Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, pp. 667-670

D-11-1

High Purity InP Growth by Low-Pressure Metalorganic Chemical Vapor Deposition

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High purity InP epitaxial layers are grown by low-pressure metalorganic chemical vapor deposition (MOCVD). Electron mobilities higher than 70,000$cm^2/V\cdot s$ at 77K for N_D-N_A lower than 1 × $10^{15}cm^{-3}$ are reproducibly achieved. Carrier concentrations decrease and electron Hall mobilities increase as growth temperatures decrease or $[PH_3]/[TEI]$ in the vapor increase. Optimum conditions are established for high purity growth, i.e., a growth temperature of approximately 550°C and a $[PH_3]/[TEI]$ larger than 150.

INTRODUCTION High purity InP growth is essential not only for the fabrication of high speed devices demanding high purity epitaxial layers but also for well-controlled doping of epitaxial layers. High purity InP epitaxial layers are usually grown by VPE or LPE. Recently, several reports have been published on the purity of InP grown by MOCVD.[1,2] However, detailed information is lacking concerning effects of growth parameters such as substrate temperatures and mole fraction ratios in the vapor on the incorporation of residual impurities.

This paper describes the effects of growth conditions on epitaxial layer purity as well as the dependence of growth rates and layer purity on the substrate position on the susceptor. Optimum conditions are established for high purity epitaxial growth.

EXPERIMENTAL The growth apparatus is similar to that developed by Fukui and Horikoshi.[3] Triethylindium (TEI) and PH_3 are used as the In source and the P source. Fe-doped semi-insulating InP substrates ((100) 3°off towards <110>) were loaded on a 15cm long SiC-coated carbon susceptor placed in a horizontal quartz reactor (diameter 40mm).

Growth conditions are summarized in Table 1. The pressure in the reactor was maintained at 0.1atm. Low-pressure MOCVD[4] was employed because high gas velocity in a low-pressure system can prevent TEI from decomposing in the vapor prior to the reaction on the substrate surface.[5] A PH_3 pyrolysis oven was not used. Growth temperatures were measured with a thermocouple inserted into the susceptor and varied between 500°C and 700°C. Mole fraction ratios $[PH_3]/[TEI]$ in the vapor were varied between 40 and 170.

Carrier concentrations and mobilities at 300K and 77K were determined by the van der Pauw method. Van der Pauw measurements were performed on cloverleaf shape samples with Sn contacts. All of the grown layers showed n-type conductivity.

RESULTS

i) Growth rates Growth rates depend on substrate positions as well as on growth temperatures. Figure 1 shows growth rates vs. substrate positions (x) measured from the susceptor front end at various growth temperatures (Tg). Tg is defined

Table 1. Growth parameters

Growth temperatures	500~700°C
Reactor pressure	0.1atm
Total gas flow rate	3.2ℓ/min
H_2 flow rate into the TEI bubbler	460cc/min
TEI bubbler temperature	30°C
PH_3 flow rate	14~60 cc/min
$[PH_3]/[TEI]$	40~170

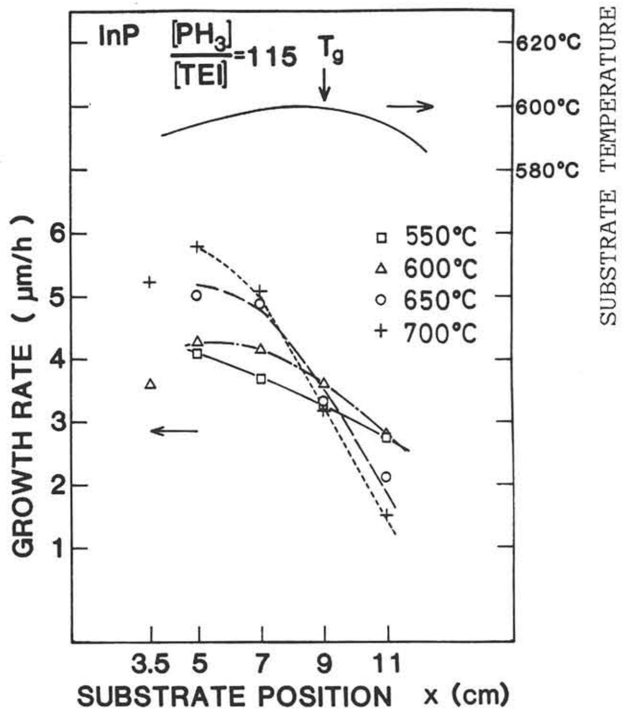

Fig. 1 Growth rate vs. substrate position x measured from the susceptor front end for various growth temperatures. The susceptor temperature profile measured at T_g = 600°C is also shown.

at x = 9cm. The temperature profile in the susceptor at Tg = 600°C is also shown in Fig. 1. Growth rates decrease as x increases due to depletion of source materials in the vapor at x > 5cm. On the other hand, at x < 5cm, growth rates increase with an increase in x. In this region, flow profile and temperature profile are not fully developed and entrance effects are evident. The lower growth rates observed at x = 3.5cm seem to be caused by the entrance effects.

