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Growth of AlGaInP in a High-speed Rotating Disk OMVPE Reactor

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In an OMVPE reactor with a high speed rotating disk, growth of a quaternary material AlGaInP is carried out after a basic investigation on the GaAs growth rate uniformity. Experimental growth rate and growth efficiency results are compared with the theoretical results obtained from an infinite diameter rotating disk model. Distributions of the lattice mismatch, PL spectra and carrier concentration were measured to clarify the disk rotation effect on these properties. The main reason for non-uniformities is not the disk rotation but the temperature distribution on a substrate carrier.

Key words: AlGaInP, OMVPE, high speed rotation

1. INTRODUCTION

AlGaInP is a quite attractive material for visible light emitting devices. Recently, this material has been grown successfully[1,2] by metal-organic chemical vapor deposition (MOCVD). However, the growth on larger substrate areas is still difficult because of the In compositional non-uniformity.

The rotating disk reactor goes back to the 1970s, when Olander grew Ge,[3] followed by Sugawara[4] who carried out silicon epitaxial growth using $SiCl_4$, along with a numerical simulation of flow and mass transport in a CVD reactor. This work showed that the growth rate was readily controlled by changing the rotation speed in the temperature range where the mass transport limits the rate. The same principle can be applied to any mass transport limited processes, such as MOCVD. However, in the case of the silicon epitaxy very little attention was paid to the gas change abruptness, which is essential to MOCVD.

As far as the film thickness uniformity is concerned, the rotating disk reactor turns out to be attractive,[5] for its theoretically one-dimensional nature, which means that there is a possibility of obtaining good uniformity in every chemical reaction taking place on/above the substrate. In addition, it is possible to obtain the gas change speed rapid enough to grow quaternary alloys which are sensitive to the gas change speed, if the reactor and operation conditions are optimized so that there is no convection.

In this paper, first, a method for the rough growth rate estimation is proposed, based on the rotating infinite diameter disk model. According to this model, operation conditions for obtaining good thickness uniformity can also be roughly predicted. After seeking conditions for uniform film thickness, epitaxial AlGaInP was grown. The results, obtained from the authors' experimental study, are reported with particular attention paid to the uniformity of the carrier concentration, lattice mismatch and photoluminescence (PL) wavelength distribution.

2. EXPERIMENTAL

A schematic of the reactor is shown in Fig. 1. The reactor shape is designed so that there is no forced convection at the inlet. A substrate carrier is heated by a carbon heater, set inside a cylindrical substrate carrier holder, in order to avoid the shaft effect on the substrate carrier temperature uniformity. Reactants diluted with a hydrogen carrier gas are introduced at the inlet from a direction tangential to the reactor axis to a 3 inch substrate, placed on the substrate carrier. Reactants used here are trimethylgallium (TMGa), trimethylaluminum (TMAl), trimethylindium (TMIn) and phosphine.

First GaAs was grown to investigate the growth rate characteristics for the reactor. Pressure was varied from 12 to 76 Torr with the total gas flow of 3.5–7 slm. The rotation speed was set in the range from 40 to 3000 rpm. After determining the conditions required to obtain a uniform growth rate, GaInP, and AlGaInP were grown on GaAs substrates, at 19–76 Torr pressure, 2000–3000 rpm rotation speed, and 100–250 V/III ratio. Total flow rate was kept at 7 slm during these experiments.

3. GROWTH RATE ESTIMATION

The flow around the infinite diameter rotating disk placed in an infinite space was originally derived by von Karman as one of the few examples of exact Navier-Stokes solution.[6] The results indicate that the velocity component, perpendicular to the disk is the same all over the disk. Sparrow[7] developed the theory incorporating heat and mass transfer, showing that the temperature and concentration distribution exists only in the z-direction, *i.e.* they are uniform across the disk.

