A Study of Deposition Mechanism of Laser CVD SiO_2 Film

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This study was performed to investigate the deposition mechanism of SiO_2 by ArF excimer laser(193nm) CVD with Si_2H_6 and N_2O gas mixture and evaluate laser CVD quantitatively by modeling. With ArF excimer laser CVD, thin films can be deposited at low temperature(below 300℃), with less damage and good uniformity owing to generation of conformal reaction species by singular wavelength of the laser beam. In this study, new model of SiO_2 deposition process by laser CVD was introduced and deposition rate was simulated by computer with the basis on this modeling. And simulation results were compared with experimental results measured at various conditions such as reaction gas ratio, chamber pressure, substrate temperature and laser beam intensity.

Keywords : Quantitative analysis, Deposition mechanism , Laser CVD

1. INTRODUCTION

Laser CVD method has been used for depositing films of good quality under less than 300 ℃. In addition, there is no mask required in such a way that it is possible to do selective deposition of the films. Recently this method has been applied to deposit SiO_2 and Si_3N_4 films and is expected to be an important tool in fabricating the next generation submicron devices. It should be admitted, however, that there is no thorough analysis on film deposition mechanism using the method so that no reliable process parameters are available to achieve repetitive and controllable quality of the films.

This study proposed a new model to quantitatively analyze the deposition mechanism of the SiO_2 film generated by laser CVD. ArF excimer Laser (193 nm: Questek series 2000) was chosen as the source with the reaction gases of Si_2H_6 and N_2O in this study. The uniform source model was assumed in the study where the intensity of the laser beam used to photolytically dissociate the gases was the same inside any arbitrary point of the beam diameter. Another assumption on the transport mechanism of reaction products was employed; diffusive model that says the gaseous collision between the primary reaction products after the photolytic dissociation generates SiH_2O [2] and all the gaseous products can only move to the surface in a vertical way, that is, no horizontal convection motion of the gases.

This study based on these assumptions compared the computer simulation results with the experimental results obtained from varying the several sets of process conditions.

2. DEPOSITION OF OXIDATION LAYER FOR THE MODELING

The ArF excimer laser with the wavelength of 193 nm was beamed at the reaction gases of Si_2H_6 and N_2O in a parallel position with the substrate surface. The moisture in a CVD reactor was removed by heating the substrate holder at 400℃ for around an hour. The pressure in the reactor was lowered down to 1 x 10^{-5} Torr so that the possibility of contamination due to oxygen and other gases in it was excluded.

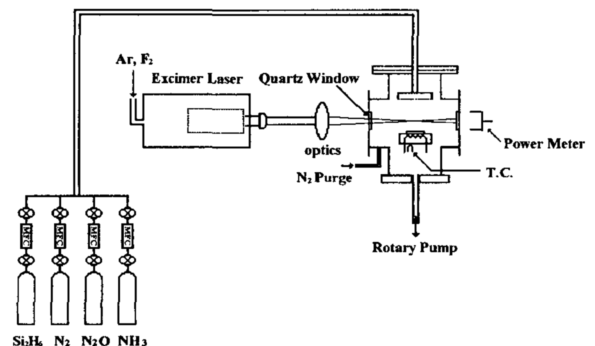


Fig. 1. Schematics of laser CVD system used in the SiO_2 film deposition.

Figure 1 shows the schematics of laser CVD system used in the SiO_2 film deposition. It consists of the vacuum reactor with the two windows attached, the laser source and related optical system, reaction gas supply, substrate heating system, and vacuum gauge. The reactor was made out of stainless steel, and the raw material of the t wo windows was artificial quartz of which transparency was very good to the wavelength of 193 ㎚. The laser beam was aimed through a circular lens at the height of 0.5 ㎜ above from the substrate so that the resultant radicals could be diffused down into 1 ㎜ below from its surface. The focal distance of the lens was 50 ㎝, while the laser repetition rate was set to be 50 ㎐. The pulse energy was varied from 90 mJ to 110 mJ which was equal to 4.5 ㎿/㎠ · pulse to 5.5 ㎿/㎠ · pulse with the beam size of 20x10 ㎜ and pulse duration time of 10 ㎱.

