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Laser MOCVD Crystal Growth in GaAs

Yoshinobu Aoyagi, Sohachi Iwai, Yusaburo Segawa,
*Atsutoshi Doi and Susumu Namba

The Institute of Physical and Chemical Research
Wako-shi, Saitama, 351-01, Japan
*International Micro Technology Corp.
2-15-2, Shinkanda Bldg. Sotokanda, Chiyoda-ku, Tokyo, 101, Japan

It has been found a growth rate of GaAs epitaxial layer is largely enhanced by CW Ar ion laser irradiation in metal organic chemical vapor deposition (MOCVD). The dominant mechanism of the enhancement is photochemical process at the surface. This technique of the crystal growth makes a patterned crystal growth possible.

1. Introduction

Many workers have much interests in a metal organic chemical vapor deposition (MOCVD) crystal growth for many advantages of this technique such as high controlability of the thickness of the epitaxial layer, possibility of making a high quality and large area epitaxial wafer. If the MOCVD crystal growth is controlled by external light or beam, many new advantages like a patterned crystal growth and/or fabrication of new devices are expected.

In this paper large enhancement of a growth rate of the epitaxial layer by CW Ar ion laser irradiation in GaAs MOCVD is reported (Laser MOCVD). Characteristics of the growth of the epitaxial layer and the mechanism of the enhancement are discussed.

2. Experimental Procedure

Our MOCVD system is operated at a pressure of 100 mb or 2 mb. The substrate is heated by a resistance heater and the furnace is a conventional transverse type as shown in Fig.1. The flow rate of the H_2, AsH_3 (20% H_2 base) and trimethyl gallium (TMG) are typically 2650, 150 and 6 sccm and the growth time is 30 min. To study characteristics of the Laser MOCVD a total flow rate and a V/III mole ratio are changed. Substrates used are Cr doped SI and Si doped n type (100)$\pm$0.5 or (100) 2° off wafers etched by an etchant (H_2SO_4:H_2O_2:H_2O=4:1:1). The laser used is a CW Ar ion laser. Each oscillation line of the laser between 514.5 to 457.9 nm is used to examine wavelength dependence of the Laser MOCVD. Samples are irradiated by the laser through a qualtz window. The laser power was changed upto 3 W for large area irradiation (about 1cm in diameter, large area Laser MOCVD) and 0.7 W for focused irradiation (350 μm diameter, focused Laser MOCVD). The substrate temperature is directly monitored by an infrared thermometer.

3. Experimental Results and Discussion

Figure 2 shows a surface of the epitaxial layer grown by the focused Laser MOCVD and the cross section observed by talystep. Under a

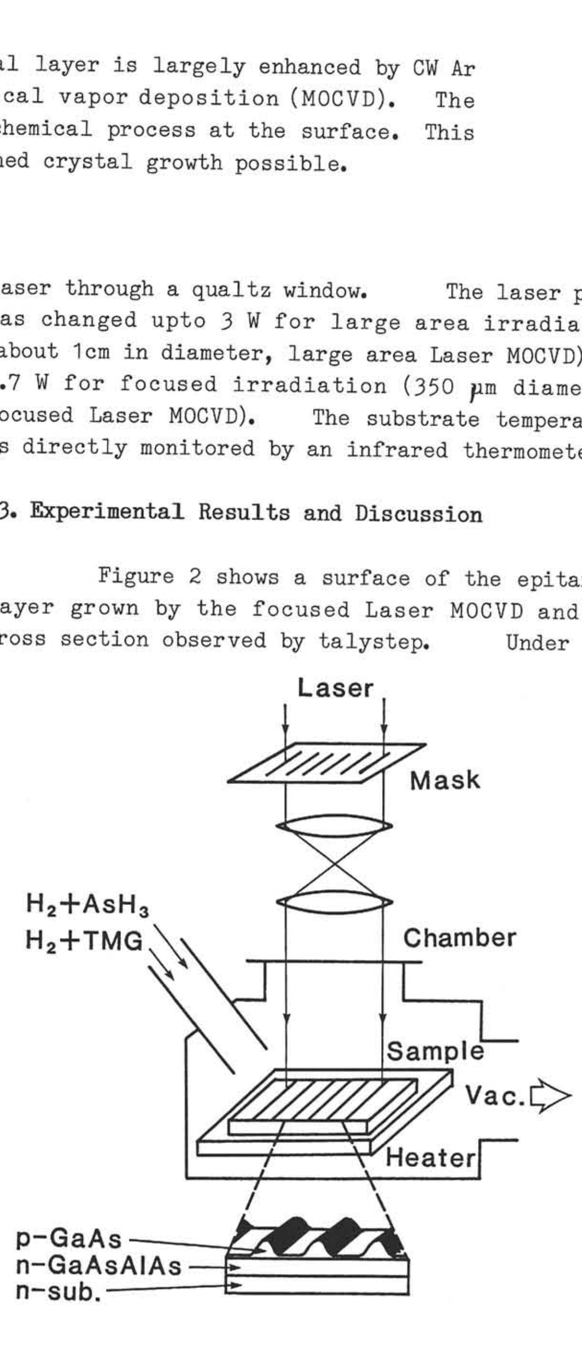
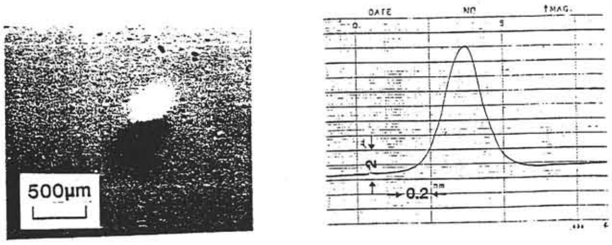