In the diffusion-limited process, the growth rate can be calculated from a non-dimensional concen-

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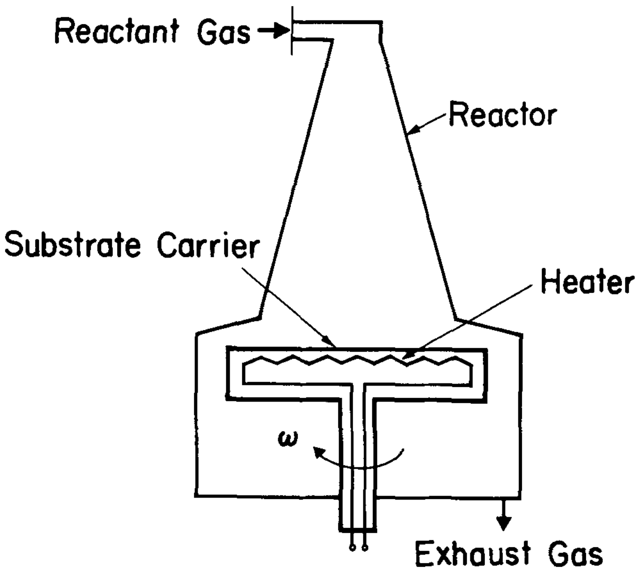

Fig. 1 — Schematic of Rotating Disk Reactor

tration parameter multiplied by the concentration gradient, as follows

$$\begin{aligned}\mathrm{Gr} &= D(\partial C/\partial Z)_{z=0}\\ &= -D(C_s - C_\infty)(d\phi/d\zeta)(d\zeta/dz)\\ &= -D(C_s - C_\infty)\phi'(0)\sqrt{\omega/\nu}\\ &= D\,C_\infty\phi'(0)\sqrt{\omega/\nu}\end{aligned} \tag{1}$$

where Gr is the growth rate

D = Diffusion coefficient

C = Concentration, C_s; at surface,

C_∞; at ∞ from surface

ϕ = dimensionless concentration

$(C - C_\infty)/(C_s - C_\infty)$

ζ = dimensionless distance, $z\sqrt{\omega/\nu}$

ω = angular velocity

ν = kinetic viscosity

Dependence of physical properties on operation parameters are

$$\begin{aligned}&D\alpha T^{1.75}P^{-1}.\\ &C\alpha f/F\cdot P\cdot T^{-1}.\\ &\nu\alpha T^{1.5}\cdot P^{-1}.\end{aligned} \tag{2}$$

where f is the reactant flow rate and F is the total flow rate. Substitution into Eq. (1) yields

$$\mathrm{Gr}\alpha\sqrt{P\omega}\cdot f/F. \tag{3}$$

This relation indicates that the growth rate is in proportion to $\sqrt{P\omega}$ and is inversely proportional to the feed carrier gas flow rate F, while it is independent of the gas temperature, with fixed reactant flow rate, f. Figure 2 shows the experimental growth rate distribution across a 3 inch substrate, with rotation speed as a parameter. The growth rates and their flatness vary with the rotation speed. Growth rates at the substrate center are plotted against the value $f\cdot\sqrt{P\omega}/F$ in Fig. 3. It is pointed out that the growth rate at the substrate center, where there is the least end effect, complies with Eq. (1), except for the low rotation speed region where the reactor shape mainly governs the flow.

Moreover, using this model, we can also roughly guess the best operation conditions to get a uniform growth rate, because a good growth rate uniformity is considered to be achieved only when the carrier gas flow rate is set equivalent to the discharging rate of the disk. The total volume flow rate, G, discharged by the rotating disk is calculated from the Eq.

$$G = H(\infty)\cdot\pi R^2\sqrt{\nu\omega} \tag{4}$$

where H = dimensionless vertical velocity, R = disk radius. On the other hand, concentration C in Eq. (1) can be replaced by $\rho\cdot f/F$

$$\mathrm{Gr} = D\cdot\rho\cdot(f/F)\cdot\phi'(0)\cdot\sqrt{\omega/\nu}. \tag{5}$$