The inner surface of the windows was purged with the N_2 gas to be free from a possible film deposit and other contaminants on it which might degrade the transmittance of the laser light through the window.

The substrate used in the film deposition was of Si(100) p-type of which resistivity was 4.5 Ω · cm to 6 Ω · cm. Prior to the sample preparation, the RCA cleaning process on the substrate was introduced to get rid of any form of contamination such as organic materials, metal ions a nd native oxide. The highly purified Si_2H_6 and N_2O gases were used as reactants and N_2 was used as a carrier gas. The flow meter and the throttle valve were used to control the gas volume and pressure in the reactor, respectively.

With the proper experimental conditions provided, the investigation on the dependence of film deposition rate on the factors such as gas flow rate, the reactor pressure, substrate temperature and laser intensity was pursued. More specifically, in order to extract the effect of each factor on the film deposition rate, the measurement was done with one factor varied and the others fixed.

3. QUALITATIVE ANALYSIS OF DEPOSITED FILM GROWTH

Figure 2 depicts the schematic view of film deposition process. The following are the proces s details. The laser beam is directed at the upper part of the reactor where uniformly mixed gases(Si_2H_6 + N_2O + N_2) are located. The radicals obtained through this photolytic dissociation are getting in unstable state so that the diffusion process takes place through consecutive collisions. As a result of the collisions, the surface precursor, SiH_2O, is formed, which migrates to the hydrogenated surface and forms the oxide layer. More specific qualitative explanation can be provided into 3 stages.

3.1 Photolytic dissociation by ArF excimer laser

The general reaction of light absorption dissociation of Si_2H_6 is as follows,

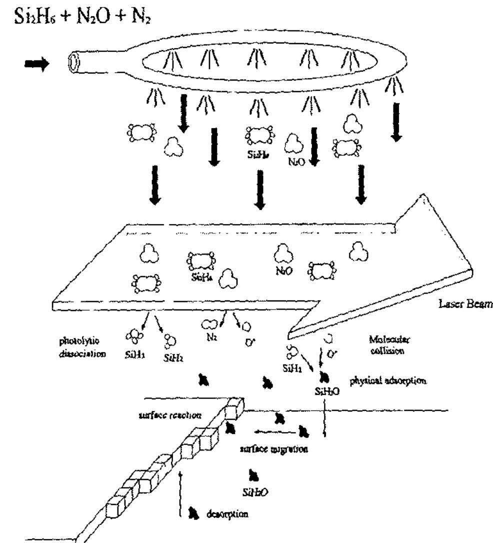
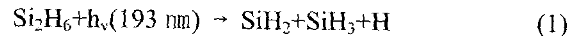
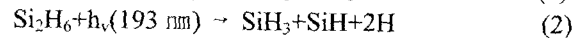


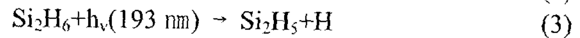
Fig. 2. Schematic view of film deposition process.



$$Si_2H_6+h_v(193\ nm) \rightarrow SiH_2+SiH_3+H \quad (1)$$

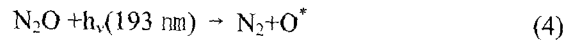


$$Si_2H_6+h_v(193\ nm) \rightarrow SiH_3+SiH+2H \quad (2)$$



$$Si_2H_6+h_v(193\ nm) \rightarrow Si_2H_5+H \quad (3)$$

The reaction generating the reactant out of the above three reactions is (1) where light absorption area is 3.4 x 10^{-18} ㎠ [3]. The N_2O gas is dissociated into N_2 and the oxygen radical, O^*, by laser beam.



