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Atomic Layer Epitaxial Growth of GaAs Using KrF Excimer Laser

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Atomic Layer Epitaxy for GaAs using KrF excimer laser has been investigated. The growth temperature range for one monolayer growth expanded under KrF excimer laser irradiation compared with that of nonirradiated growth. Using rate equations based on a selective absorption at surface arsenic atoms, the enhanced decomposition of TMG on the surface due to laser irradiation was analyzed. The result indicated that the activation energy for TMG decomposition decreased due to the laser irradiation.

1. Introduction

Atomic Layer Epitaxy (ALE) is a new growth technique in which only one monolayer is deposited per growth cycle in a self-limiting manner. Therefore, ALE is considered to be one of the ultimate growth control processes for compound semiconductor films.

Growth of III-V compound semiconductors by ALE method has been reported by many groups.[1)~6)] Particularly, photoirradiation is expected to increase the controllability of ALE growth. An ALE growth using Ar ion laser was demonstrated successfully.[3)] It was reported that surface morphorogy was improved by KrF excimer laser irradiation in molecular layer epitaxy.[1)] Excimer lasers operate only in short pulses. Moreover, there were not so many irradiated photons during one growth cycle, because the duty cycle is low. Therefore, the effect on ALE may not be necessarily as expected in KrF excimer laser irradiated ALE, as well as an Ar ion laser irradiated ALE.[3)] Recently, the authors have investigated the ALE growth using KrF excimer laser[7)]. This presentation reports the KrF excimer laser irradiation effect on GaAs ALE, and growth rate dependence on pattern configuration for SiO_2.

2. Experimental procedure

Source gases were trimethylgallium(TMG) and arsine(10% AsH_3 in H_2). Hydrogen was used as a carrier gas. The growth reactor consisted of a vertical stainless steel tube. It was designed to suppress gas flow convection. The growth pressure was 10 to 20 Torr.

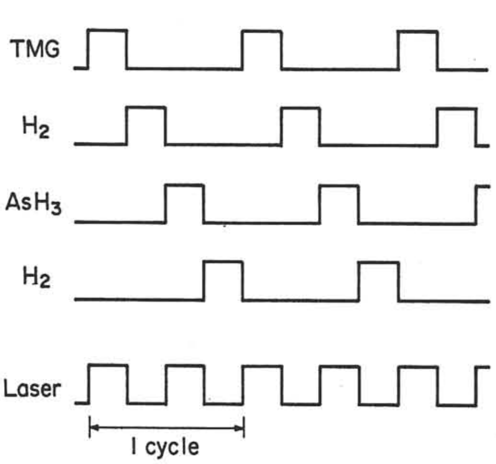

Fig.1 Time sequences for gases and laser irradiation

Typical time sequences for the gases and laser irradiation are shown in Fig.1. TMG and AsH_3 gas were alternately introduced onto the GaAs growing surface. These source gases were separated by H_2 purging to prevent mixing. The substrate was perpendicularly irradiated by KrF excimer laser synchronized with the introduction of both source gases. The laser power density was $12 \sim 15 mJ/cm^2$ at the substrate surface, and the repetition rate was 80 pulses per second. One growth cycle comprises TMG flow period, H_2 flow period, AsH_3 flow period and H_2 flow period. Typical growth duration was 600 cycles. Substrates were GaAs(100) wafers, which were partially masked with SiO_2 deposited by CVD. After the growth, the SiO_2 masks on the substrate were removed. The step heights were measured by a surface roughness profiler. Growth rate was determined by dividing the step height by the growth cycle number.

3. Results and discussion

3.1. The KrF excimer laser irradiation effect

Figure 2 shows the growth rate as a function of growth temperature for laser irradiated and nonirradiated growths. The

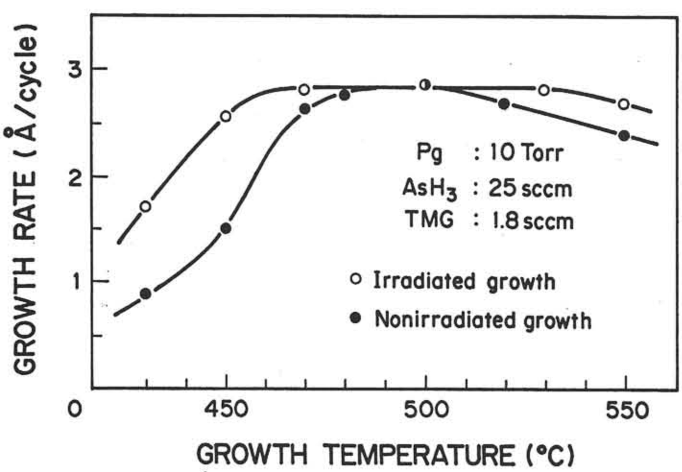

Fig.2 Growth rate as a function of growth temperature for laser irradiated growth

