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MOCVD of GaAs-AlGaAs —Homogeneous Nucleation in the Growth of AlGaAs—

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We have investigated the effect of growth temperature on growth rate, alloy composition and crystal quality of AlGaAs grown by MOCVD under atmospheric pressure. The growth rate and the alloy composition were found to change remarkably with growth temperature under a relatively low flow rate of hydrogen carrier gas. The change in the growth rate against the growth temperature could be interpreted by homogeneous nucleation of GaAs and AlAs at high temperature. Al composition in solid was not the same as that in vapor phase and the difference changed with the growth temperature. This phenomenon and the fluctuation of the alloy composition over the wafer were correlated with the homogeneous nucleation.

§1. Introduction

GaAs/AlGaAs double-heterostructure lasers with a low threshold current density have been made by several research groups using metalorganic chemical vapor deposition(MOCVD). AlGaAs/AlGaAs visible lasers have also been fabricated by Mori et al.[1], Burnham et al.[2] and other groups using this technology. Systematic life tests have been carried out for visible wavelength lasers, and showed very long lifetime comparable to those of lasers grown by liquid phase epitaxy[3]. The MOCVD is now one of the most useful technology for production of large-scale laser wafers with excellent performance and reliability.

Furthermore, MOCVD has high potential to grow other sophisticated structure devices, such as multi-quantum well[4], symmetric distributed-Bragg-confinement[5], graded refractive index SCH[6] lasers and GaAs/AlGaAs modulation doped structure devices[7]. It is necessary to control alloy composition precisely and to avoid alloy clustering in AlGaAs to make a sharp hetero-interface for fabricating such sophisticated devices with good characteristics.

It is most important to understand growth kinetics in MOCVD to overcome above serious problems. Unfortunately, only few works have been done concerning this problem up to now. Lays et al.[8] have studied on growth rate of GaAs as a function of growth temperature and total hydrogen flow rate in MOCVD. They found that the growth rate of GaAs decreased at temperature above 750°C. Though the similar results have been reported by some authors[9], it has not yet been interpreted why the growth rate decreased at high temperature.

We studied systematically on the relations of the growth rate and the alloy composition in AlGaAs to the growth temperature and to a molar ratio of Al to Ga in the vapor phase. We found, through the growth experiment, that homogeneous nucleation of GaAs and AlAs played a decisive role in the growth of AlGaAs.

In this paper, we first present the data on the change of the growth rate and the alloy composition against the growth temperature for different arsenic over pressure and total hydrogen flow rate. The relation of the alloy composition versus the molar ratio of Al to Ga in the vapor phase is shown for several different combination of the growth parameters. Finally, we discuss on the homogeneous nucleation and its role in the MOCVD.

§2. Experiment

AlGaAs was grown by MOCVD in a conventional vertical reactor using trimethyl-gallium (TMG), trimethyl-alluminum (TMA) and arsine (AsH_3) at temperature from 620°C to 920°C under atmospheric pressure. The flow rates of TMG, TMA and AsH_3 for the growth of $Al_{0.3}Ga_{0.7}As$ were 0.526, 0.118 and 23.85 ml/min, respectively.

AlGaAs was grown under two distinctly different total gas flow rate conditions: a relatively low hydrogen flow rate of 6 l/min, and a high rate of 12 l/min. Upward thermal convection of the hydrogen gas around the susceptor was observed in the former condition, while no appreciable perturbation was observed in the latter.

The AlGaAs layers doped with selenium were grown on Si or Cr doped subtrates oriented to (100), (111)B, (311)A and (311)B. Thickness of the grown layer was measured from an image of a scanning electron microscope. Carrier concentration was measured by a Hg contacted C-V profiling technique and a room temperature photoluminescence (PL) spectra of the layer was observed under excitation with a 5145 A argon ion laser with incident power density of about 25 W/cm^2. The alloy composition was evaluated from a band-edge peak wavelength of the PL spectra using band parameters deduced by Casey and Panish[10]. The alloy composition for the layer with the indirect band edge was measured with an electron probe mass analysis.

