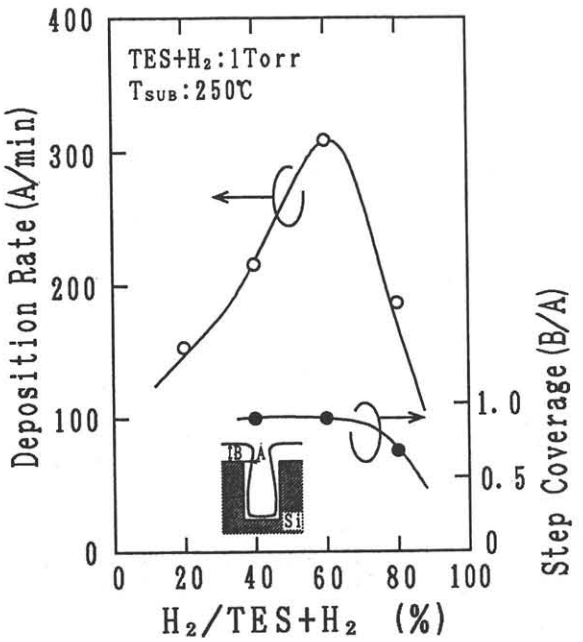
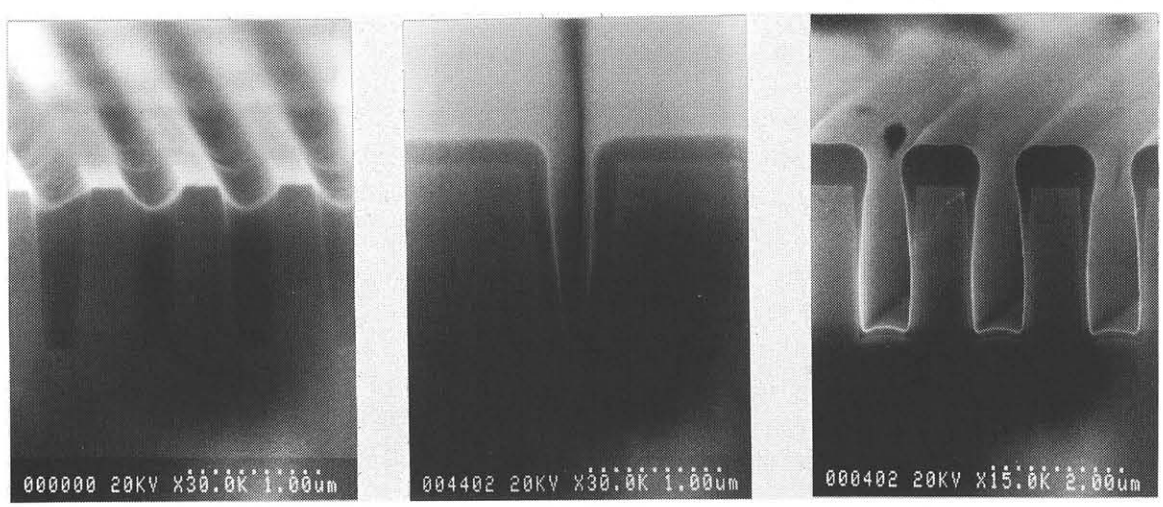


Fig.1 A deposition rate of films and step coverage vs. H_2 concentration in TES.

A drastic variation was found in features filled at room temperature shown in Fig.2 (a,b,c). A trench was filled like liquid from the bottom at 40% H_2 concentration, (a). With increasing H_2 concentrations, the step coverage changed from conformable at 60%, (b) to overhang features at 80%, (c). When the deposition temperature was elevated to 100 °C at 40% H_2 concentration, a conformable feature like (b) was obtained. In addition, absorbance of specific 2962-2872 cm^{-1} in the FTIR spectrum for these films increased with decreasing temperature and H_2 concentration.

An in-situ FTIR measurement in the gas phase was also carried out for the reaction systems of TES/hydrogen. In the experiment, TES and H_2 with or without discharge were introduced by quartz tubings to a reactor whose both sides were shielded with a Si wafer window set in an optical path of infrared light. Appreciable differences between both systems were not detected for a widely changed conditions of pressure and gas composition. This result is likely to imply that the reaction of adsorbed TES with hydrogen radical occurs predominantly on the surface. Although the presence of oligomers should be detected by a chromatography, it



(a) (b) (c)

Fig.2 Cross-sectional SEM micrograph of the features filled at room temperature in a trench at 40%,(a) 60%,(b) and 80%,(c) H_2 concentration.

cannot be now concluded that these films including organic species originate from oligomers generated in a gas phase.

