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Digital CVD of SiO_2

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Digital CVD method , in which one cycle consisting of deposition of microwave-discharged silane mono-layer and its subsequent oxidation is repeated, is developed for the formation of SiO_2 films. The deposition rate of 3 A/pulse is achieved by controlling the flow velocity of SiH_4 gas jet and the pulse width of O_2 radicals. The deposition species ejected with supersonic velocity into a high vacuum reactor fills successfully SiO_2 film into a trench.

1. INTRODUCTION

In usual plasma CVD technologies, the dominant gas phase species in the plasma have been degradated the step coverage to cause harmful voids in deep trenches and holes, which should be refilled by insulators or metals with high aspect ratio (depth/line-width). Therefore, in order to avoid such degradation and to realize the conformable CVD, it is of crucial importance to suppress a gas phase reaction and in turn to enhance a surface reaction.

To meet this requirement, a layer by layer process such as that has been studied in the atomic layer epitaxy (ALE) of GaAs and AlGaAs[1] and the cryogenic laser CVD[2] also should be applied to the insulator deposition. This report proposes a new digital CVD of SiO_2. In this method, SiO_2 film is deposited by repetition of one-cycle of silane radical and its subsequent oxidation with oxygen radical, which are generated by upstream microwave-discharges[3] of SiH_4 and O_2, respectively.

2. EXPERIMENTAL

Figure 1 shows a schematic illustration of the digital CVD apparatus. The SiH_4 (18.5%; He dilution) and O_2 gases, which flow by adding pulse signals on each piezo-valve set in two gas lines, are introduced independently into microwave (2.45 GHz) discharge portions. Then, upstream-excited silane and oxygen radicals are alternately blown upon a Si wafer into the reactor through a sloped nozzle tube and a straight (13 mmϕ) quartz tube. In order to restrain a drop of SiH_4 gas temperature due to an adiabatic expansion, and also to relax a velocity of its gas jet, a buffer tube equiped with a fin is connected to an outlet of the piezo-valve. The wafer temperature can

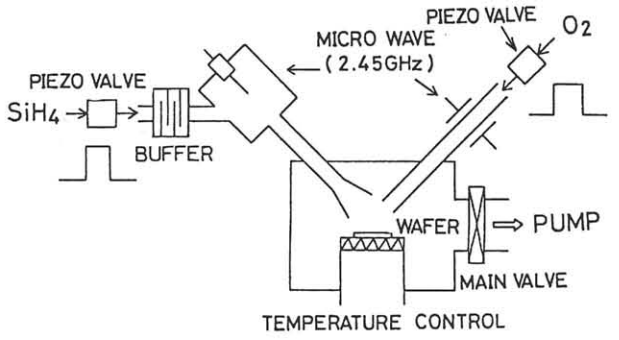


Fig.1 A schematic illustration of the digital CVD apparatus.

be controlled in the range from 400 °C to -20 °C. Both distances between these tube edges and a wafer surface are 40 mm. Flow pulse widths for SiH_4 and O_2 are 50 msec and 1-10 sec, and interval between both gas flows is 1 sec. During the deposition experiments, the reactor is evacuated by a turbo-molecular pump as keeping opening a main valve.

3. DEPOSITION PROPERTIES

First, the SiH_4 gas without a discharge was investigated. However, any films have been not obtained in the temperature range from 600 °C to -20 °C. Eventurely, SiH_x radical with a high sticking probability[4], which was generated by microwave discharge using a coaxial type waveguide, was obliged to be used, thus SiO_2 film was formed successfully at the room temperature (R.T). However, it was found out in the case without the buffer that a supercooled SiH_x radical was deposited locally on a wafer with high deposition rate of 40 A/pulse at R.T. Figure 2 shows the deposition profiles in the cases with and without the buffer. The W-shaped steap profile in the case without the buffer is improved greatly by this equipment. Figure 3 shows the SiO_2 film thickness as a function of the buffer temperature. As the gas temperature is increased, the film thickness is decreased, while this film area enlarges, because of lowering of sticking probability with SiH_x radicals.

