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Atomic Layer Growth of Silicon by Excimer Laser Induced Cryogenic CVD

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Silicon atomic layer growth has been achieved by controlling the thickness of Si_2H_6 adsorbates on a cooled substrate. The first monolayer of Si_2H_6 in contact with the growing silicon surface is extremely reactive under ArF (193 nm) excimer laser irradiation, and hence shot by shot atomic layer growth proceeds on the surface. The effective photodissociation reaction rate for the first layer Si_2H_6 molecules is estimated to be about 40 times faster than that of an isolated Si_2H_6 molecule.

1. INTRODUCTION

Recent progress in thin film technology has enabled us to grow an atomically smooth crystalline layer. Atomic layer epitaxy (ALE)[1] and molecular layer epitaxy[2] have been developed as a new growth technique for II - VI and III - V compound semiconductors. In these systems, a self-limiting process controls the growth rate. Namely, the strong chemical bond formation between group VI (or V) surface atoms and adsorbed group II (or III) metal organic radicals suppresses the multilayer adsorption in the proper temperature range. Also, it is reported that in the Ar^+ laser induced ALE of GaAs the chemical reaction rate of Ga organic radicals on the As surface atoms is significantly enhanced with laser irradiation[3]. More recently Ge ALE has been carried out by using $GeEt_2H_2$[4]. The monolayer growth of Si or Ge without using organic compounds has never been reported. In this paper, it is shown that the reaction rate of the first monolayer of Si_2H_6 adsorbed on Si surface is significantly enhanced with 193 nm laser irradiation. This leads to the Si atomic layer growth.

2. EXPERIMENTAL

The details of the laser-induced CVD of silicon from Si_2H_6 have been described elsewhere[5]. Also, the as grown Si layer is polycrystalline[5]. An ArF excimer laser (193 nm) beam was incident perpendicularly to a silicon or quartz substrate. The flow rate of 1% disilane diluted with He was 12 sccm. The substrate temperature, the Si_2H_6 partial pressure, the laser power and the repetition rate were in the range of -69 ∿ 19 °C, 0.01 ∿ 0.05 Torr, 10 ∿ 60 mJ cm^{-2}/shot and 0.66 ∿ 20 Hz, respectively. The thickness of the deposited films was measured using a high resolution surface-roughness measuring

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instrument and the surface morphology was examined using a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

The Si_2H_6 condensation process onto a cooled substrate has been studied by measuring the silicon growth rate as a function of the pulse to pulse interval by changing the repetition rate of the excimer laser as shown in Fig. 1. It is evident that the Si deposition occurs after the incubation time τ_i in the range of 10 ∿ 500 msec. No thin film growth took place at laser repetition rate faster than $1/\tau_i$. Also, τ_i increases with decreasing the Si_2H_6 partial pressure. This implies that the two dimensional silicon nuclei created by the laser induced dissociation of adsorbed Si_2H_6 do not exceed the critical radius r_c when the Si_2H_6 coverage is smaller than a certain value. The free energy of a two dimensional disk shape nucleus G(r) with the radius r is given by:

$$G(r) = \gamma\frac{2\pi r}{a} - \Delta\mu\frac{\pi r^2}{a^2} \quad . \qquad (1)$$

Here, γ is the step energy for the periphery atoms of the nuclei. $\Delta\mu$ is the chemical potential difference being equal to $\mu_v - \mu_c$, where μ_v is the gas phase chemical potential and μ_c the solid phase, and a is the atom size. Equation (1) indicates that the two dimensional nuclei smaller than the critical radius $r_c = \gamma a/\Delta\mu$ are unstable and no overgrowth takes place. The growth rate per laser shot saturates with increasing the pulse to pulse interval and the saturated value increases with the Si_2H_6 partial pressure. It is likely that the growth rate per shot is dependent on the adsorbed Si_2H_6 layer thickness which is controlled by the substrate temperature and the Si_2H_6 partial pressure. Therefore, the monolayer growth can be achieved by controlling the adsorbate thickness as shown in Fig. 2, where the silicon monolayer thickness is indicated in