§3. Result and Discussion

We investigated efficiency of Se doping from H_2Se into $Al_{0.3}Ga_{0.7}As$ grown on the GaAs substrate with various surface orientations as a function of the growth temperature. Fig.1 shows the carrier concentration against the growth temperature. The layers were grown under relatively low hydrogen flow rate of 6 l/min. Temperature dependence of the carrier concentration in the layer grown on the (311)B substrate was almost the same as that on the (100) substrate in the temperature range from 620°C to 870°C. They have a minimum value about $1.5\times10^{17}cm^{-3}$ at the temperature about 750°C. The carrier concentrations in the (111)A and (311)A layers, however, increased monotonically from 620°C to 870°C. While the dependence of the doping efficiency of Se on the growth temperature is different among the (100)/(311)B, (111)A and (311)A layers at temperature below 750°C, it is almost the same at higher temperature. The result seems to suggest the difference in a growth kinetics between two temperature regions divided at about 750°C.

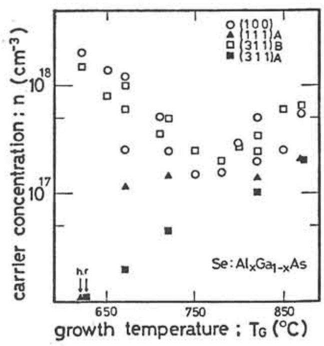

Fig.1 Carrier concentration against growth temperature for Se doped $Al_{0.3}Ga_{0.7}As$ grown on (100),(111)A, (311)A and (311)B oriented substrates.

The growth rate, band-edge PL wavelength, λ_{PL}, and the band-edge PL intensity normalized by its carrier concentration, I_{PL}/n, for the layer grown on the (100) substrate are shown in Fig.2. The growth rate was independent of temperature from 600°C to 700°C and it decreased drastically with increasing temperature above 720°C. Dependence of λ_{PL} on the growth temperature was similar to that of the growth rate. This implies that the decrease in the growth rate of GaAs is larger than that of AlAs in the alloy crystal grown in the high temperature region.

We calculated each growth rate of GaAs and AlAs in the alloy separately from the data of λ_{PL} and the growth rate of the alloy. The growth rates of GaAs and AlAs normalized by the rates at a low temperature are shown in Fig.3. Though the decrease in the growth rate of GaAs is much more drastic, the growth rate of AlAs also decreases with increasing temperature . The specific temperature at which the minimum carrier

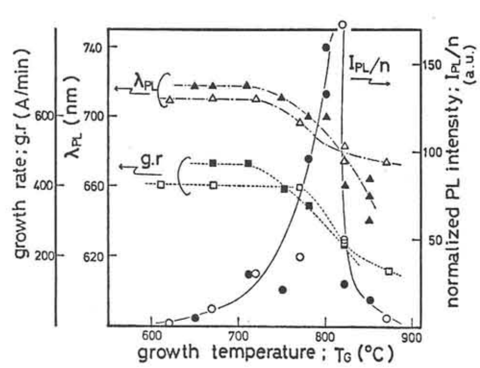

Fig.2 Temperature dependence of growth rate, band-edge PL peak wavelength, λ_{PL}, and normalized PL intensity, I_{PL}/n, of Se-AlGaAs on (100) substrate. Growth was carried out under relatively low hydrogen flow rate 6 l/min.

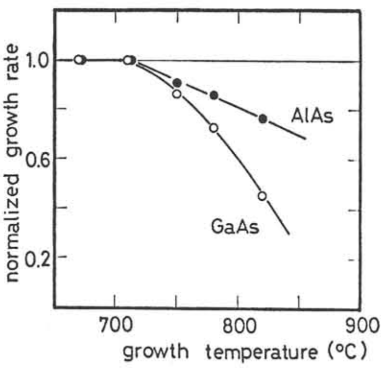

Fig.3 Calculated growth rate of GaAs and AlAs in AlGaAs aginst the growth temperature.