Using the mass transfer model,[5,6] growth rates are calculated to be

$$G(x) = 1.34\times10^{7}\frac{D_0 p(0)}{T_0{}^2\delta}\,T_s(x)$$

$$\times \exp\left[-\frac{D_0}{T_0 V_0 b\delta}\int_0^x T_s(x)\,dx\right] \qquad (1)$$

where G(x) is the growth rate (μm/h); D_0 is the diffusion coefficient of TEI in H_2 at 300K and 0.1atm (cm^2/s); p(0) is the partial pressure of TEI at the inlet of the reactor (atm); T_0 = 300K; δ is the stagnant layer thickness estimated using the results of Eversteyn et al.[6] (δ ≅ 0.55cm); Ts(x) is the substrate temperature at x (K); V_0 is the mean gas velocity calculated from the incoming carrier gas flow rate and the free cross section of the tube (V_0 = 83.3cm/s); b is the free height above the susceptor (b = 2.0cm). $D = D_0(T/T_0)^2$ is assumed for the temperature dependence of the diffusion coefficient of TEI.

D_0 is estimated to be 2.7cm^2/s using the following relation:[7]

$$D_0 = D_0{}'\left(\frac{300K}{273K}\right)^2\left(\frac{1atm}{0.1atm}\right) \qquad (2)$$

where $D_0{}'$ = 0.2231cm^2/s,[7] which is the diffusion coefficient of TEI at 0°C and 1atm.

Good agreement exists between Eq. (1) and the results measured at 550°C (Fig.2) when p(0) is assumed to be 1.1×10^{-5} atm (mole fraction = 1.1×10^{-4}), which corresponds to a TEI vapor pressure

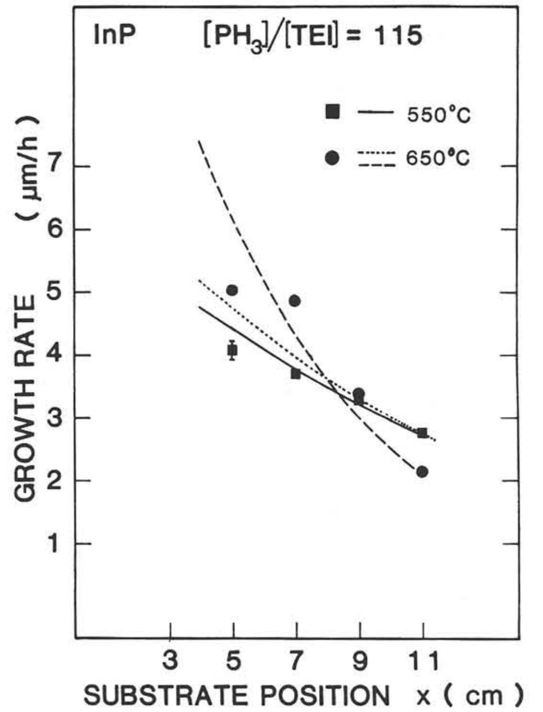

Fig. 2 Comparison of experimental growth rates and calculated growth rates using the mass transfer model. ■ : experiment at 550°C, ● : experiment at 650°C, solid line : calculation at 550°C for D_0 = 2.7cm^2/s, dotted line : calculation at 650°C for D_0 = 2.7cm^2/s, dashed line : calculation at 650°C for D_0 = 5.4cm^2/s.

of 0.6Torr in the bubbler. Calculated growth rates, however, deviate significantly from those measured at $T_g \geqq 600°C$.

