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# $SiO_2$ Deposition by Photo-initiation

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Thin films of silicon dioxide ($SiO_2$) was photochemically deposited by photo-initiation at low substrate temperatures in a $SiH_4+O_2+N_2$ system. Deposition of $SiO_2$ film continued without subsequent UV light irradiation, if film deposition was initiated by UV light irradiation for a short time at an early stage. Photo-initiation condition is closely related with parameters such as substrate temperature, chamber pressure and $O_2/SiH_4$ gas ratio. $SiO_2$ films with high resistivities and breakdown fields can be deposited using photo-initiation. The films have been characterized using etch rate, IR spectra and C-V measurements.

## 1. Introduction

Recently, photo-CVD(chemical vapor deposition) processes are widely studied for VLSI fabrication as a new low temperature processing. Deposition of $SiO_2$ films have been carried out by irradiation of UV light from a low pressure Hg-lamp,[1] $D_2$-lamp[2] or ArF excimer laser.[3] Although photo-CVD method using Hg-sensitization[4] have been reported for depositing $SiO_2$ films, Hg should be avoided in a system not to bring contamination into semiconductor processing. We previously reported $SiO_2$ film deposition by KrF excimer laser irradiation.[5] We found a new phenomenon of photo-initiation for $SiO_2$ deposition by irradiating UV light to a $SiH_4+O_2+N_2$ system. Photo-initiation means the following: Keep the system not to make deposition of a $SiO_2$ film without irradiation of UV light, once the deposition occurs by UV light irradiation, it continues even if the light irradiation is stopped. In this report, we describe a new film deposition method by photo-initiation for $SiO_2$ films and evaluation of the films in detail.

## 2. Experimental

A stainless-steel chamber with three windows for UV light irradiation was used for experiment . A silicon(Si) substrate with 10x10 $mm^2$ was mounted on a stainless-steel pedestal which had a heater in the inner side. The Si substrate was irradiated by a low pressure Hg-lamp through a synthetic quartz window. The distance between the lamp and the Si substrate was 10 cm. Reaction gases were flowed through a special nozzle which was designed to make a laminar flow pattern above the Si substrate. The gas flows of 4-14 sccm $SiH_4$(10% in $H_2$), 2-40 sccm $O_2$, and 170 sccm $N_2$ were used. Chamber pressure was changed in the range of 6 to 30 Torr. The pressure was measured by a Pirani gauge. In-situ thickness measurement for the depositing $SiO_2$ film was employed using He-Ne laser light reflection from the surface. The thickness and the refractive index of the deposited film on Si substrates were precisely measured by ellipsometry. The deposition rate is defined by the ratio of the film thickness to the deposition time. For evaluating film properties, annealing was done at a temperature of 400 °C for 1 hour in Ar ambient.

## 3. Results and discussion

### 3.1 Film deposition

Photo-initiation phenomenon was observed in the following sequence. After a Si substrate was set on the susceptor, the reaction chamber was pumped down to $10^{-2}$ Torr. First, $N_2$ gas for dilution of $SiH_4$ and window purge was introduced. Then, the Si substrate was heated up , and $O_2$ gas was introduced. After that, $SiH_4$ gas was added to the chamber and pressure P was precisely adjusted for a desired condition. A typical condition is $T_s$=230 °C ( substrate temperature: $T_s$), P=10 Torr and gas ratio of $O_2/SiH_4$=10. The reaction gases were flowed for 90 minutes before photo-irradiation to confirm that film deposition did

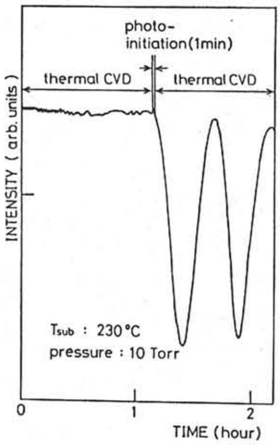


Fig.1 Photo-initiated film deposition.

not occur thermally. When the light was irradiated for only 1 minute, film deposition started and continued even without subsequent UV light irradiation as shown in Fig.1.

To clarify the role of UV light irradiation, the following experiments were carried out under the condition of $T_s$=175 °C, P=20 Torr and the gas ratio of $O_2/SiH_4$=10;

a) UV light irradiation for 16 minutes,
b) leave it without UV light irradiation for next 10 minutes,
c) reaction gas was shut off for 4 minutes, and
d) reaction gas was flowed again.

The result of each step is shown in Fig.2. After photo-initiation, $SiO_2$ deposition continues

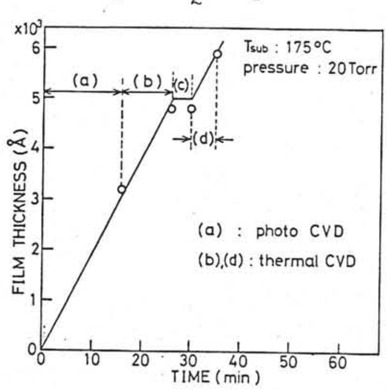


Fig.2 Photo-irradiation effect.

without photo-irradiation during the gas flow by thermal CVD(step b). The film thickness increases linearly with reaction time. At step c, film deposition ceased because of no reaction gas flow. However, once the reaction gas was flowed again, the deposition again occured without photo-irradiation(step d). These results indicate that active sites for $SiO_2$ deposition are formed on the Si substrate by UV light irradiation in the early stage, and for subsequent film deposition UV irradiation is not necessary.

