

Invited

Recent Progress in Low Temperature Photochemical Processes

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In photochemical processes, a sort of specific radical or ion can be selectively formed without defect generation and pure reactions can be accelerated even at lower temperatures. Fundamental superiorities of photochemical processes are discussed emphasizing their importance in crystal growth process. The photochemical induced effects on the epitaxial growth of GaAs layers have been demonstrated. The growth rate has been enhanced by irradiation with an excimer laser.

§1. Introduction

High reliability and high reproducibility in semiconductor technology are mainly based on perfect crystal technology. By minimizing the deviations from the perfect crystals, the reduction of characteristic fluctuations can be realized as well as the improvement of performance in semiconductor devices because of the reduction of defects and its propagation. High temperature processing, which is usually used, frequently causes defect generation and propagation, thermal wafer warpage and impurity redistribution. Therefore, the development of low temperature processing techniques is increasingly required in the manufacture of semiconductor devices.

Plasma assisted chemical techniques have been developed as low temperature processing. In these techniques, however, defects are generated near the semiconductor surface due to plasma ion bombardment and complexed reactions are induced due to the simultaneous production of many sorts of reacting species. Moreover, process parameters such as rf power, rf frequency, electrode spacing, gas flow, total pressure, and substrate heating are all interrelated and difficult to be individually controlled. As an alternative approach, photochemical techniques have been receiving increasing attention in semiconductor processes. Deposition, etching and doping can be carried out at low temperatures by utilizing photochemical reactions. Photochemical processes have the potential for becoming ideal processing techniques because they have few drawbacks such as defect generation.

The author (J. Nishizawa) has first proposed photochemical technique in 1961¹⁾, and applied this technique to the vapor phase epitaxial growth of Si²⁾. High quality Si epitaxial layers were grown at lower temperatures by irradiating with UV light. This method called photoepitaxy will become important technology for growing perfect crystals, which are essential to high performance semiconductor devices. This paper describes the potentiality of photochemical processes and the results of its application to the vapor phase epitaxial growth of GaAs.

§2. Potentiality of Photochemical Processes

In photochemical processes, reactions are less complex and fewer defects are generated due to excess energies unlike plasma excitation because pure radicals and ions can be formed by selecting the photon energy. Moreover, photochemical processes have the possibility that each elementary process can be individually controlled among the competitive processes by using monochromatic light of which wavelength is suited to the activation energy of the process. Photochemical processes can be carried out at low temperatures and it is expected that monitoring and controlling the system will be relatively easy. Therefore, photochemical processes seem to be a more promising technique to achieve precise control. Another advantage of photochemical processes is the ability to localize spatially the reaction region by using a tightly focused laser beam.

The application to crystal growth from the vapor phase will be briefly discussed. In the vapor phase crystal growth, the species adsorbed on the substrate surface are transported by surface migration to kink sites where they are bonded to the crystal lattice, as shown in Fig.1. Therefore, energies for vapor phase reaction, adsorption, surface migration, surface reaction and bond to the crystal lattice are needed at each process step. For example, in the case of growth of Si crystals, there should be a suitable wavelength for each reaction such as $\text{SiCl}_4 + \text{H}_2 \rightarrow \text{SiHCl}_3 + \text{HCl}$ and $\text{SiHCl}_3 + \text{H}_2 \rightarrow \text{SiHCl}_2 + \text{HCl}$ and also for the dissociation of impurity gas. The composition of species adsorbed on the substrate surface can be controlled by using these wavelengths properly. In order to grow high quality crystals, energy for accelerating surface migration is required and thermal energy is usually used. However, vacancies and interstitials become to be formed and then imperfections are increased with raising temperature. Therefore, it is necessary to accelerate the surface migration without raising temperature and photons seem to be most suitable as above-mentioned energy source.

As aforementioned, overall reaction is composed of many process steps and there should be the wavelength which

is most suitable to the activation energy of the process step. Therefore, by irradiating with multiwavelength light and controlling the intensity of each wavelength light, every process step can be individually controlled. Although the irradiation with only the wavelength which activates the rate-determining step is adequate, multiwavelength irradiation is of great promise because the amount of dopant can be also controlled by the relative intensity of irradiated light.