Fig.1 Schematic diagram of the Laser MOCVD system.



(a) (b)

Fig.2 (a) Surface pattern of the epitaxial layer grown by the focused Laser MOCVD at 550°C, 514.5 nm and 774 mW. (b) Talystep trace of the pattern.

condition of the focused irradiation of 350 μm diameter (~35 W/cm^2) the enhancement is about 8.4 μm and the enhancement factor ($\Delta d/d_{nor}$) is more than 100. The observed spot size is in agreement with the spot size of the irradiation laser beam. The surface of the layer grown by the large area Laser MOCVD is a mirror like as same as that grown by the conventional MOCVD but small surface hillocks are observed. The hillocks seem to be due to an inhomogeneity of the laser intensity due to a speckle pattern.

Usually the crystal growth mechanism in MOCVD is considered as a transport limit of Ga material pyrolitically decomposed from TMG. Therefore, the growth rate is independent of the substrate temperature(1). However, in our system the growth rate strongly depends on the substrate temperature as shown in Fig.3 in the temperature range of 500 to 680°C and is given by

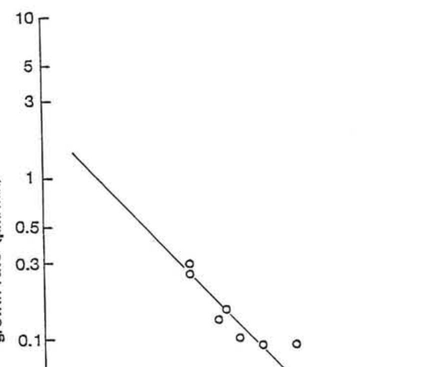


Fig.3 Temperature dependence of the growth rate of our MOCVD without laser irradiation.

$$d_{nor}=d_0\exp(-E/kT), \qquad (1)$$

where E=0.33 eV in our observed temperature range. This result suggests that some reaction limit growth mechanism should be considered in our system. The laser enhanced crystal growth was mainly observed in this temperature region. If we use a substrate temperature larger than 750°C, only a little enhancement is observed. Around this temperature, a transport limit crystal growth mechanism is dominant. The enhancement factor has

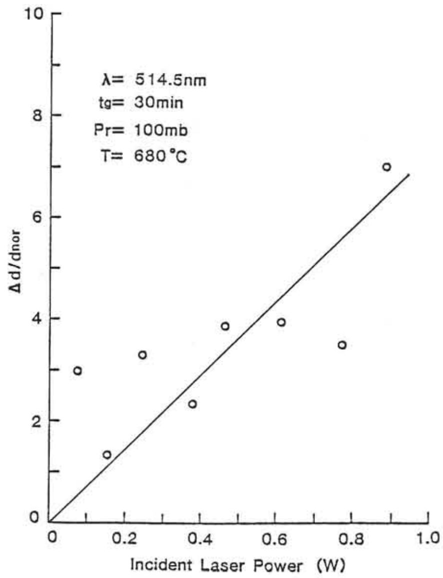


Fig.4 Enhancement factor as a function of incident laser power. d is the thickness enhanced by the laser irradiation and d_{nor} is the thickness of the epitaxial layer grown by the MOCVD without the laser irradiation.