Calculated and measured growth rate variations at 650°C are also shown in Fig.2. Apart from the entrance effect, which is more evident at 650°C than at 550°C, the measured growth rate at 650°C decreases more rapidly with increases in x than the calculated rates for $D_0 = 2.7cm^2/s$ (dotted line). If we increase D_0 from $2.7cm^2/s$ to $5.4cm^2/s$ in the calculations, the agreement will be better (dashed line). These results seem to suggest that the diffusing species at 650°C are different from those at 550°C.[8)]

ii) Electrical properties Dependence of electrical properties on the substrate positions was investigated. Carrier concentrations (N_D-N_A) and electron Hall mobilities vs. substrate positions (x) are shown in Fig. 3 for the growth temperature of 575°C. When Tg = 575°C, $N_D - N_A$ does not depend on x, while the mobility at 77K slightly increases as x decreases, which indicates purer layers are obtained at a smaller x. When $T_g \geqq 600°C$, $N_D - N_A$ increases gradually as x increases.

The effects of the growth temperatures on residual impurities incorporation were investigated for a fixed substrate position. Figure 4 shows $N_D - N_A$ and electron Hall mobilities vs. T_g (the susceptor temperature at x = 9cm). Substrates are placed at x = 9cm. $[PH_3]/[TEI]$ in the gas phase is fixed at 170. When T_g > 550°C, $N_D - N_A$ at 300K as well as at 77K increases as T_g increases. Correspondingly the Hall mobilities decrease as T_g increases. It has been reported[9)] that with increasing T_g, $N_D - N_A$ increases at growth temperatures between 550°C and 650°C. In the present experiments, layer purity has been improved using a higher purity TEI lot and $N_D - N_A$ is ten times lower than before. The variation of $N_D - N_A$ with the growth temperatures is , however, similar to the previous one, which suggests donor impurities are incorporated mainly from the TEI source.

At temperatures below 550°C, the mobility decreases rapidly. This rapid decrease seems to be caused by defect formation due to incomplete PH_3 pyrolysis and a reduction in [P]/[In] at the growing surface.

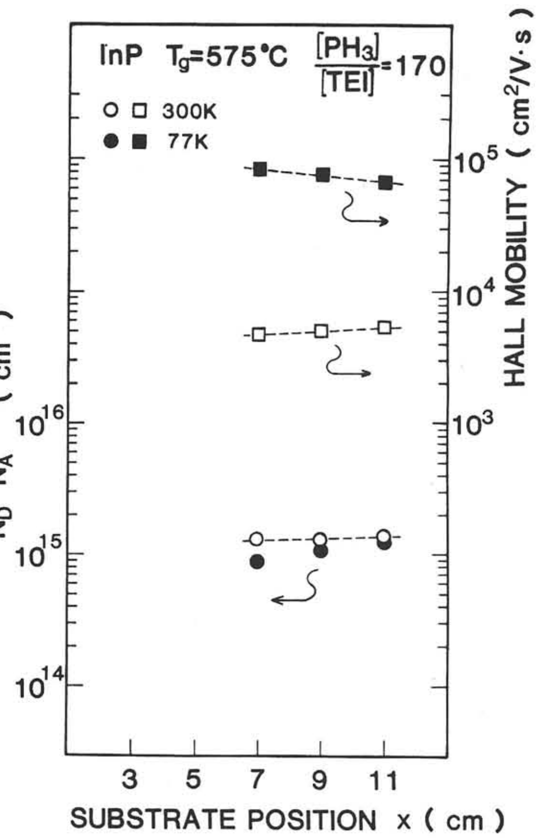

Fig. 3 $N_D - N_A$ and electron Hall mobilities at 300K and 77K vs. substrate position x measured from the susceptor front end; T_g is 575°C and $[PH_3]/[TEI]$ is 170.

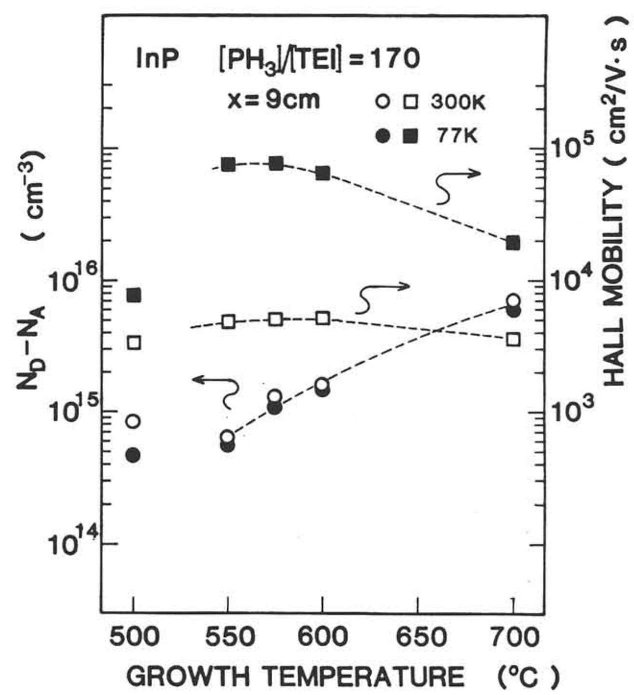

Fig. 4 $N_D - N_A$ and electron Hall mobilities at 300K and 77K vs. growth temperature.