§3. Photoepitaxy of GaAs

The photo-excitation effects on the vapor phase epitaxial growth of GaAs have been demonstrated. The growth of GaAs epitaxial layers was carried out by using a conventional AsCl_3 - Ga - H_2 system. A schematic diagram of the growth apparatus is shown in Fig.2. The temperature of the AsCl_3 bubbler was kept to 0°C and the flow rate of hydrogen through the AsCl_3 bubbler was kept to $100\text{cm}^3/\text{min}$. The substrates were Cr-doped semi-insulating GaAs, oriented 4° off the (100) toward (110). An excimer laser and a high pressure mercury lamp were mainly used as a light source for irradiation during crystal growth. The light was introduced into the growth zone without any focusing.

Figure 3 shows the growth rate as a function of incident excimer laser wavelength for an incident power of $\sim 1.7\text{W}$. The growth rate was increased by 248nm (KrF) irradiation but scarcely changed by other wavelength irradiation. Moreover, no enhancement of growth rate was obtained by irradiation with an argon-ion laser light. These results indicate that the growth rate enhancement is not caused by thermal-induced reactions but by photo-induced reactions.

The growth rate for no irradiation and irradiation with the 248nm laser is plotted in Fig.4 as a function of the reciprocal growth temperature. In this experiment, the temperature difference between the source and the growth zone was kept to 50°C . In the absence of irradiation, the growth rate decreased with lowering the growth temperature from 700°C , but increased slightly below 600°C and then decreased again below 550°C . No crystal growth was obtained below 500°C . This growth rate behavior seems to depend on the degree of AsCl_3 decomposition. Namely, AsCl_3 is not completely decomposed for the source temperature below 700°C and the source reacts not only with HCl but also directly with AsCl_3 .³⁾ In the case with irradiation, however, the growth rate decreased slightly with lowering the growth temperature and the growth was obtained above 480°C . The growth rate was found to be enhanced over the whole of temperature range of $480 \sim 700^\circ\text{C}$ by irradiation with 248nm laser. The growth rate can be controlled by changing the incident laser power because the growth rate increases in proportion to the incident power, as shown in Fig.5.

Figure 6 shows the growth temperature dependence of Hall mobility for GaAs layers grown with irradiation of high pressure mercury lamp light and without irradiation. In this experiment, the source temperature remained unchanged at 720°C . Although the mobility decreased rapidly with lowering the growth temperature, the layers grown with irradiation have 10~15% higher mobility than that of the layers grown without irradiation.

The mechanisms of irradiation effects have not been clear yet, but the growth rate enhancement is presumably associated with the absorption by GaCl because GaCl has the absorption band at 248nm.⁴⁾

§4. Future Prospects

Photochemical processes has the potential for becoming useful processing techniques because they possess indispensable conditions for realizing high performance semiconductor devices. The combination of photochemical technique and molecular (atomic) layer epitaxy⁵⁾ is expected to enable high quality and exactly thickness controlled very thin layers to be grown at low temperatures and the crystal growth mechanism to be clarified.⁶⁾ Moreover, photochemical processing technique is expected to be used for synthesis of the materials which can not be synthesized by thermal chemistry without accelerating unnecessary reactions such as autodoping.

References

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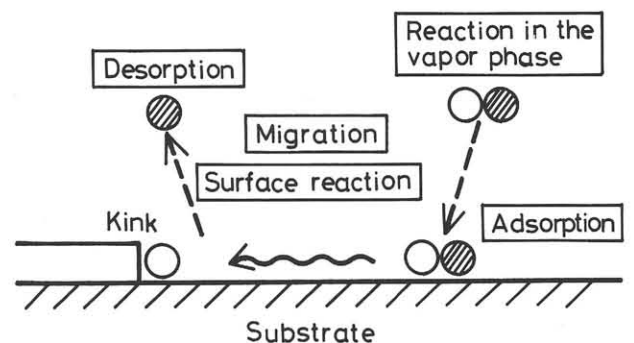


Fig.1 Process steps of crystal growth from the vapor phase.