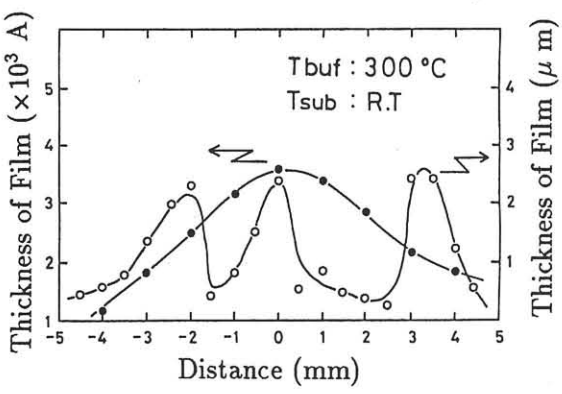


Fig.2 Deposition profiles in the cases with and without the buffer at buffer temperature T_{buf}=300°C and wafer temperature T_{sub}=300°C.

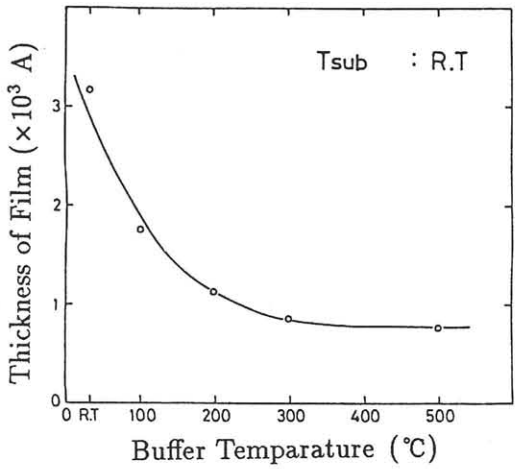
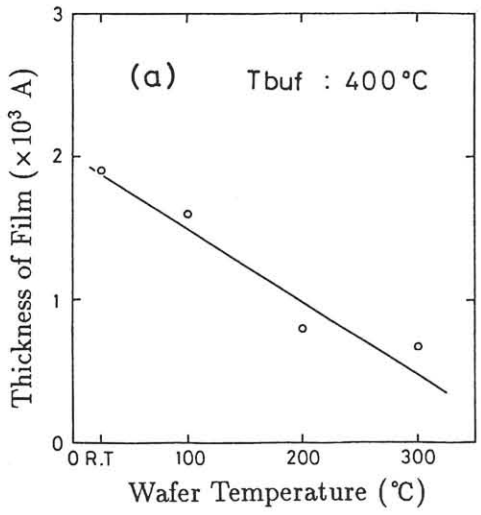


Fig.3 SiO_2 film thickness as a function of the buffer temperature at wafer temperature T_{sub}=R.T.

The refractive index and the quality of the SiO_2 films were estimated with the ellipsometry and FT-IR measurements. Figures 4(a) and 4(b) show the SiO_2 film thickness and ratio of integral absorption coefficient for Si-OH to Si-O bonds, as a function of the wafer temperature, respectively. Deposition rates demonstrates an increase with decrease in wafer temperature, while absorption coefficient of Si-OH bond goes up considerably. This is ascribed to formation of the film involving poly-silane structure[5] and poor oxidation ability of oxygen radicals for hydrogen atoms. In Fig.5, $\int\alpha_{Si\text{-}OH}/\int\alpha_{Si\text{-}O}$ is shown as a function of the pulse width of O_2 gas. The Si-OH bond is decreased with long irradiation by the oxygen radicals. Figure 6 shows the SiO_2 film thickness as a function of number of the pulse at the wafer temperature of R.T and 300 °C. Then, the deposition rate of SiO_2 film on a wafer area of 1 cm^2 can achieve 3 A/pulse under the conditions of pulse width for SiH_4 and O_2 gases of 50 msec and 5 sec, respectively, and at the wafer temperature of 300 °C. The value of 3 A/pulse is defined by dividing a maximum film thickness by number of the pulse.