In the conditions where the uniform growth can be achieved, F in Eq. (5) is replaced by $\rho\cdot G$

$$\mathrm{Gr} = D\cdot f\cdot\phi'(0)/(\pi R^2\cdot H(\infty)\cdot\nu). \tag{6}$$

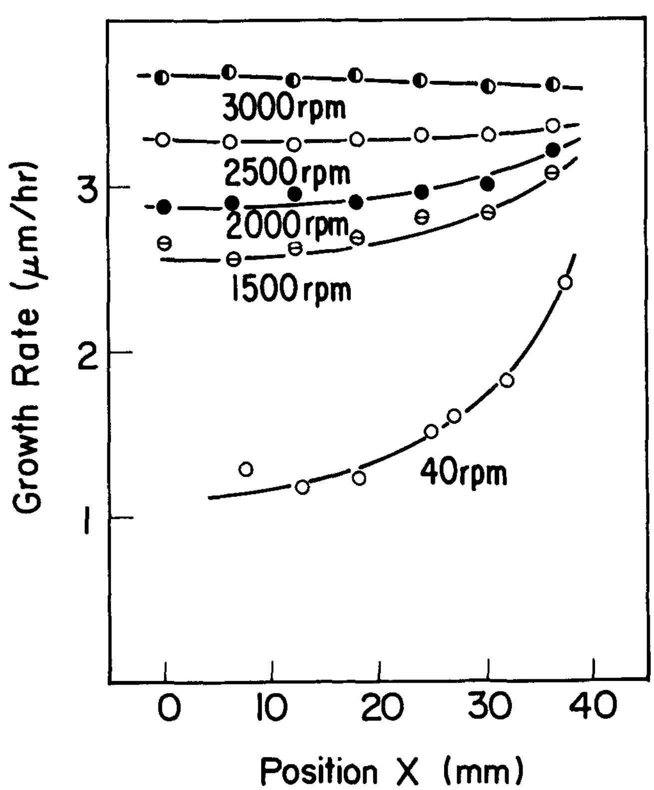

Fig. 2 — Growth rate distribution

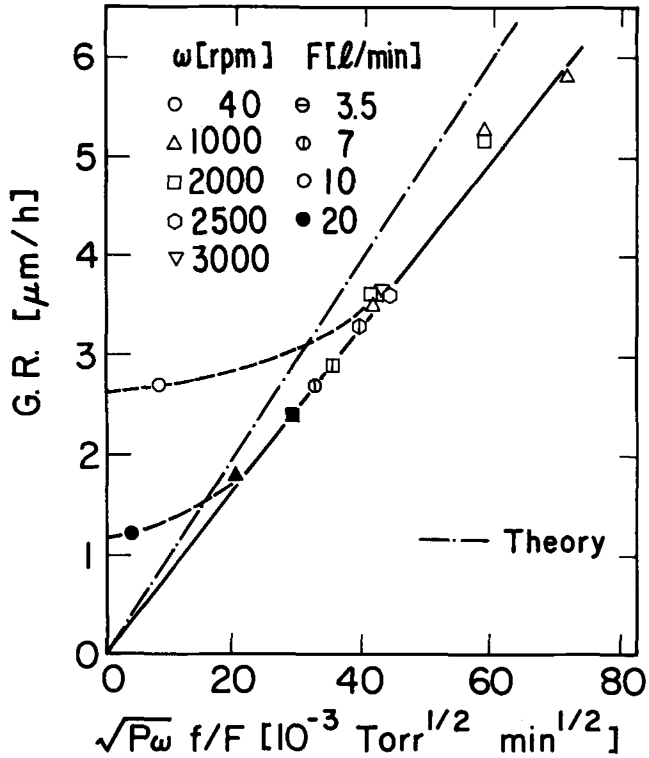

Fig. 3 — Effect of operation conditions on growth rate

The growth efficiency η is calculated by dividing Gr by the reactant flow rate per unit area.

$$\eta = \mathrm{Gr}/(f/\pi R^2) = \phi'(0)/(H(\infty)\cdot \mathrm{Sc}). \quad (7)$$

In this case Schmidt number, Sc = 2.9, then the growth efficiency can be calculated from Eq. (7) as 0.26 which is close to the experimentally obtained value of 0.32. It should be noted that in the conditions of uniform growth rate profile, the growth efficiency settles into one value.