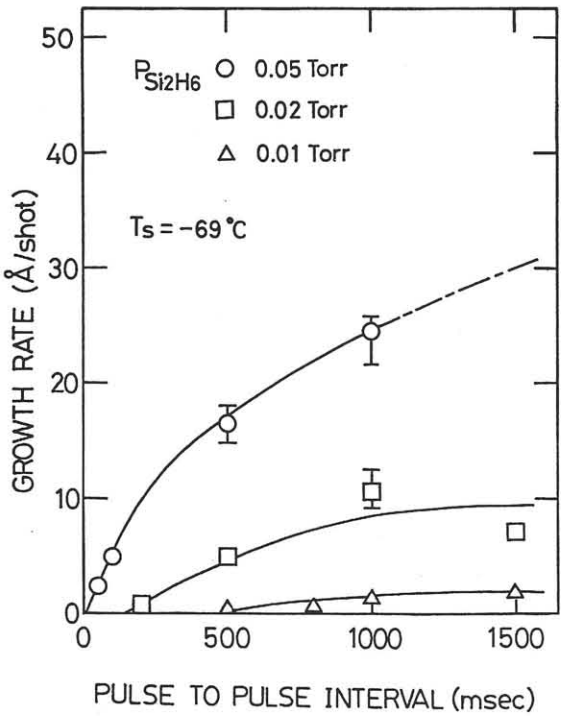

Fig. 1 Silicon growth rate plotted against pulse to pulse interval of laser irradiation at Si_2H_6 partial pressures of 0.01, 0.02 and 0.05 Torr.

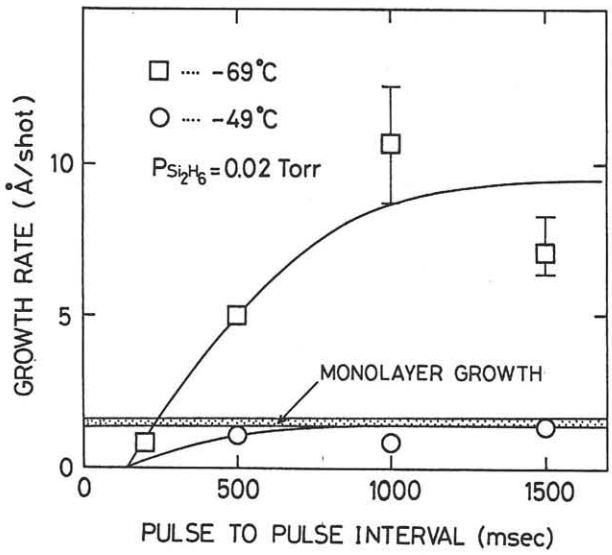

Fig. 2 Silicon growth rate versus pulse to pulse interval at temperatures of -49 °C and -69 °C.

the range 1.36 A for Si(100) to 1.57 A for Si(111) because the grown film is polycrystalline under the present conditions.

In order to get further insight on a possible mechanism of monolayer growth, the temperature dependence of the growth rate was measured as shown in Fig. 3. In the plateau region at temperatures - 40 to - 50 °C the atomic layer growth condition appears to be satisfied. It is interesting to note the fact that no Si deposition takes place when the cooled quartz substrate is exposed to Si_2H_6 and subsequently the reaction chamber is evacuated before laser irradiation. In contrast with this, once the silicon layer is grown on the quartz by laser irradiation in Si_2H_6 ambient, the Si_2H_6 exposure/evacuation/laser irradiation cycles lead to the film growth. This clearly shows that the residence time of Si_2H_6 adsorbed on the silicon layer is considerably long with respect to that on the quartz. Therefore, it is likely that the photodissociation rate of the first one monolayer of Si_2H_6 on the silicon surface is significantly high compared to that of the second and third monolayers.

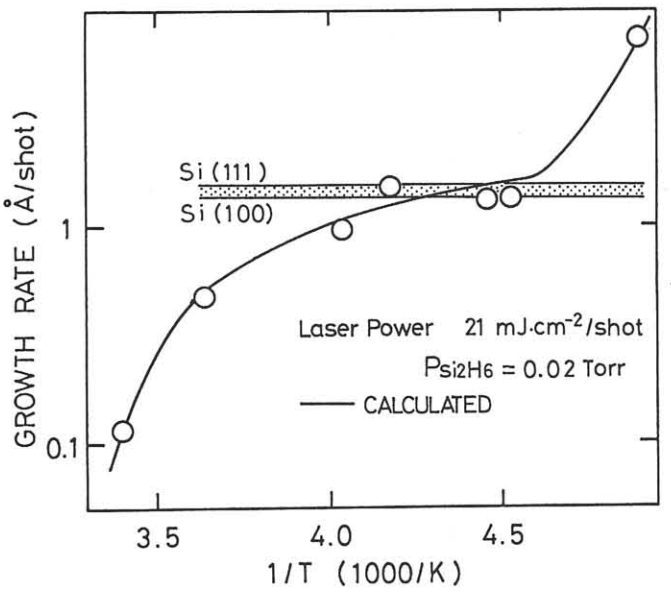

Fig. 3 Silicon growth rate as a function of reciprocal temperature. The solid curve is the calculated growth rate.