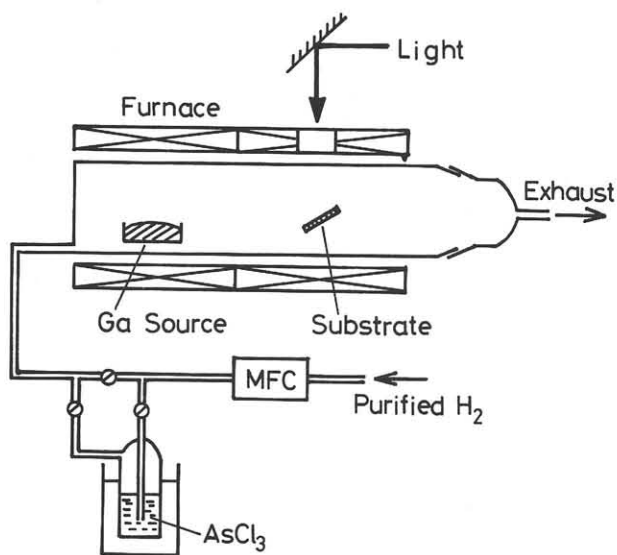


Fig.2 Schematic diagram of the growth apparatus.

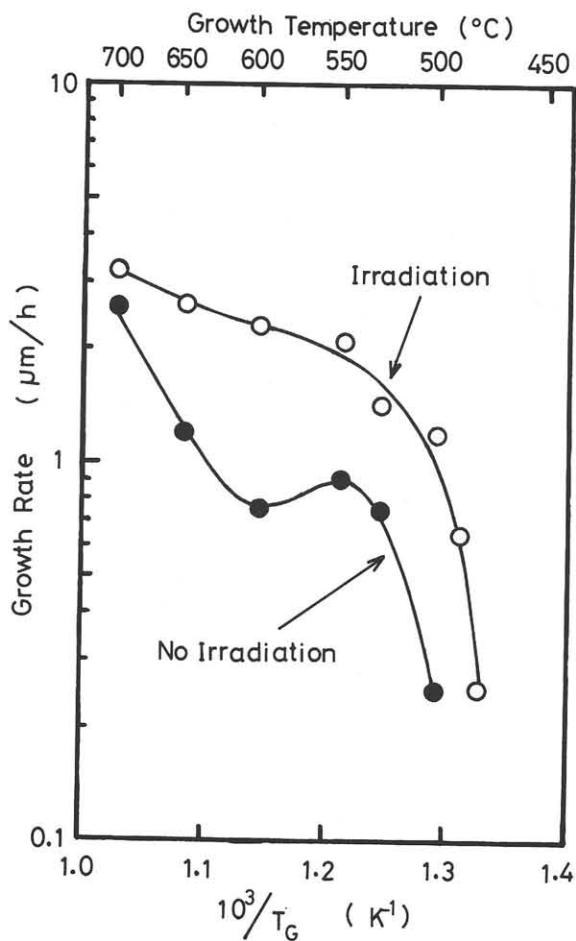


Fig.4 Temperature dependence of growth rate for GaAs epitaxial layers.