Figure 4 shows theoretical flow rate (*Ft*) contours calculated from Eq. (4) plotted on a pressure-rotation speed plane. Experimental conditions where the uniform growth rate distribution is obtained are also plotted. As is obvious in the figure, the agreement between them is fair, with the flow rate difference of about a constant 30%.

4. GROWTH OF QUATERNARY ALLOY

4.1 Morphology

A mirror like surface was obtained within almost all the operation conditions mentioned above. However, it seemed that the lower pressure is better in terms of microscopic morphology. The rotation speed has little effect on the surface, as long as it is above 2000 rpm.

4.2 Lattice Mismatch

Lattice mismatch between GaAs substrate and epitaxial AlGaInP was measured using double crystal x-ray diffraction. Results are shown in Fig. 5 as a function of the position on a substrate, with the disk rotation speed as a parameter. The distribution of the lattice mismatch is almost the same among the 3 different rotation speeds. The lattice mismatch of 2500 rpm is a little lower than the others, but it is considered that rather unstable behavior of the TMIn bubbler is responsible. In this region of the rotation speed, it is considered that the In/Ga ratio is not affected by the disk rotation, while the growth rate distribution is quite sensitive to it. There is a slight distribution of lattice mismatch across a 3 inch substrate, as is shown in the figure. The main reason for this nonuniformity is a substrate carrier temperature distribution, since the temperature of the substrate carrier periphery is lower than the center, which results in a richer Indium composi-