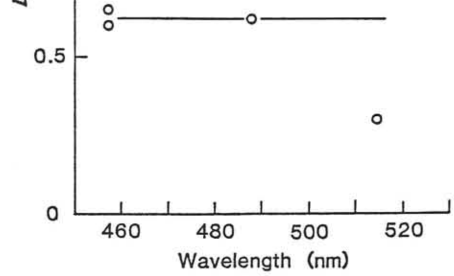


Fig.5 Enhanced thickness of the epitaxial layer as a function of the wavelength of the incident laser.

linear dependence on the incident laser power in the observed range from 50 mW and 700 mW for the focused Laser MOCVD as shown in Fig.4. This result suggests the enhancement is a linear process. We can not observed wavelength dependence of the enhancement for each line of the Ar ion laser from 457.9 nm to 514.5 nm as shown in Fig.5.

Figure 6 shows an enhancement factor as a function of the growth temperature. The lower the growth temperature is, the larger the enhancement factor is. If the enhancement is a pure pyrolitic effect, the enhancement factor $\Delta d/d_{nor}$ is given by

$$\Delta d/d_{nor}=(\exp(-E/k(T+\Delta T)-\exp(-E/kT))/\exp(-E/kT) \quad (2)$$

from eq.(1). The observed enhancement factor at the low temperature is larger than 100. The temperature increase ΔT under the laser irradiation estimated from eq.(2) would have to be about 2×10^4°C to get the observed enhancement factor of 100 at the temperature of 530° In this case the substrate temperature would be much higher than the melting point (1238°C) of the GaAs wafer. Moreover, the observed spot size is almost same as the irradiation spot size. If the pyrolitic reaction is dominant, the enhanced area would be much larger than the irradiation spot size due to the high thermal conductivity of GaAs. These results suggest the enhancement process is not a pure pyrolitic effect.

Figure 7 shows a growth rate of the epitaxial layer grown by the Laser MOCVD as a function of V/III mole ratio. As shown in this figure the growth rate increases with decreasing the ratio of V/III.

Figure 8 shows a enhancement factor as a function of the total flow rate with keeping a constant V/III ratio. This result shows that increasing the total flow rate the enhancement factor increases but saturates at a large flow rate region. These two results suggest that supply of the large amount of the TMG (or partially decomposed TMG) to the surface is important to the large enhancement of the Laser MOCVD.

In our experiment the enhancement factor of the Laser MOCVD grown on the n type substrate is two or three times larger than that grown on the SI substrate. This substrate dependence of the enhancement factor is quite surprising phenomena, because the temperature of the substrate is quite high and at the temperature both of the n and SI substrate should become intrinsic. If electron at the surface is related to this enhancement phenomena, the electron of the substrate should

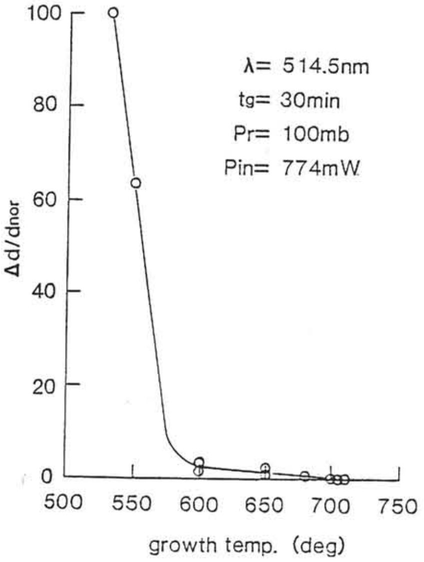


Fig.6 Enhancement factor as a function of the growth temperature.

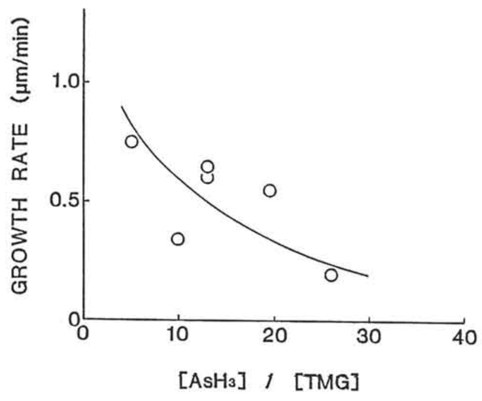


Fig.7 Growth rate of the epitaxial layer under the laser irradiation as a function of V/III mole ratio.