$$N_2O+h_v(193\ nm) \rightarrow N_2+O^* \quad (4)$$

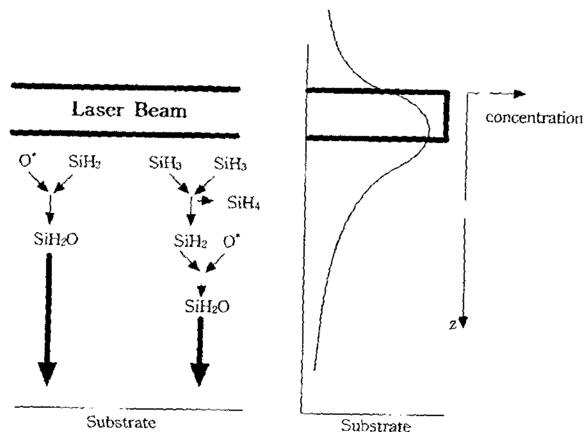


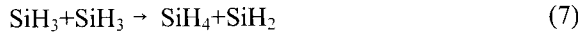
Fig. 3. Nucleation of surface precursors and their diffusion.

3.2 Generation of surface precursor and its diffusion

Deposition of oxide layer is not mad e directly through SiH_2 and SiH_3 that are generated by the dissociation process, but through a series of interim reaction processes. These reactants experience the gaseous collisions during the transport that results in yielding surface precursors which, in turn, react with hydrogen on hydrogenated surface. The following gives a tip of reactions which generates surface

precursor, SiH_2O.

$$H+Si_2H_6 \rightarrow SiH_3+SiH_4 \quad (5)$$

$$H+SiH_4 \rightarrow SiH_3+H_2 \quad (6)$$

$$SiH_3+SiH_3 \rightarrow SiH_4+SiH_2 \quad (7)$$

$$SiH_2+O^* \rightarrow SiH_2O \quad (8)$$

The generation and diffusion of this precursor is illustrated in Fig. 3.

3.3 Deposit reaction of the reactants

Film deposition occurs through the substitution process breaking the bond of Si-H on hydrogenated surface, and then being oxidized by the oxygen in the reactants. This reaction pretty much depends on the substrate temperature which affects the penetration depth of oxygen and its reactivity as well. So this reaction is very important in analyzing the oxygen and hydrogen contents inside the film. This procedure is well shown in Fig. 4.

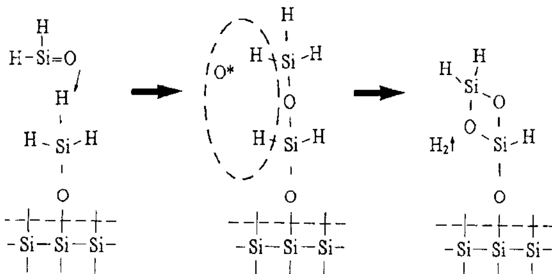


Fig. 4. Reaction process of surface precursors for film growth.

4. QUANTITATIVE ANALYSIS

To estimate the growth rate of oxide layer, it is necessary to have a mathematical model on how many precursors generated via collision and diffusion processes would reach the substrate. These precursors, of course, are the output of the primary reactants photolytically dissociated by the laser.

In this study, a mathematical model was proposed under the uniform source model and the diffusion model based on a certain set of assumption.

4.1 Assumption set

1) Film deposition forms in terms of surface reaction with oxygen radicals (O^*) after substitution of surface hydrogen with the precursors where any by-product due to gaseous reaction between the precursors can be ignored.
2) The precursor in the surface reaction is only SiH_2O and the reverse reaction should be negligible because the in- and out-gas flow is assumed to be stationary.
3) The primary reactants obtained from photolytic dissociation of the laser beam would be only in vertical motion, not in horizontal motion.
4) The process controllability on the generation rate due to dissociation process is limited to the reaction gases of Si_2H_6 and N_2O, which are directly dissociative by ArF excimer laser.
5) The laser beam has a constant intensity in its cross sectional area. The intensity of the beam itself forms the Gaussian distribution, but extending its area, the intensity can be regarded as a constant at any point inside the diameter. This means that the photolytic dissociation rate should be constant inside the beam area