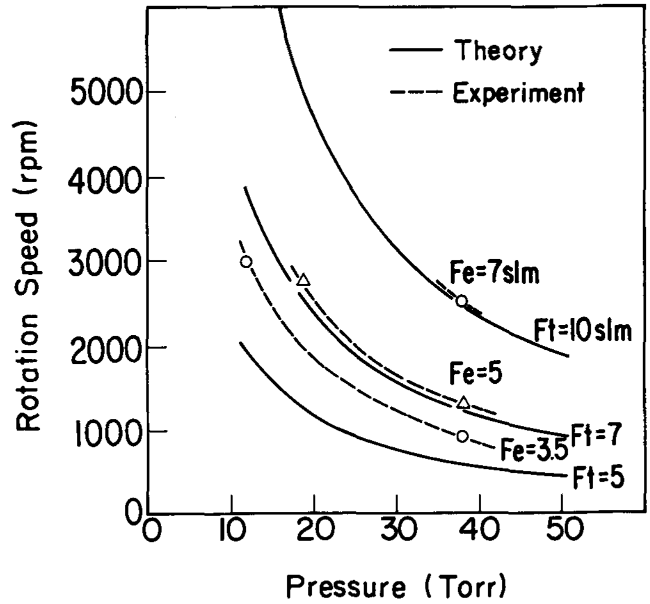

Fig. 4 — Calculated and Experimental conditions for uniform growth rate profile

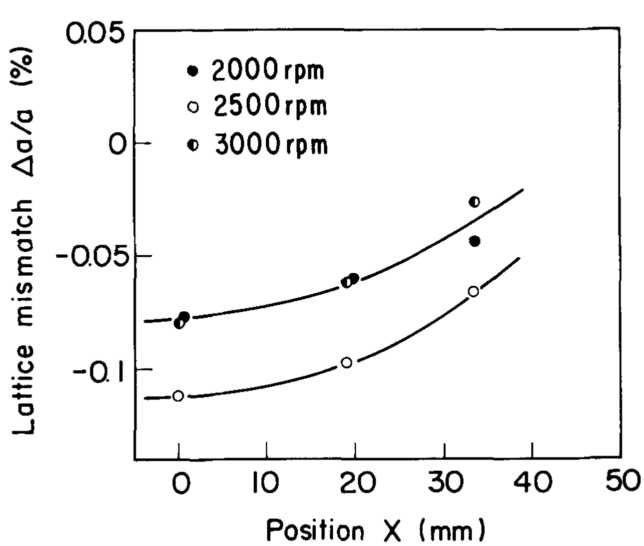

Fig. 5 — Lattice mismatch distribution of $Ga_{0.5}In_{0.5}P$

tion. This temperature distribution is the result of heat loss through ambient hydrogen to the reactor wall which is near the substrate carrier at the periphery. Calculated substrate carrier temperature distribution is shown in Fig. 6. The distribution is qualitatively consistent with the lattice mismatch distribution.

4.3 *Photoluminescence*

PL measurements were carried out for $Ga_{0.5}In_{0.5}P$ at room temperature and at 77 K. Once again, there was no function of the rotation speed, as is shown in Fig. 6. The uniformity is allowable, but this slight distribution is similar to that for the lattice mismatch distribution. Using the temperature dependence of the PL spectrum data,[8] the temperature difference between the center and peripheral part of the substrate carrier, corresponding to the PL wavelength difference of this work, was estimated as 15° C, which is consistent with the numerically calculated temperature distribution of the substrate carrier shown in Fig. 6.

PL wavelengths at 77 K are plotted vs V/III ratio in Fig. 7. The wavelength becomes longer with increasing V/III ratio, while the ratio did not affect the In/Ga ratio. It is considered that phosphine or decomposed phosphine adsorbed on a substrate surface may limit the free movement of the III group species on the surface, which may result in the In-Ga ordering. As reported by Nozaki,[8] the disordering causes the band gap energy increase for the material to shorten the PL wave length.

4.4 *Doping*

Silicon was used as an *n*-dopant in AlGaInP using silane, fixing all the operating conditions but rotation speed. The carrier concentration decreased and the profile uniformity became better with increasing rotation speed, as is shown in Fig. 8. However, the Si incorporation rate; a product of the carrier concentration and the growth rate (see Fig. 9), did not depend on the rotation speed. This indicates that the Si incorporation rate is constant, independent of the growth rate. Decreasing carrier concentration at the outer part of a substrate is explained by the above mentioned temperature distribution of the substrate carrier, since silane cracking is considered to limit the Si incorporation rate.[9,10]

On the other hand, in the case of *p*-doping by dimethylzinc, the rotation speed did not affect the *p*-carrier concentration, as shown in Fig. 10. This indicates that zinc gets into the crystal with a constant ratio of zinc to a total amount of III group species. This may imply that the zinc is incorporated in the form of adduct which is formed in the gas phase reaction with the III group sources. Because, judging from the excessive amount of supplied DMZn, compared with incorporated zinc amount, it is dif-