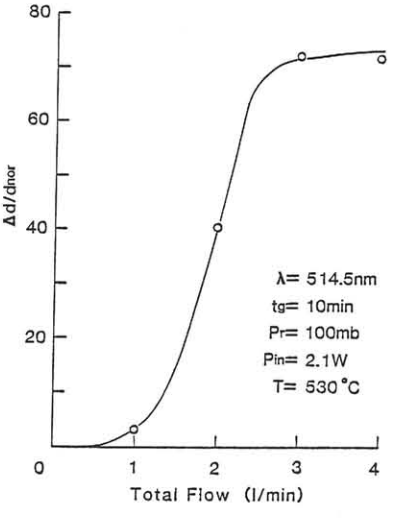


Fig.8 Enhancement factor as a function of the total flow rate.

diffuse onto the surface where the epitaxial crystal growth is going on. It is very interesting that the enhancement of the crystal growth by the Laser MOCVD is quite resemble to the laser induced chemical etching in the point of view of the dependence of the type of the substrate. All of these results, that is, an anomalously large enhancement of the epitaxial layer by the laser irradiation, keeping the small spot size crystal growth under the focused laser irradiation, the dependence of the type of the substrate, prove that the enhancement process is not a pyrolitic effect but photo surface effect.

In our system the distance between the nozzle and the sample is short. In this design TMG or AsH_3 (or partially decomposed TMG or AsH_3) should diffuse to the surface before pyrolitic decomposition. If the TMG or AsH_3 diffuses to the GaAs wafer, TMG or AsH_3 may be easily decomposed by the catalytic effect(2) of GaAs surface. The irradiation of the laser light may enhance the decomposition by a photoassisted catalytic effect(3) at the surface or some photo surface effect schematically shown in Fig.9. The photon energy of the irradiation laser is too small to decompose directly the Ga-C bond, but is enough to decompose TMG or AsH_3 at the surface by the photo catalytic or surface effect, if a catalytic activation energy is the observed activation energy of 0.33 eV. Therefore we have observed a largely enhanced crystal growth which is more than that expected by the pure pyrolitic effect and we do not observe a wavelength dependence of the enhancement. The temperature dependence of the enhancement factor may be explained as follows. If the temperature is high, TMG and/or AsH_3 is decomposed before diffusing to the sample surface and the amount of TMG or AsH_3 decreases at the sample surface. Therefore the enhancement of the crystal growth by laser light decreases if the temperature is raised.

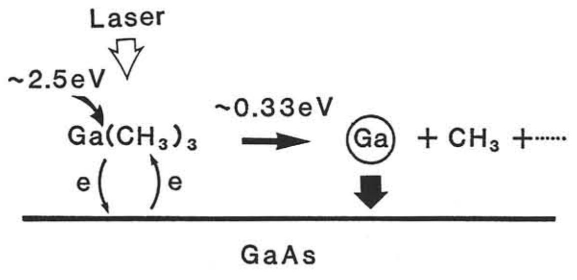


Fig.9 Schematic diagram for the mechanism of the Laser MOCVD.

At a temperature around 500°C the crystal growth rate without the laser irradiation is very small and the enhancement by the laser irradiation is large in this temperature region. This result suggests that patterned crystal growth, that is, a rigid waveguide construction or the crystal growth in small areas by the Laser MOCVD becomes possible in contrast with the conventional MOCVD.

The optical and electrical characteristics of the epitaxial layer grown by the Laser MOCVD are almost equivalent to those grown by the conventional MOCVD but under some condition of the growth the photoluminescence of the epitaxial layer becomes stronger than that grown by the conventional MOCVD and doping is modulated by the laser irradiation. Details are now under the examination.

It should be emphasized that the crystal growth can be controlled by the visible CW laser irradiation. If we use an excimer laser we can easily decompose the TMG bond directly but a duty cycle of the pulse laser is low. In the case of the excimer laser irradiation the enhancement effect should be small.

4. Conclusion

We have observed the large enhancement of the crystal growth in the MOCVD by the Ar ion laser irradiation. The experimental results show the photochemical effect like the photo catalytic or photo surface effect is the dominant mechanism for the Laser MOCVD.

References

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