4.2 Uniform source and flux model

We see the intensity of the laser beam follows the Gaussian distribution shown in Fig. 5 in which the intensity is decreasing as it moves away from the focal center point. The formula for the distribution is as follows.

$$I(\gamma) = I_0 \exp\left(\frac{-2\gamma^2}{\omega_o^2}\right) \quad (9)$$

The change in the intensity like this causes one to model the laser CVD process with great difficulty so that the uniform model simplifies the situation a lot with a great deal of ease. Assuming the beam intensity takes form of $I=I_o/e$ of cylindrical shape, it is possible to model the cylinder with the radius of $\sqrt{2}W_0$ [4]. Fig. 6 shows a schematic diagram of the uniform model for the Gaussian distribution of the laser intensity.

In case of the laser (Questek series 2000) used in this study, the focused beam shape was rectangular, of which dimension was 5 x 2 mm. So applying the uniform model, the model dimension of the beam became $5\sqrt{2}$, $2\sqrt{2}$ mm.

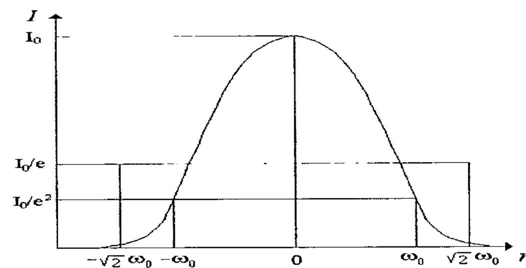


Fig. 5. Gaussian distribution of laser beam intensity.

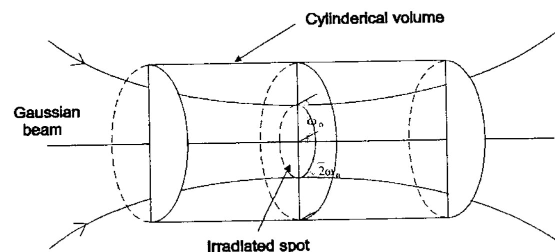


Fig. 6. Schematic diagram of the uniform model of the laser intensity.

4.3 Diffusion transport model

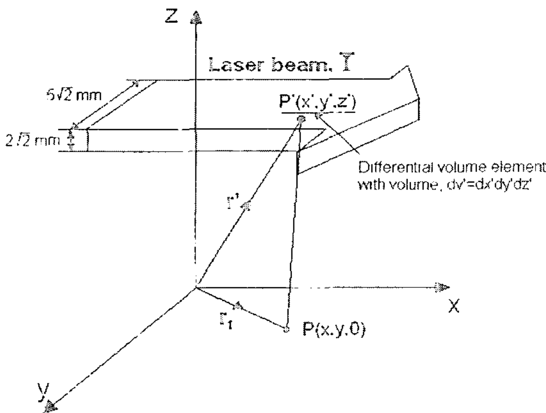


Fig. 7. The coordinates system for diffusion transport model.

The transport mechanism of the reactants obtained from the dissociation process presupposed no lateral convection motion, but vertical diffusion motion. Using the coordinates system specified in Fig. 7, the following equation was obtained.

$$\frac{\partial N_{ir}}{\partial t} + \nabla \cdot (N_{ir} u) = -\nabla \cdot J_{ir} + S_{pir} \tag{10}$$

where N_{ir} is the concentration of the i species in the r area, J_{ir} is the mass flux and S_{pir} is the generation rate of the i species in the r area. Using the conditions of 1) no convection and 2) the stationary state in this mass conservation equation, the diffusion equation was found below.

$$D\nabla^2 n_p(r) = S(r) \tag{11}$$

where $S(r)$ is the total sum generated per unit time and unit volume, $r = xi + yj + zk$.