pulse durations for individual source gases and purge H_2 gas were 2 seconds. In nonirradiated growth, monolayer growth was achieved only for an extremely narrow temperature range around 500°C. On the other hand, in laser irradiated growth complete monolayer growth was obtained over a relatively wide temperature range, from 470°C to 530°C. In both laser irradiated growth and nonirradiated growth, the growth rate increased as the growth temperature increased in the lower temperature range, but the growth rate decreased as the growth temperature increased in the higher temperature range. It is considered that the growth rate was controlled by the TMG decomposition rate on the surface in the lower temperature range, while the growth rate was controlled by the TMG desorption rate on the surface in the higher temperature range. The growth temperature range for monolayer growth under laser irradiation expanded not only to lower temperature but also to higher temperature, compared with that of nonirradiated growth. This result suggests that KrF excimer laser irradiation enhanced the decomposition of TMG on the surface.

Figure 3 shows the growth rate as a function of the TMG pulse duration for laser irradiated and nonirradiated growths. In both laser irradiated growth and nonirradiated growth, the growth rate was saturated completely at one monolayer. In laser irradiated growth, one monolayer growth was achieved by shorter TMG pulse duration than that in nonirradiated growth.

The growth rate is shown as a function of the TMG flow rate for nonirradiated growth in Fig.4. One complete monolayer growth was achieved independently from TMG flow rate. This result suggests that most of species, supplied from the vapor phase, were TMG. If species supplied from the vapor

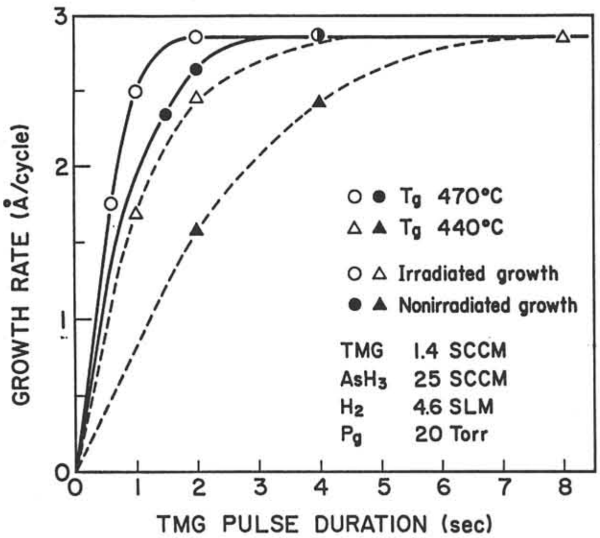

Fig.3 Growth rate as a function of TMG pulse duration for laser irradiated growth and nonirradiated growth

phase contained dimethylgallium, methylgallium or gallium, these species strongly adsorbed on Ga atoms at surface. In that case, one monolayer growth could not be achieved.

In order to investigate the enhanced TMG decomposition on the surface due to KrF excimer laser, the authors analyzed the data presented in Fig.2, using the surface process model, including the adsorption, desorption and decomposition of TMG on the surface. TMG from the vapor phase was assumed to be adsorbed weakly on the surface As atoms at the adsorption rate k_s, and then to be desorbed from the surface at the desorption rate k_{ds} or to decompose at the decomposition rate k_{dc}. If TMG is decomposed into methylgallium or gallium on the surface, they are adsorbed strongly at the surface and not desorbed from the surface. Therefore, the rate equations follow as,[6)]

$$\frac{d\theta_{TMG}}{dt}=k_s(1-\theta_{TMG}-\theta_{Ga})-k_{dc}\theta_{TMG}-k_{ds}\theta_{TMG}$$

$$\frac{d\theta_{Ga}}{dt}=k_{dc}\theta_{TMG}$$

where θ_{TMG} was surface coverage for TMG, and θ_{Ga} was surface coverage for methylgallium or gallium. The methylgallium or the gallium were strongly adsorbed at the surface, and were unable to be desorbed from the surface. The authors considered that the growth rate was in proportion to θ_{Ga}.