Substrate temperature dependence of the film deposition is shown in Fig.3. After UV light irradiation for only first 1 minute, the film thickness was continuously monitored. The thickness increased linearly with reaction time at $T_s$=175 °C. After deposition for 13 minutes, substrate

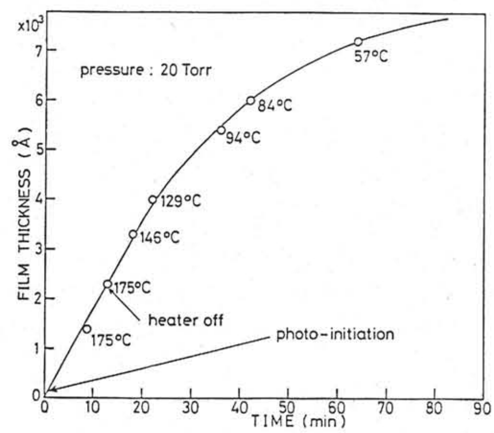


Fig.3 Substrate temperature dependence.

temperature was gradually decreased. The film deposition continued to a substrate temperature of 57 °C, though the deposition rate seemed to decrease. Thus, once the film deposition occurs by photo-initiation, it continues thermally without UV light irradiation even though the substrate temperature is decreased.

Temperature dependence of the deposition rate at 30 and 10 Torr is shown in Fig.4. The film deposition occured by photo-initiation in the A and B regions in the figure, but thermal deposition did not occur in these regions. High deposition rates of 300 A/min and 150 A/min were obtained for chamber pressures of 30 Torr and 10 Torr, respectively, in the photo-initiation dominant region. In C and D regions, the film deposition occured by thermal CVD process. When the UV light was irradiated during deposition in regions C and D, the deposition rate increased by about 10 %(not shown in the figure). At a chamber pressure of 10 Torr, activation energies of 0.016 eV for region B and 0.21 eV for

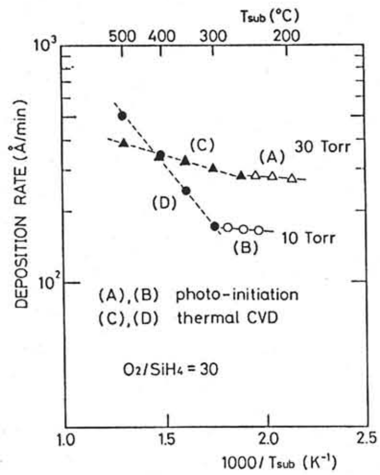


Fig.4 Temperature dependence of the deposition rate.

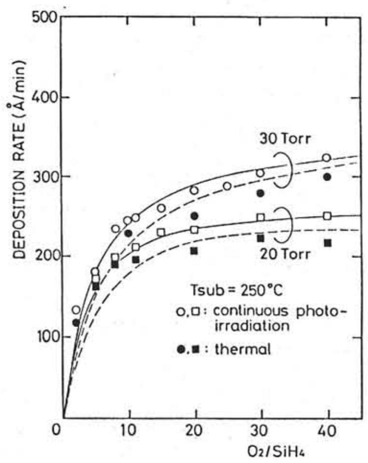


Fig.6 $O_2/SiH_4$ gas ratio dependence.

region D were obtained. The activation energy for photo-initiated deposition is lower than that for thermal deposition.

Pressure dependence of the deposition rate is shown in Fig.5. In the lower part of the dotted line in Fig.5 , deposition by photo-initiation occured, whereas thermal CVD occured in the upper part . At the substrate temperature of 250°C, there was no deposition at a pressure less than 6

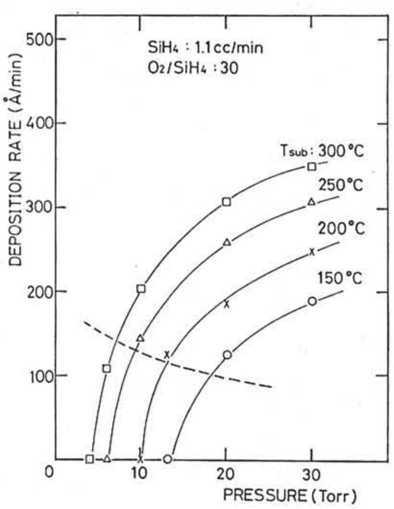


Fig.5 Pressure dependence of the deposition rate.

Torr even under UV light irradiation. When the pressure was increased more, deposition occured suddenly at 10 Torr. Beyond this pressure, the deposition rate increased gradually. At higher substrate temperatures, the deposition rate reached a saturable value in the higher pressure range. Once the substrate temperature is chosen, there seems a threshold pressure for the film deposition. Substrate temperature and pressure are closely related with each other for film deposition by photo-initiation.