4.4 Quantitative analysis of film deposit rate

In order to get the solution of the diffusion equation, the equation describing the flow flux of incident particles to the substrate surface was employed.

$$j_f = D\frac{\partial n_p}{\partial z} = \frac{1}{4}\gamma_s n_p \bar{v} \quad \text{at z=0} \tag{12}$$

where γ_s is the surface sticking coefficient and $\bar{v}$ is the average velocity of the reactants.

As it could be seen in the equation, since the surface impingent flux was linearly proportional to the film deposit rate, the film deposit rate could be expressed as follows, considering the temperature dependence of the surface sticking coefficient and dividing the impingent flux by oxide layer density.

$$\frac{dh}{dt} = \frac{j_f}{\rho}\gamma_s \exp(-E_a / kT) \tag{13}$$

where γ_s is the surface sticking coefficient, ρ is the oxide layer density and E_a is the activation energy.

The simulation program for the process based on the above mathematical model was made in C language. In order to justify the simulation validity, the same conditions applied to the experiment were loaded to the simulation with which the effect of each parameter including gas flow rate, pressure, substrate temperature and beam intensity on the growth rate was investigated.

5. RESULTS AND DISCUSSION

Figure 8 illustrates the dependence of the ratio of the reaction gases, N_2O/Si_2H_6, on the growth rate. The experiment indicated that the SiO_2 deposition rate in Si_2H_6+N_2O system was low at the low reaction gas ratio and it was getting higher at the higher reaction gas ratio, while there was a maximum deposition rate at around 100 whereafter the film growth rate was decreasing. These results were in excellent agreement with our simulation. The feasible conjecture behind this result was two-fold; firstly, the light absorption coefficient of N_2O excited through light absorption was 40 times as low as that of dissociated Si_2H_6, and also N_2O^* could be dissociated into N_2+O and return to the stable state during its short life time so that the actual number of N_2O that collided with SiH_2 and/or SiH_3 was reduced.

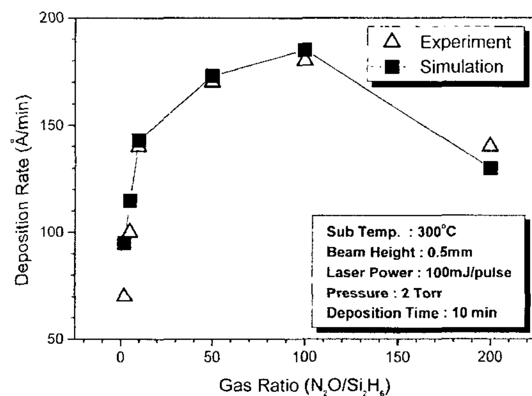


Fig. 8. Dependence of the ratio of the reaction gases, N_2O/Si_2H_6, on the growth rate.

The dependence of the deposition rate on reaction gas pressure is shown in Fig. 9. According to the experiment, as the gas pressure increased, the film growth rate also almost linearly increased, which agreed well with the simulation as well. This phenomenon happened because the number of gas particles per unit volume increased proportional to the pressure increased, in case of direct dissociation of Si_2H_6 by

laser beam. This pressure dependence might be an important clue to find the light absorption cross section.

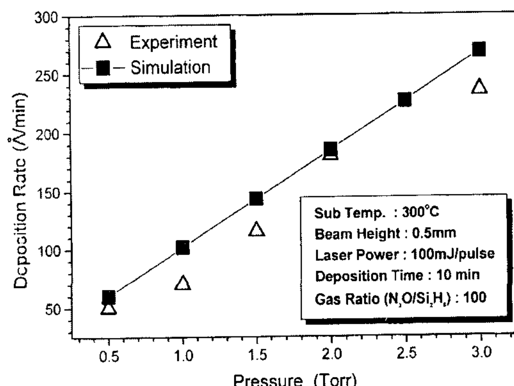


Fig. 9. Dependence of the deposition rate on reaction gas pressure.