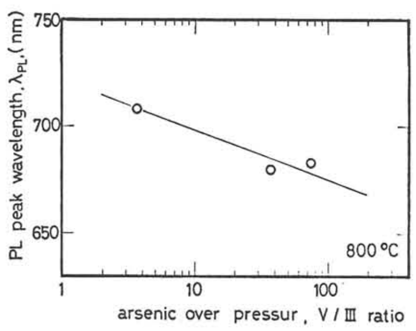

Fig.4 Relation of PL peak wavelength, λ_{PL} to arsenic over pressure.

concentration is observed agrees well with the temperature where the growth rate begins to decrease. The PL intensity reflecting the crystal quality increases sharply from 620°C to about 800°C, and it falls drastically with further increase of temperature. The PL intensity and the λ_{PL} fluctuated over the wafer in high temperature growth above 800°C.

The decrease in the growth rate at high temperature can possibly be explained by one or the other of the following mechanisms; 1) decomposition of arsenic from the epitaxial surface, 2) increase in thickness of a stagnant boundary layer and 3) homogeneous nucleations of GaAs and AlAs. Change in the thickness of the boundary layer (2) is estimated to be too small to explain the experimental results in Fig.2. The rate of decomposition of arsenic from the surface (1) decreases and the homogeneous nucleation (3) increases with the increased arsenic over pressure during growth. Fig.4 shows the λ_{PL} against the arsenic over pressure at growth temperature about 800°C. The λ_{PL} shifted to shorter wavelength with arsenic pressure. Fluctuation of the λ_{PL} was observed over the wafer grown under arsenic over pressure above 37.

Furthermore, we grew AlGaAs under high hydrogen flow rate 12 l/min. Both the growth rate and the λ_{PL} did not change even when the growth temperature exceeded 900°C. The PL intensity increased monotonically with temperature up to 900°C.

Through the above experiment, we concluded that the decrease in the growth rate at high temperature growth under a relatively low hydrogen flow rate is due to the homogeneous nucleation of GaAs and AlAl during growth.

It was, then, investigated whether the homogeneous nucleation developed even at a lower growth temperature. Relation of the alloy composition to the molar ratio of TMA to TMG is shown in Fig.5, where the vertical axis represents the ratio of alloy composition, X_{Al}, to the molar ratio of the input gas composition, γ, and the horizontal axis γ. Solid lines in the figure represent the relation $X_{Al} = \alpha P_{TMA} / (\alpha P_{TMA} + P_{TMG})$, where α means an incorporation rate of Al. The incorporation rate of Al atom to the solid was about twice larger than that of Ga atom. This indicates that the Al compound was introduced as a dimer, $(CH_3)_6Al_2$.

The incorporation rate of Al atom is, however, not unity even if the Al compound was assumed to be introduced as a dimer. The relation similar to Fig.5 is plotted in Fig.6, assuming Al is introduced as a dimer. The incorporation rate of Al decreased gradually with increasing molar ratio of Al to Ga compounds. The cross point is found to be at nearly equal amount of Al and Ga atoms in the vapor phase.

A similar result for high temperature growth, in which the homogeneous nucleation clearly occurred, is also plotted in the same figure. As seen in the figure, while the general tendency of the change in the incorporation rate of Al against the Al mole fraction is similar between the two cases, the difference is very great. The deviation of X_{Al} / γ' from unity could be considered to reflect the degree of the homogeneous nucleation. Figure 6, then, implies that the rate of

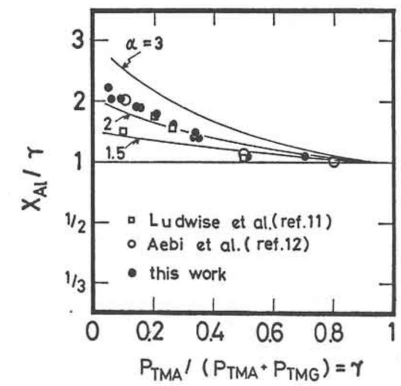

Fig.5 Relation of Al composition between solid and vapor phases. AlGaAs layers were grown at temperature about 700°C. Solid lines represent the relation $X_{Al} = \alpha P_{TMA}/(\alpha P_{TMA} + P_{TMG})$ (α=1.5, 2, 3).

the degree of homogeneous nucleation of GaAs and AlAs changes with the ratio of Al and Ga atoms in the vapor phase.