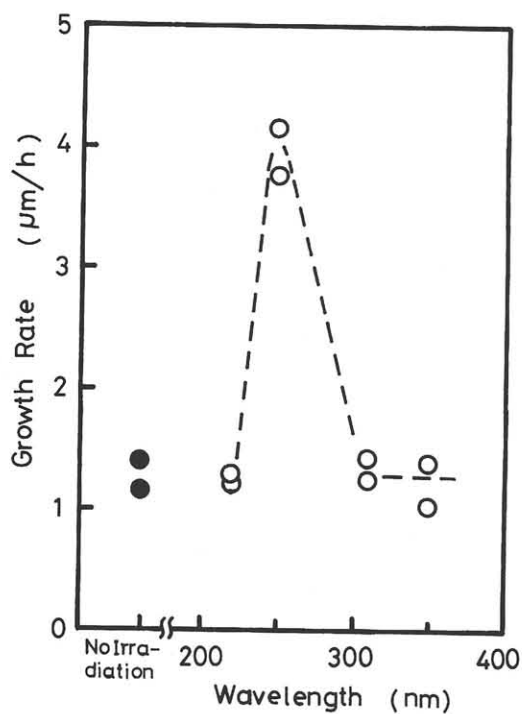


Fig.3 Wavelength dependence of growth rate for GaAs epitaxial layers grown by irradiation with an excimer laser.

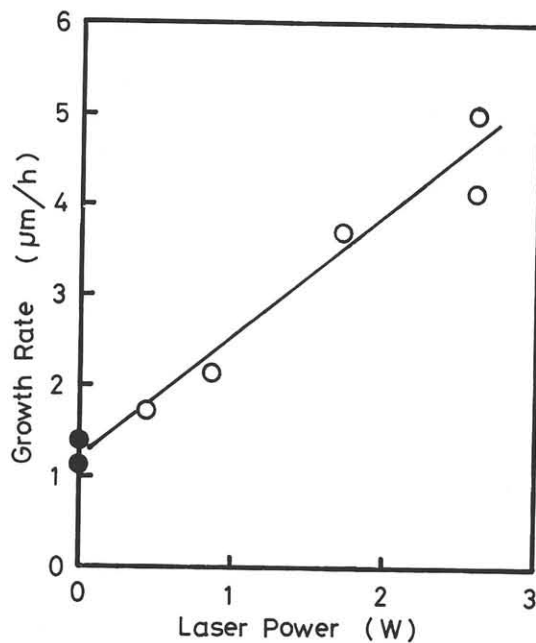


Fig.5 Incident laser power dependence of growth rate for GaAs epitaxial layers.

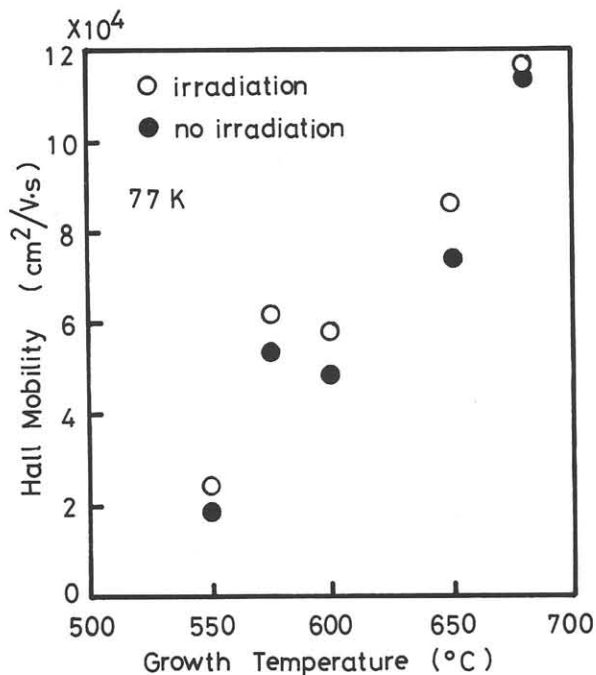


Fig.6 Growth temperature dependence of Hall mobility for GaAs epitaxial layers.