Figure 10 depicts the temperature dependence of film deposition. The Arrhenius plot helps see better the effect of the activation energy on the film growth. The temperature was in the range of 150 to 350 ℃ and was picked every 50 ℃ in the range, that was, 5 sample temperature points. Experimental finding said that there was a drastic change in the activation energy at the substrate temperature of around 200 ℃. At the temperatures less than 200 ℃, Ea was 0.22 eV while at more than 200 ℃, it was 0.61 eV. This was thought to be because at more than 200 ℃ the dissociation characteristic due to surface heat itself was not negligible. The simulation results also said the almost same thing.

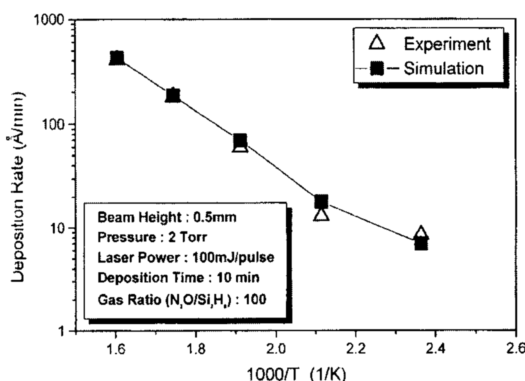


Fig. 10. Temperature dependence of film deposition.

Figure 11 depicts the laser power dependence of film deposition. As shown in Fig.11, the film deposition rate increased linearly as the laser power increased. it seem that this phenomenon happened because the reaction gases use d in this study were dissociated with single photon process. There was a good agreement between the experiment and the simulation.

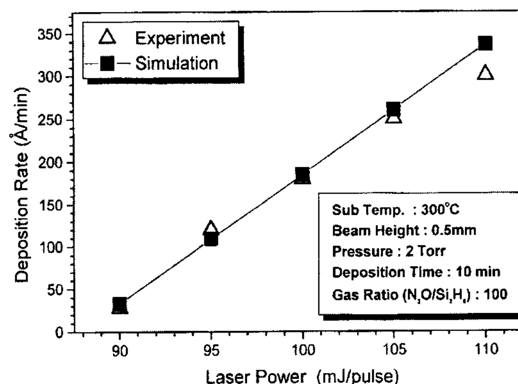


Fig. 11. Dependence of oxide film deposition rate on the laser power.

6. CONCLUSION

In this study to do quantitative analysis of deposition mechanism of laser CVD SiO_2 film, the uniform source model and the diffusion model were introduced to simplify the mathematical model on the photolytic dissociation process and the transport mechanism, respectively. Based on the model, we found that the quantitative process simulation was feasible to the film deposition analysis with several parameters varied. Our simplified model justified its validity through good agreements with the experiment.

There were some discrepancies between simulation and experiment. The simulation values were a little bigger than the experimental ones, which was reasoned to come from no lateral convection motion considered.

The future item to be pursued more after this study should be a quantitative analysis of the refraction index indicating the film density.

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Instructions for the Preparation of Article for Transactions on Electrical and Electronic Materials (bold, 15 points)

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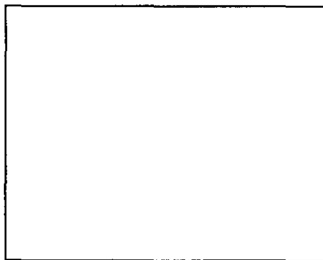

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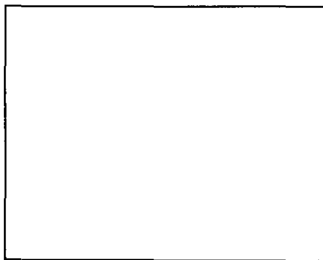

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$$H_{\alpha\beta}(\omega) = E_\alpha(0)\delta_{\alpha\beta} + \langle \alpha : W_\pi : \beta \rangle \qquad (1)$$

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ACKNOWLEDGMENTS

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