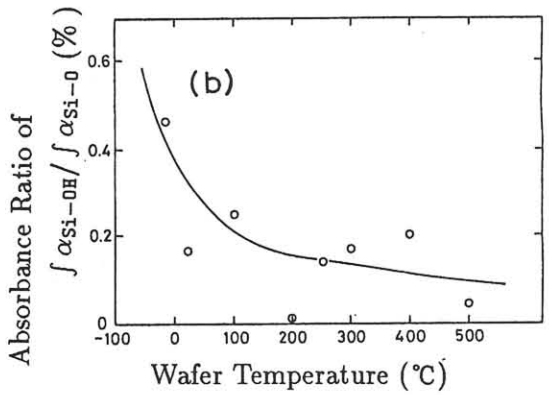


Fig.4 (a) SiO_2 film thickness and (b) ratio of integral absorption coefficient for Si-OH to Si-O bonds as a function of wafer temperature at buffer temperature T_{buf}=400°C.

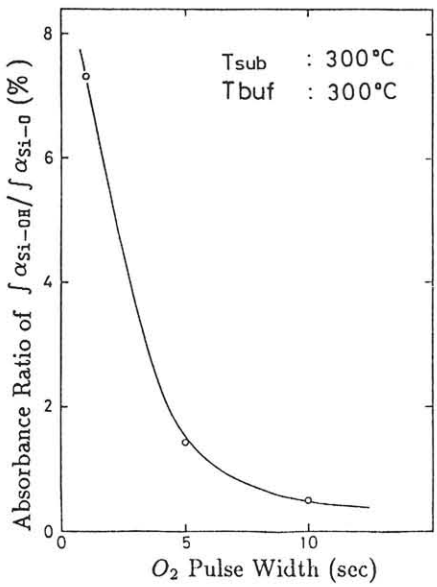


Fig.5 Ratio of integral absorption coefficient for Si-OH to Si-O bonds as a function of pulse width of O_2 gas at buffer temperature T_{buf}=300°C and wafer temperature T_{sub}=300°C.

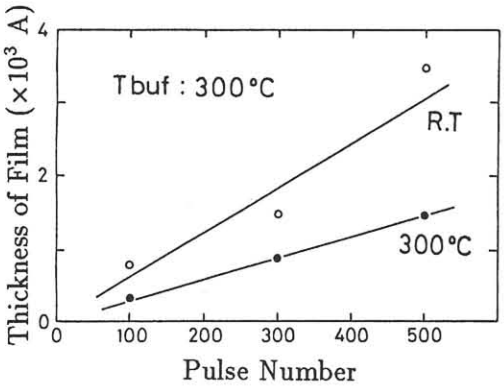


Fig.6 SiO_2 film thickness as a function of number of pulse at buffer temperature T_{res}= 300°C.

In the course of this study, SiH_4 radicals which impinged obliquely on a wafer as shown in Fig.1 was found to reflect on a wafer surface and deposit on an opposite side viewing window. As shown in Fig.7, deposition rates decrease with leaving from the normal incidence angle of the SiH_x radical beams and in addition, thicker film deposition on the sidewall is observed at higher angle of incidence. Hence, deposition rates become high with increasing the radical beam flux of SiH_x. It is also suggested from this result that, althrough the flow velocity of SiH_4 gas decelerated conciderably by the addition of the buffer, neutral SiH_x beams have still near a supersonic velocity, because the SiH_4 gas is injected in pulse and its radicals are transported at lower pressure of 10^{-6} Torr into the reactor. As another examination of the intense radical beams with a supersonic velocity and the directionality, upstream-excited argon radicals were irradiated upon the present SiO_2 film. As a result, any loss of this film thickness was not observed in spite of longer irradiation of argon radicals. Therfore, these intense radical beams does not play an essential role in occurrence of physical sputtering. It should seem that a magnitude of normal component of a momentum having SiH_x radicals dominates the chemical reaction velocity caused the film deposition.