To understand the mechanism of film deposition, $O_2/SiH_4$ gas ratio dependence of the deposition rate for two chamber pressures was studied as shown in Fig.6. The deposition rate increased as the gas ratio increased, and it tended to saturate in the higher gas ratio. The saturable deposition rate increased as the chamber pressure increased. The deposition rate under UV irradiation was always larger than that under non-irradiation. From the gas ratio dependence, the deposition mechanism of the $SiO_2$ film at low pressure using $SiH_4$+$O_2$+$N_2$ mixture gas can be explained by applying a bimolecular surface reaction theory used for thermal CVD at atmospheric pressure.[6)]

3.2 Physical properties

The etch rate of the $SiO_2$ film was studied by using an etchant of HF:$H_2O$=1:40 at 13 °C. As the substrate temperature increased, the etch rate decreased. The etch rate of the film deposited at 210 °C was about 8 A/s, which was about 5 times larger than that (1.75 A/s) of the $SiO_2$ film by thermal oxidation (wet 1000 °C). The increase in the etch rate for the film deposited at lower temperature is due to porosity of the films, though the refractive index of 1.46 did not change with the substrate temperature. $O_2/SiH_4$ gas ratio dependence of the etch rate was also examined for the $SiO_2$ film deposited at 250 °C. The etch rate decreased with increasing the gas ratio. Under the higher oxygen condition ($O_2/SiH_4$=40), the deposited film became dense. The etch rate of the film was not influenced by preparation conditions with or without UV light irradiation.

Infrared spectra of the $SiO_2$ films of as-deposited and after annealing were measured. There were three main absorption bands(wave numbers:460, 800, and 1080 $cm^{-1}$) related to Si-O vibrational modes. There was a peak at 3300 $cm^{-1}$ in the as-deposited film, which is associated with absorbed water. This peak vanished after annealing . The peak at 1050 $cm^{-1}$ was shifted to the higher energy side, indicating decrease of atomic vacancy and /or bond strain in the film.

3.3 Electrical properties

Electrical properties of the deposited films were evaluated by fabricating MOS diodes ($Al/SiO_2/n\text{-}Si$). The diameter of a metal electrode was 1.5 mm. The thickness of the $SiO_2$ film was about 1000 A. Temperature dependence of the film resistivity at 1 MV/cm was measured. The films deposited above 250 °C had sufficiently higher resistivities, and higher resistivity could be obtained by elevating the substrate temperature. Breakdown fields were 6.2 MV/cm and 9.6 MV/cm for the films deposited at 250 °C and 400 °C, respectively. The breakdown field of 9.6 MV/cm was comparable with that of thermally oxidized silicon. The breakdown field was defined as the gate bias where leakage current reached 1uA. Although the breakdown field of the film deposited at 250 °C was 6-7 MV/cm, it was improved to 8.1 MV/cm after annealing. $O_2/SiH_4$ gas ratio dependence of the resistivity was also examined, but the resistivity did not depend on the gas ratio ($O_2/SiH_4$=2-40).

The dielectric constant was not influenced by the preparation conditions such as the substrate temperature and the gas ratio of $O_2/SiH_4$. Average value of the dielectric constant of the film was about 4.5. Although the dielectric constant of the film deposited at 250 °C was about 5, after annealing it approached the value of 4 for the film prepared by thermal oxidation.

C-V characteristics at 1 MHz were also measured for MOS diodes. Fixed charge density was calculated from the flat band shift of the C-V curve, and it decreased with increasing the substrate temperature. C-V characteristics of the MOS diodes with as-deposited $SiO_2$ showed an injection type hysteresis. However, the width of the hysteresis became narrow for the film deposited at higher substrate temperature. For the gas ratio of $O_2/SiH_4$ of about 20-30, the width of the hysteresis became minimum. And, this width of the hysteresis decreased after annealing. The minimum surface state density calculated from the C-V curve was $1.4\times10^{12}$ $cm^{-2}$ $eV^{-1}$ for the $SiO_2$ film deposited at 250 °C, and $6.6\times10^{11}$ $cm^{-2}$ $eV^{-1}$ for the annealed $SiO_2$ film. An appropriate in-situ cleaning of the Si surface prior to film deposition will be necessary for obtaining lower surface state density and fixed charge in the film.

4. Conclusion

Direct photochemical deposition of $SiO_2$ at low temperatures by UV light irradiation to a $SiH_4+O_2+N_2$ gas mixture was carried out without using any Hg photosensitization. Photo-initiation effect was observed in this system. Film deposition continues without continuous UV light irradiation and even though the substrate temperature is lowered from the initial temperature. This phenomenon is applicable for film deposition at lower substrate temperatures. Substrate temperature, pressure and gas ratio of $O_2/SiH_4$ are key parameters for $SiO_2$ deposition by photo-initiation. These parameters are found to be closely related with each other. Physical and electrical properties of the $SiO_2$ films deposited by photo-initiation were evaluated. Resistivity of the film is high enough for use of an insulator.

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