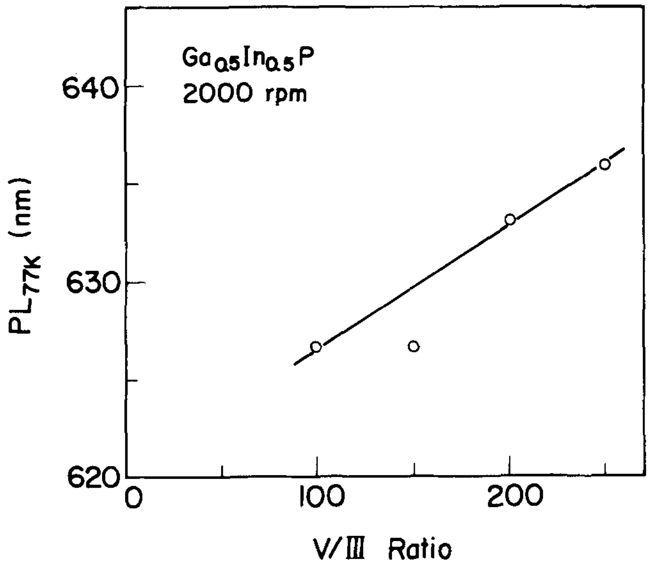

Fig. 7 — PL_{77K} wave length as a function of V/III ratio

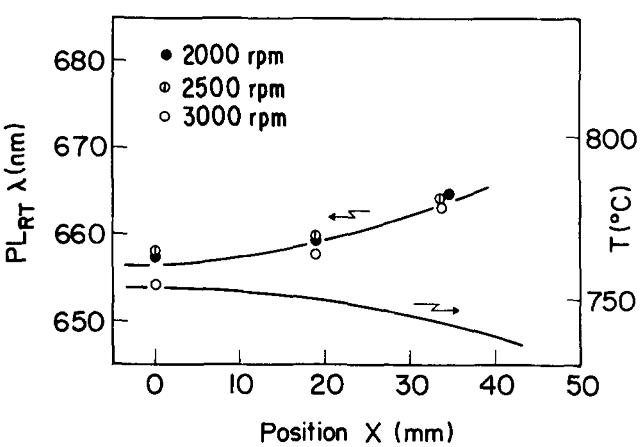

Fig. 6 — PL distribution of $Ga_{0.5}In_{0.5}P$ and substrate carrier temp. distribution

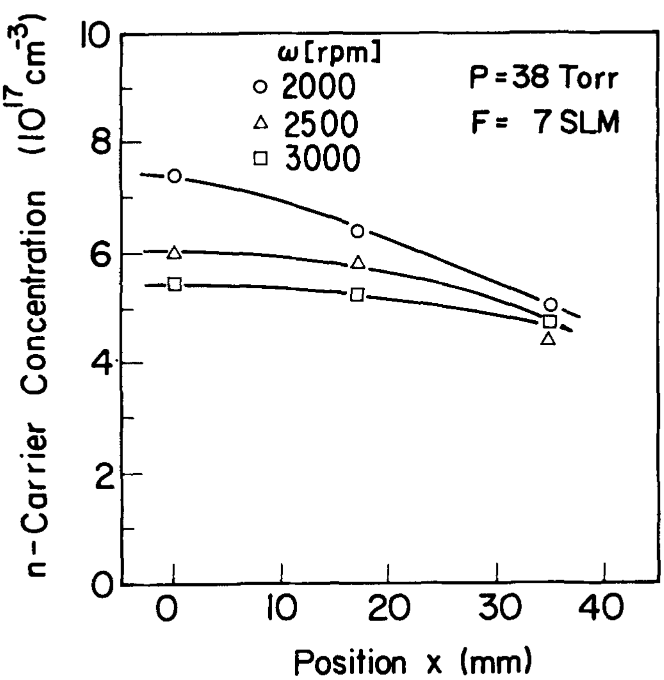

Fig. 8 — *n*-Carrier concentration profile of AℓGaInP (Si Dopant)