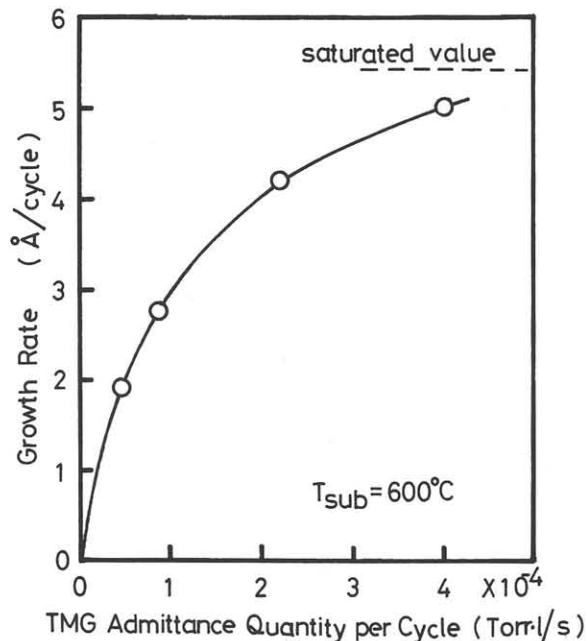


Fig.8 Growth rate of GaAs layers grown by molecular layer epitaxy as a function of TMG admittance quantity per cycle. (By J. Nishizawa, H. Abe and T. Kurabayashi).

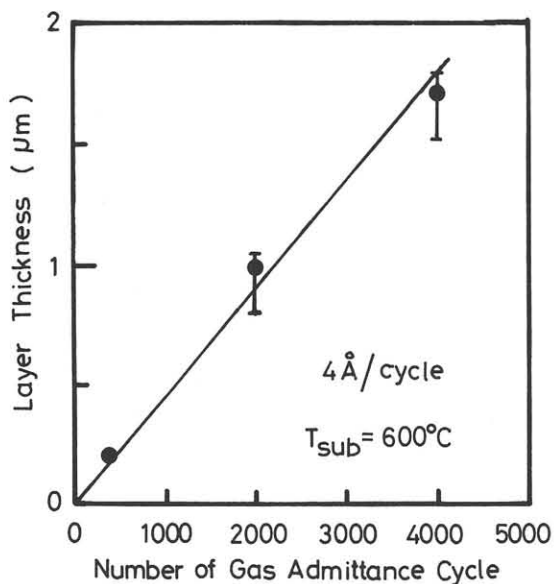


Fig.7 Thickness of GaAs layers grown by molecular layer epitaxy as a function of number of gas admittance cycle. Gas admittance conditions are as follows; After AsH₃ is admitted with $p \approx 5 \times 10^{-5}$ Torr for 20sec, a pause is inserted in gas exchange 1sec long and TMG is admitted with 1×10^{-4} Torr l/s for 4 sec. (By J. Nishizawa, H. Abe and T. Kurabayashi).

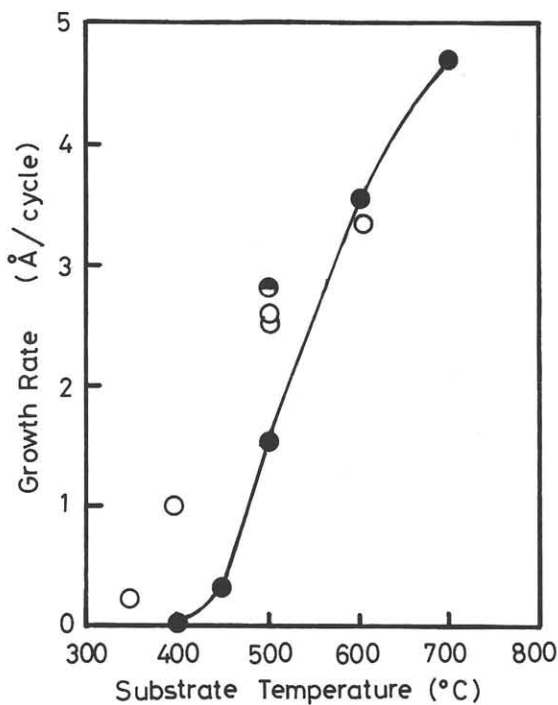


Fig.9 Growth rate of GaAs layers grown by molecular layer epitaxy as a function of the substrate temperature. ●: no irradiation, ○: irradiation by a high pressure Hg-lamp, ●: irradiation by 257nm laser (By J. Nishizawa, H. Abe and T. Kurabayashi).