These changes of the filling profiles are considered as follows according to above results: In Fig. 2 (a), the low viscosity film involving organic species such as CH_2 and CH_3 with high concentration condenses first at trench bottom edges with lowest equilibrium vapor pressure[5] and then is filled like water poured into a glass. For relatively high viscosity film obtained at 60% H_2 concentration, surface tension makes conformable on the trench sidewall as shown in (b). The source of the degraded step coverage for the higher concentration of H_2 might be ascribable to production of an atomic Si dominant film as a result of extraction reaction of CH_2, CH_3 and C_2H_5 group, which reduces the surface migration. The more efforts should be made for the reaction mechanism and the film characteristics.

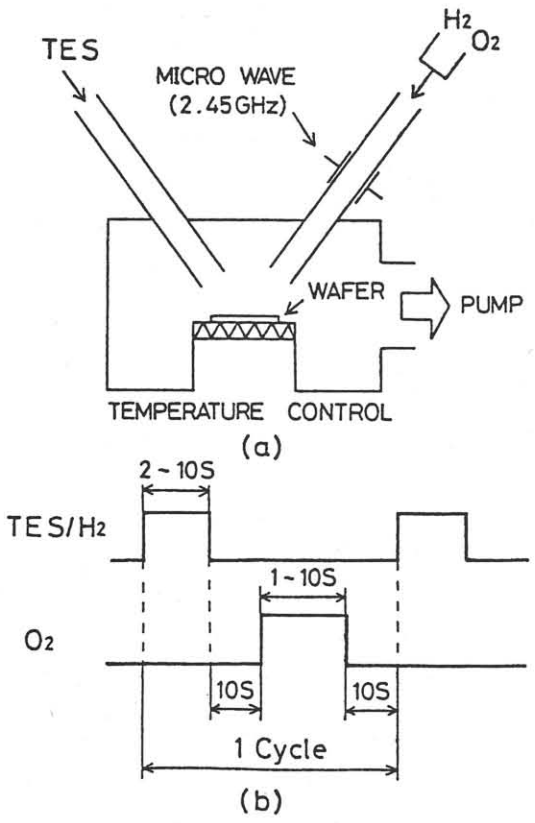


Fig.3 Schematic illustration of the experimental apparatus and time sequence of the introduction of gases.

2.2. Digital CVD of SiO_2

The layer-by-layer technique called by the digital CVD has been applied to oxidizing a lot of C_xH_y groups included in the TES/H_2 reaction film, fabricating high quality SiO_2 film. This method was carried out by repetitive reactions of first TES/hydrogen radicals and subsequently oxidation of this film with oxygen radicals generated from a remote microwave plasma of O_2. Figure 3 illustrates the experimental apparatus and time sequence of the introduction of gases. TES/H_2 and O_2 gases were introduced using a

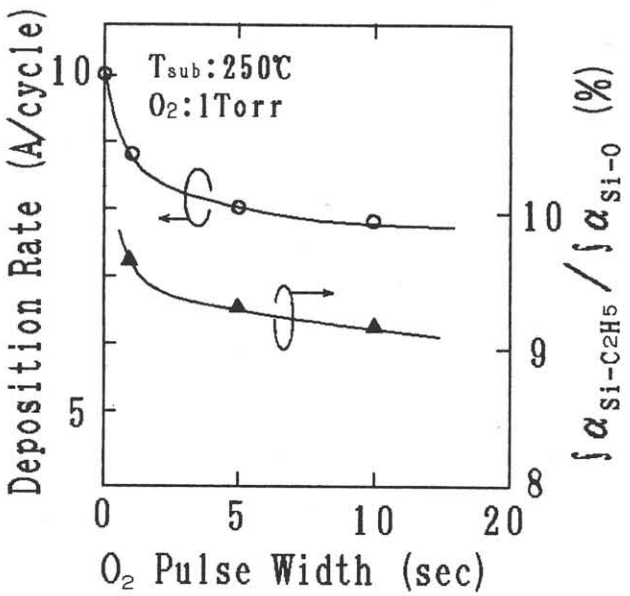


Fig.4 The deposition rate per cycle vs. O_2 pulse width, where the initial thickness of the layer deposited by TES/hydrogen reaction per one cycle is 10 A.