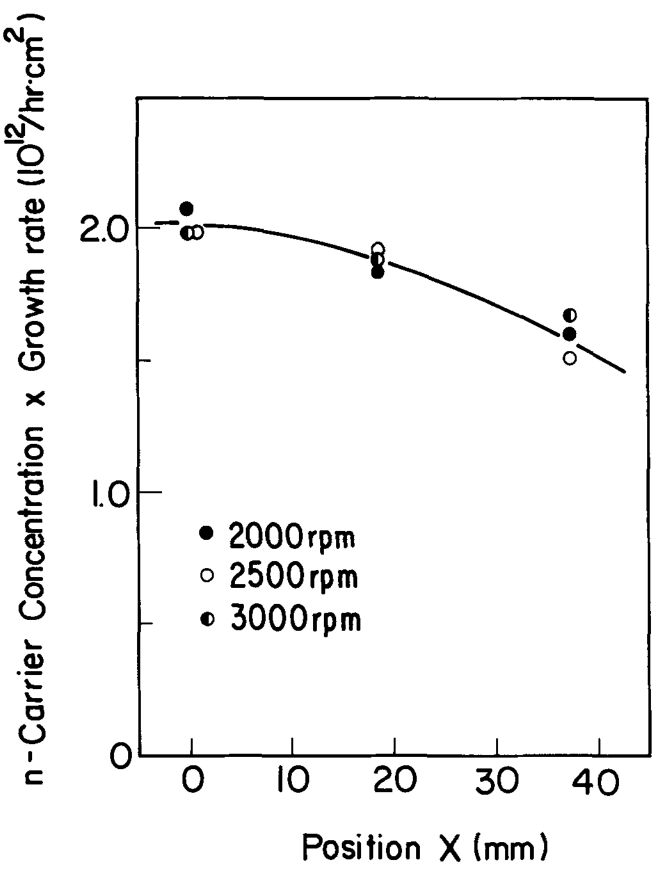

Fig. 9 — n-Carrier incorporation rate

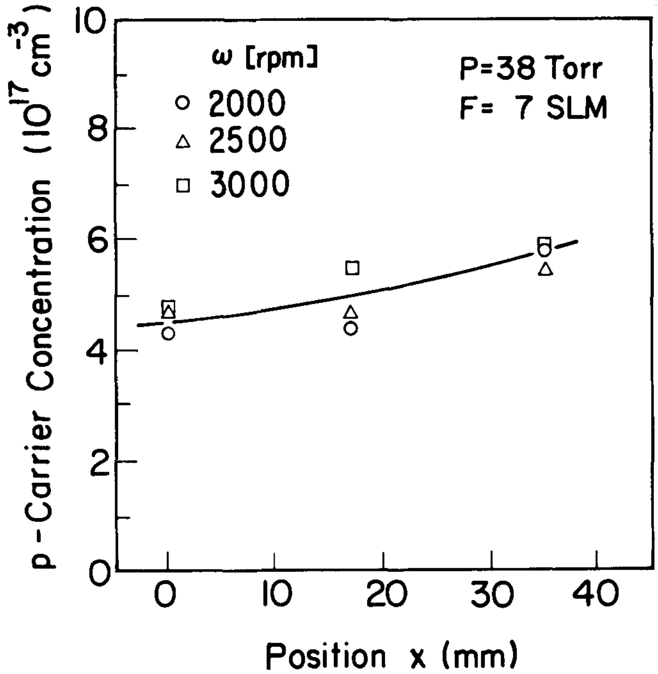

Fig. 10 — p-Carrier concentration profile of AℓGaInP (Zn Dopant)

ficult to consider that the zinc incorporation rate is diffusion-limited. If the rate is limited by the surface reaction of DMZn, the carrier concentration should be a function of the growth rate. Further study is necessary to understand the zinc incorporation mechanism. The tendency of increasing hole concentration at the outer position is also thought to be caused by the substrate carrier temperature distribution, since Zn incorporation rate increases as the temperature drops.[11]

5. CONCLUSION

In a high speed rotating disk reactor, the growth of a quaternary material AlGaInP has been carried out, after basic investigation on GaAs growth rate uniformity. The growth rate, predicted from the theory of the infinite-diameter rotating disk, turned out to agree well with the growth rate at the substrate center. From this theory, the growth conditions where the uniform growth can be achieved, has also been shown to be roughly predicted. The equation for the growth efficiency has also been derived from the model to show that it is a constant in the conditions of a uniform growth rate profile, independent of individual values of the pressure or the rotation speed.

A mirror-like AlGaInP surface has been obtained in a wide range of operation conditions. Distributions of the lattice mismatch, PL wave length, and p-, n-carrier concentration have been shown to be caused by the temperature distribution of the substrate carrier, while it has been found that the disk rotation speed, as long as it is above 2000 rpm, does not directly affect all of these properties except n-carrier concentration. Incorporation of Si is affected by the disk rotation through the growth rate change. It has been shown that the use of high speed rotation is a promising method for the growth of materials which demand severely rapid compositional change and high uniformity.

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