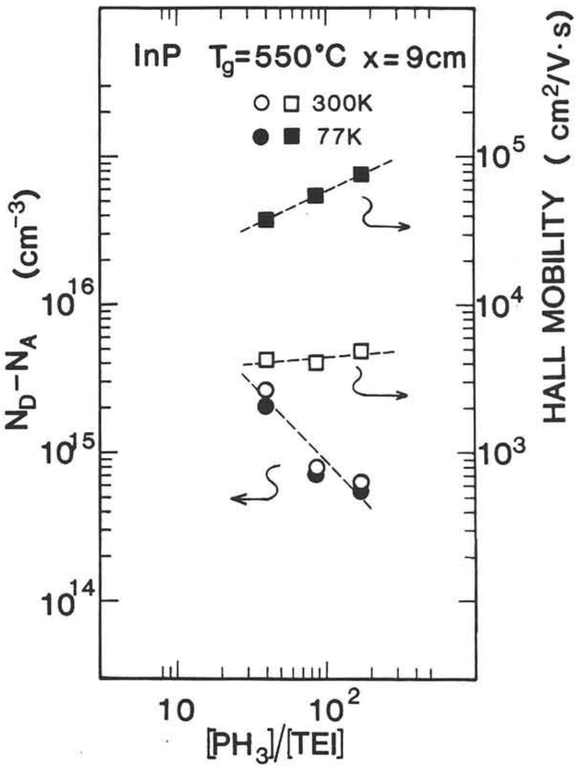

Fig. 5 N_D - N_A and electron Hall mobilities at 300K and 77K vs. mole fraction ratio $[PH_3]/[TEI]$

The effect of the mole fraction ratio $[PH_3]/[TEI]$ in the gas phase on epitaxial layer purity was also investigated. PH_3 flow rates were varied while TEI flow rates were held constant. $[PH_3]/[TEI]$ was varied between 40 and 170.

Figure 5 shows N_D - N_A and electron Hall mobilities at 300K and 77K vs. $[PH_3]/[TEI]$. N_D - N_A decreases and 77K Hall mobility increses as $[PH_3]/[TEI]$ increases. Similar dependence of N_D - N_A on phosphorus partial pressure was observed in VPE InP growth.[10] High phosphorus pressure may suppress defect formation.

The authors previously reported[9] that N_D - N_A as well as electron mobilities does not show a significant variation when $[PH_3]/[TEI]$ is varied between 65 and 325 at the growth temperature of 600°C. In those experiments, N_D - N_A was approximately 1∿2 × $10^{16}cm^{-3}$ and the number of the residual donor impurities incorporated from the TEI source seemed to be much larger than the number of defects induced by lack of phosphorus. In the present experiments, N_D - N_A is reduced to $10^{15}cm^{-3}$; therefore N_D - N_A dependence on PH_3 partial pressure is evident.

CONCLUSION In conclusion, InP epitaxial layers have been grown by low pressure MOCVD without a PH_3 pyrolysis oven. The growth rates can be estimated by the mass transfer model at a growth temperature of 550°C. The electrical properties are fairly independent of the substrate positions on the susceptor. N_D - N_A decreases and electron mobilities increase as the growth temperatures decrease up to a growth temperature of approximately 550°C while $[PH_3]/[TEI]$ was held at 170. At a fixed growth temperature of 550°C, N_D - N_A decreases and mobilities increase as $[PH_3]/[TEI]$ increases. The highest purity layers are obtained at growth temperatures between 550°C and 575°C and $[PH_3]/[TEI]$ of 170. Epitaxial layers with N_D - N_A at 300K less than $1 \times 10^{15}cm^{-3}$ and electron mobilities at 77K higher than 70,000cm^2/V·s are reproducibly obtained.

ACKNOWLEDGMENT The authors wish to thank Drs. Hiroshi Kanbe and Takashi Fukui for their helpful discussions and Mr. Kimio Sakai of Kyushu University for the Hall measurements.

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