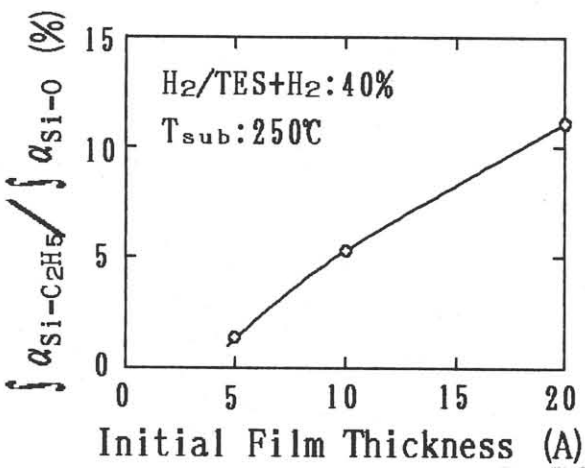


Fig.5 The ratio of $\int\alpha_{Si-C_2H_5}/\int\alpha_{Si-O}$ vs. initial film thickness of 5, 10 and 20 A.

piezo-valves and were alternately blown on a Si wafer in the reactor through quartz tubes. The reaction chamber was exhausted to 10^{-7} Torr before experiments and gases during deposition were evacuated by a rotary pump.

As shown in Fig. 4, the deposition rate per cycle decreases with O_2 pulse width, where the initial thickness of the layer deposited by TES/hydrogen reaction per one cycle is 10 A. O_2 gas was introduced manually because the piezo-valve was not used for long pulse discharge. Both film thickness and ratio of integral absorption coefficient of $Si-C_2H_5$ to Si-O ($\int\alpha_{Si-C_2H_5}/\int\alpha_{Si-O}$) in the FTIR spectrum decreased with O_2 pulse width. This drop characteristics demonstrate the removal of C_xH_y group due to oxidation by oxygen radicals, leading to integrity of SiO_2 film quality. Variation in the ratio of $\int\alpha_{Si-C_2H_5}/\int\alpha_{Si-O}$ as a function of initial film thickness of 5, 10 and 20 A were shown in Fig. 5. In this case, O_2 of 1 second pulse was introduced at 3 Torr using a piezo-valve. This demonstrates a reasonable result that the thinner thickness of the film is oxidized easily. The buffered HF (HF/H_2O = 1/50) etch rate was about 1000A/min for a film of initial thickness of 5A. However, the etch rate was 10 times higher than thermal SiO_2 with etch rate of 110 A/min. Much more improvement should be made for the high quality oxide. Accordingly, the filled SiO_2 feature into the deep trench has been achieved as shown a SEM micrograph in Fig. 6.

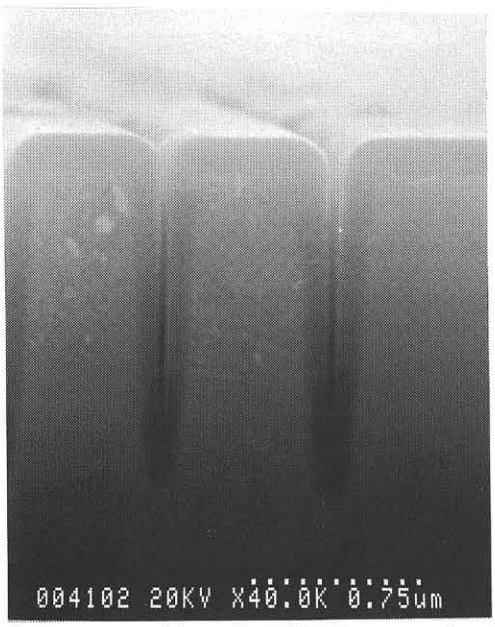


Fig.6 Cross-sectional SEM micrograph of the completely filled SiO_2 feature into the deep trench.

3. Conclusion

It was found that extraction of hydrogen in TES with hydrogen radicals generated by a remote plasma of H_2 led to conformable deposition of a $Si-C_xH_y$ film. Hence, the layer-by-layer CVD which is done by repeating one cycle consisting of this film deposition and its subsequent oxidation was developed for growing the SiO_2 films. The SiO_2 film of 5 A initial thickness deposited at 250 °C and 1 second oxidation demonstrated low concentration of C_xH_y groups and relatively low BHF etch rate. However, more efforts should be made for improvement of the film quality.

Acknowledgement

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