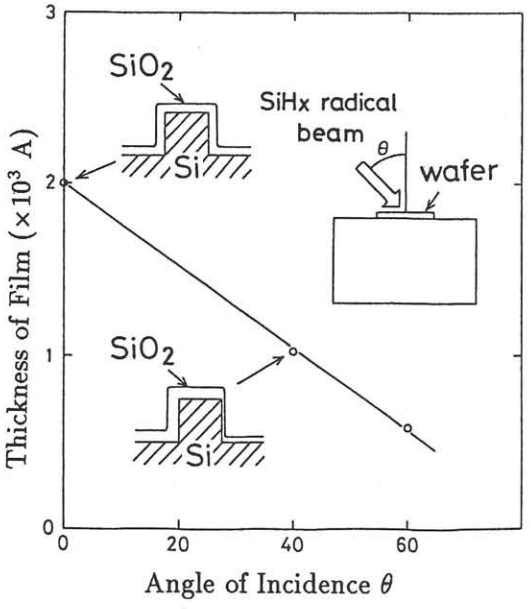


Fig.7 Film thickness and cross-sectional illustration of SiO_2 as a function of an incidence angle of SiH_x radicals.

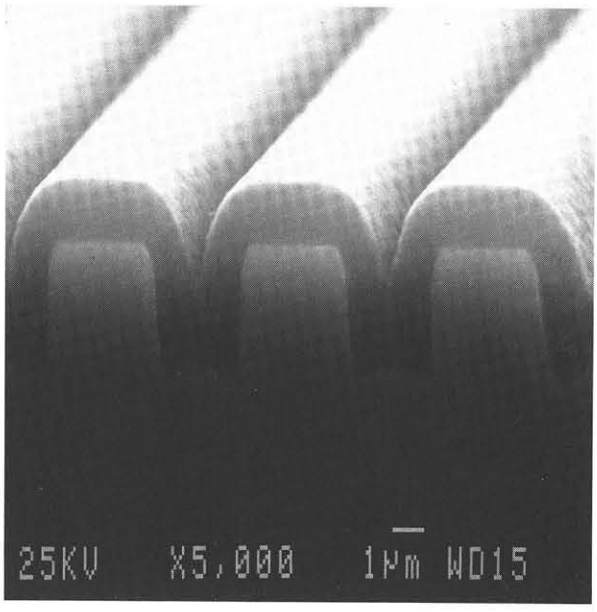


Fig.8 Cross-sectional SEM photograph of SiO_2 film filled in the trench with aspect ratio of 2.

Figure 8 shows cross-sectional SEM photograph of the SiO_2 film filled in the trench with aspect ratio being 2. Observation of the filling process demonstrates that the SiO_2 film deposits on the bottom more larger than the sidewall in the trench. This seems to result from that SiH_x radicals with normal incident beams deposit on the both upper and bottom surfaces in the trench, and simultaneously the radical beams reflect mostly on the sidewall.

At present stage, SiO_2 was not filled in trenches with aspect ratio more than 3. According to primal aim of the conformable CVD, the film deposition study based on the complete surface reaction will be continued by any means for decelerating gas velocity.

4. SUMMARY AND CONCLUSION

The digital CVD method, which was performed by repetition of alternate reaction of upstream microwave-discharged SiH_4 and O_2, was tried out on the formation of SiO_2 film deposition. To restrain a drop of SiH_4 gas temperature due to an adiabatic expansion, also to relax a velocity of its gas jet, a buffer is combined into the SiH_4 jet entrance. This provides the deposition rate of 3 A/pulse and an improvement of film characteristics along with the control of the pulse width of O_2. Moreover, the intense SiH_x radical beams with directionality fill successfully SiO_2 in the trench as a result of major reflection on the sidewall.

5. REFERENCES

1) A. Usui, and Sunakawa; Jpn. J. Appl. Phys. 25(1985) 212.
2) T. Tanaka, K. Deguchi, S. Miyazaki, and M. Hirose; Jpn. J. Appl. Phys. 27(1988) 2149.
3) M. Shibagaki, Y. Horiike, and T. Yamazaki; Jpn. J. Appl. Phys. 17(1978) 215.
4) S. Miyazaki, H. Hirata, and M. Hirose; Extended Abstracts of the 16th Conf. on SSDM (1984) 447.
5) M.H. Brodsky, M. Cardona, and J.J. Cuomo; Phys. Rev. B 16(1977) 3556.