We conclude, therefore, that the homogeneous nucleation is present even at a growth temperature as low as 700°C. We think that the species like $(GaAs)_m$ and $(AlAs)_n$ molecules diffuse through the boundary layer. Fluctuation of the alloy composition over the wafer and also a size of alloy clustering might be influenced by the degree of the homogeneous nucleation.

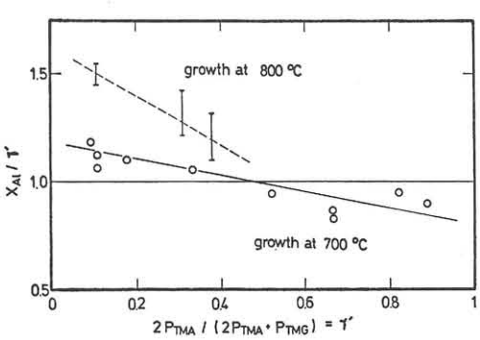

Fig.6 Alloy composition against the ratio of Al and Ga atoms in the vapor phase.

§4. Conclusions

We have investigated the effect of the growth temperature on growth rate, alloy composition and crystal quality in MOCVD growth of AlGaAs under atmospheric pressure. The growth rate and the alloy composition were strongly influenced at temperature above 750°C under relatively low flow rate of hydrogen carrier gas. The change in growth rate could be interpreted as increased gas phase reaction between decomposed III and V elements, that is homogeneous nucleation. The alloy composition was found to be different from molar ratio of Al to Ga atoms in the vapor phase. The discrepancy in the Al composition between two phases was considered to be due to the homogeneous nucleation. The size of the alloy clustering as well as the fluctuation of the alloy composition over the wafer are thought to be influenced by the homogeneous nucleation.

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References

1) Y. Mori, H. Sato, M. Ikeda, O. Matsuda, K. Kaneko and N. Watanabe; Appl. Phys. Lett., 40 (1982) 293.
2) R. D. Burnham, D. R. Scifres and W. Streifer; Appl. Phys. Lett., 40 (1982) 118.
3) Y. Mori, O. Matsuda, M. Ikeda, K. Kaneko and N. Watanabe; J. de Physique Coll. c5, suppl. no 12 (1982) 271.
4) N. Holonyak, Jr., R. M. Kolbas, W. D. Laydig, B. A. Vojak, R. D. Dupuis and P. D. Dapkus; Appl. Phys. Lett., 33 (1978) 737.
5) R. D. Dupuis and P. D. Dapkus; Appl. Phys. Lett., 33 (1978) 68.
6) S. D. Hersee, SM. Baldy, P. Assenat; J. de Physique Coll. c5, suppl. no 12 (1982) 193.
7) P. M. Frijlink and J. Maluenda; J. de Physique Coll. c5, suppl. no 12 (1982) 185.
8) M. R. Lays and H. Veenvliet; J. Cryst. Growth 55 (1981) 145.
9) A. L. Lin, V. Dao and F. Donaghey; Proc. 6th Int. Conf. on CVD (1977) 264.
10) H. C. Casey and M. B. Panish; "Heterostructure Lasers", Academic Press (1978) 192.
11) M. J. Ludwise, C. B. Cooper III and R. R. Saxena; J. Electro. Materials 10 (1981) 1051.
12) V. Aebi, C. B. Cooper III, R. L. Moon and R. R. Saxena; J. Cryst. Growth 55 (1981) 517.