The amount of photodecomposed species estimated from the optical absorption coefficient of an isolated Si_2H_6 molecule is only a few percent of the condensed Si_2H_6 molecules and hence a few tens of monolayers are needed for one atomic layer growth. This is very unlikely under the present experimental conditions and also such simple photochemical decomposition scheme involves no self-limiting process. This implies that the first one monolayer of Si_2H_6 adsorbates is almost completely decomposed by a single shot of laser pulse.

The other implication of the high reactivity of the first one monolayer Si_2H_6 on Si is obtained by measuring the silicon growth rate as a function of laser power. As shown in Fig. 4, the atomic layer growth is achieved in the laser power range 40 to 50 mJ cm^{-2} /shot. By comparing this result with the result of Fig. 3 where the atomic layer growth condition is not satisfied at -26 °C with a laser power of 21 mJ cm^{-2}/shot and also by considering the growth rate enhancement at high laser powers in Fig. 4, we may conclude that the thickness of adsorbates is not one monolayer but a little beyond when the atomic layer growth is achieved and that the reaction rate of the first monolayer of Si_2H_6 on the silicon surface is estimated to be as high as ∿ 40 times compared with the second and third Si_2H_6 layers. From the results of Figs. 3 and 4, it is shown that the surface coverage of Si_2H_6 increases with decreasing the substrate temperature through the saturated monolayer adsorption and that the high reaction rate of the first monolayer of Si_2H_6 in contact with the silicon surface leads to the monolayer growth in the saturated or a little

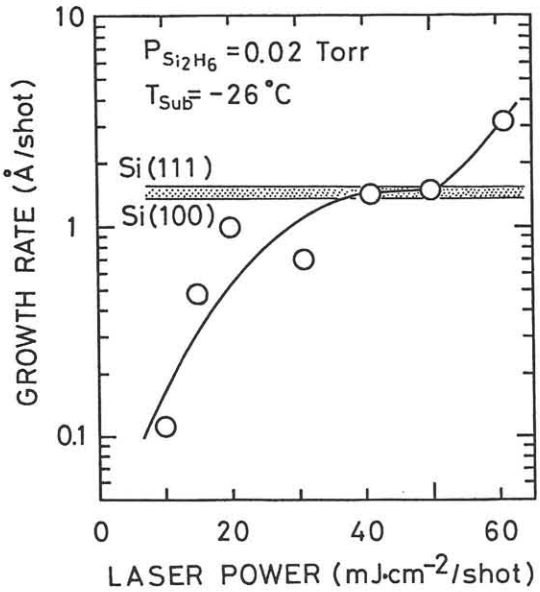

Fig. 4 Silicon growth rate as a function of laser power.

supersaturated adsorption region.

Along with this model the growth rate has been calculated as a function of temperature. The result is indicated by the solid curve in Fig. 3, being in good agreement with the experimental result.

The surface morphologies for the samples produced under the monolayer growth conditions at (a) - 69 °C and an Si_2H_6 partial pressure of 0.01 Torr and (b) - 49 °C and 0.02 Torr are shown in Fig. 5.

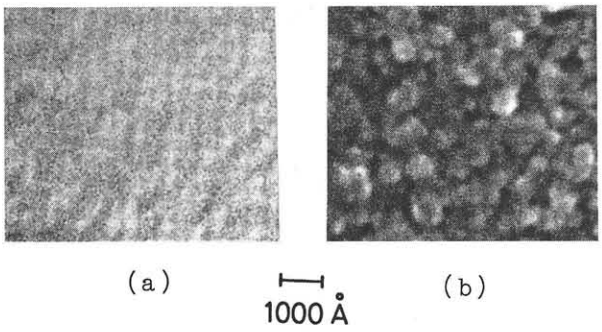

Fig. 5 SEM photographs of as-deposited Si films produced under monolayer growth conditions at (a) - 69 °C and 0.01 Torr of Si_2H_6 and (b) - 49 °C and 0.02 Torr.

There is no grain structure in (a), while in (b) many grains with a size of about 500 A are observed. Note that the surface morphology is improved by lowering the substrate temperature although the cause is unknown.

The surface morphology was also examined by a scanning tunneling microscope, showing the roughness of ± 10 A for a 3000 A thick film obtained under monolayer growth conditions. This value is significantly small compared to the value (± 50 A) for plasma enhanced CVD silicon[6].

4. CONCLUSION

Atomic layer growth of silicon is possible by controlling the Si_2H_6 adsorbed layer thickness because the photodissociation reaction rate for the first monolayer of Si_2H_6 is estimated to be ∿ 40 times faster than that of the second and third layers.

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