Decomposition rate k_{dc} for TMG on the surface is shown as a function of growth temperature in laser irradiated and nonirradiated growth in Fig.5. The k_{dc} was increased by the laser irradiation, and the activation energy for TMG decomposition

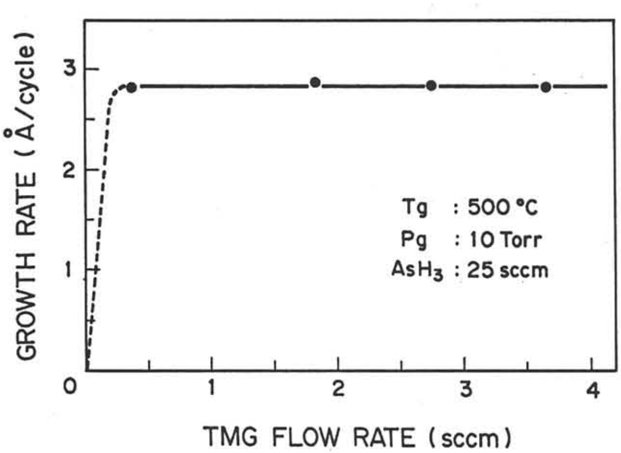

Fig.4 Growth rate as a function of TMG flow rate for nonirradiated growth

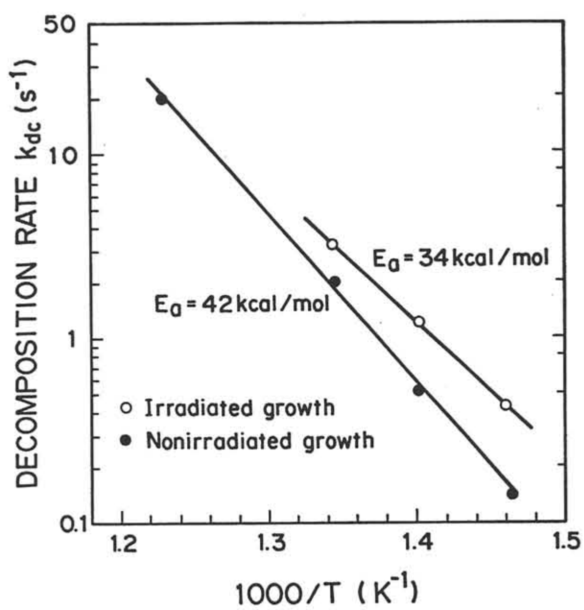

Fig.5 Decomposition rate k_{dc} for TMG on the surface, as a function of growth temperature

decreased from 42kcal/mol to 34kcal/mol due to the laser irradiation.

3.2. Growth rate dependence on pattern configuration for SiO_2

In conventional MOCVD for selection growth, the growth rate depends strongly on the ratio R(GaAs/SiO_2) for the GaAs window area to the SiO_2 masked area on the substrate.[8] In order to investigate this effect in ALE growth, two substrates with different pattern configurations were used. They were R=0.03(substrate A) and R=38(substrate B). Figure 5 shows temperature dependences for growth rate for both substrates under laser irradiation. The growth rate for substrate A(R=0.03), whose SiO_2 masked area was larger than the GaAs window area, was larger than that for substrate B(R=38) for temperature below 500°C. The monolayer growth temperature range for substrate A(R=0.03) was rather wider than that for substrate B(R=38). These results suggest that a considerably large number of TMG molecules diffused to the GaAs window surface from the SiO_2 mask. However, in the high temperature range, no distinguishable difference in the growth rate for the two substrates was observed. In this temperature range, the growth rate was decreased due to the desorption of TMG adsorbed on the surface. This suggests that very little TMG diffused to the GaAs surface from the SiO_2 mask in the high temperature range.

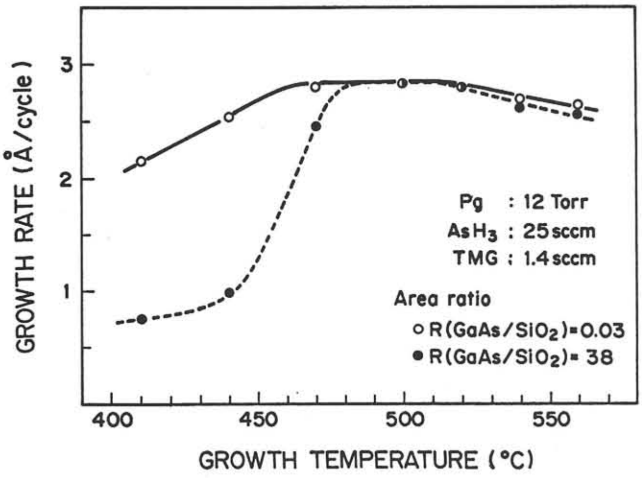

Fig.6 Growth rate temperature dependence for two substrate with different pattern configurations

4. Conclusion

The atomic layer epitaxy for GaAs using KrF excimer laser has been demonstrated. The temperature range for monolayer growth was expanded due to KrF excimer laser irradiation. It was found that the KrF excimer laser irradiation was effective for GaAs ALE. Analysis was carried out on growth processes using the surface process model. The results indicated that the excimer laser irradiation decreased the activation energy for TMG decomposition. In selective growth, it was found that only very little TMG molecules diffused to the GaAs surface from the SiO_2 mask in a high temperature range.

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