

## Chloride Atomic Layer Epitaxy of InGaP

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Atomic layer epitaxy of ternary InGaP layers using InCl, GaCl and  $\text{PH}_3$  has been studied. The growing surface is exposed to these source gases alternately in order to grow (InP)(GaP) structures. Under sufficient InCl partial pressure conditions, the In composition of grown layers is insensitive to the InCl partial pressure and  $\text{In}_x\text{Ga}_{1-x}\text{P}$  having  $x(\text{In})=0.5$  can be grown. In spite of a low growth temperature of  $450^\circ\text{C}$ , a featureless mirror surface is obtained. InGaP/GaAs/InGaP single quantum well structures are demonstrated. Sufficiently narrow photoluminescence spectrum with FWHM of 9.8 meV at 4K can be obtained.

### 1. INTRODUCTION

Atomic layer epitaxy(ALE) is a very attractive atomic-scale growth technology for II-VI and III-V compound semiconductors. Recently, GaAs-ALE with the monolayer-unit growth nature has been reported by many researchers<sup>1-4)</sup>. In the chloride-ALE using GaCl and InCl, the authors have so far reported the monolayer-unit growth over a wide range of growth conditions, so-called digital epitaxy, for various III-V compound semiconductors, such as GaAs, InP, InAs and GaP<sup>5)</sup>. However, no systematic study regarding ALE of ternary materials has yet been reported, except for quite a few papers on InGaAs<sup>6)</sup>, AlGaAs<sup>7)</sup> and the authors report of preliminary results for InGaP<sup>5)</sup>.

InGaP is expected to be used for HEMT devices<sup>8)</sup>, combined with GaAs, where the chemically active species, as Al in the AlGaAs/GaAs structures, is not contained, and the effect of DX centers, which reduce the carrier concentration, should be excluded for InGaP lattice-matched to GaAs substrate<sup>9)</sup>. Applications to optical devices in the visible wavelength region, due to

having 1.9 eV high bandgap energy, are also expected. Furthermore, due to the low temperature growth nature for ALE, a more abrupt hetero-interface should be obtained.

This paper reports details on chloride InGaP-ALE using a triple-chamber reactor. It also reports the growth of single quantum well, consisting of ALE-InGaP barrier and ALE-GaAs well, as an application.

### 2. EXPERIMENTAL

InGaP ALE was accomplished by using a triple-growth-chamber reactor, as shown in Fig.1. InCl, GaCl and  $\text{PH}_3$  gas flows were completely separated by using different chambers. The substrate was transferred between these three chambers. For comparison, another method for InGaP ALE was also tried, where both GaCl and InCl were

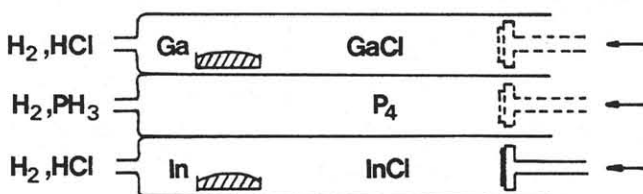


Fig.1 Growth apparatus for InGaP ALE.

simultaneously supplied to the substrate surface through a single chloride source chamber. In this case, InGaP layers, in which In and Ga atoms exist in the same group-III sub-lattice sites, can be grown.

The substrate used here was GaAs(100)  $\pm 0.5^\circ$ . Typical growth conditions are summarized in Table 1. The substrate temperature was typically raised to 600  $^\circ\text{C}$  prior to the growth and then a slight amount of HCl( 5 cc/min) was added to the carrier  $\text{H}_2$  gas to remove a several-thousand-Å-thick GaAs layer from the surface. The ALE cycle was typically repeated 300 times. The degree of lattice-match to the substrate was evaluated by X-ray diffraction measurement. The photoluminescence measurement was also carried out to determine the bandgap energy and to examine optical properties of grown layers.

Growth temperature	450 $^\circ\text{C}$
GaCl partial pressure	$4.3 \times 10^{-5}$ atm
InCl partial pressure	$0.2\text{--}11 \times 10^{-3}$ atm
$\text{PH}_3$ partial pressure	$5.3 \times 10^{-3}$ atm
Exposure time to GaCl & InCl	7 sec
Exposure time to $\text{PH}_3$	7 sec
1 ALE cycle time	45 sec
Total flow rate	4.7 l/min
Reactor Pressure	1 atm

Table 1. Typical growth conditions for InGaP.

### 3. RESULTS AND DISCUSSION

Figure 2 shows how the In composition for InGaP layers changes with the InCl partial pressure at the growth temperature of 450  $^\circ\text{C}$ . The GaCl partial pressure was kept constant at  $4.3 \times 10^{-5}$  atm during the entire experiment. Increasing the InCl partial pressure from  $2.1 \times 10^{-4}$  atm, an increase in the In content was clearly observed by X-ray diffraction measurement. At about  $3 \times 10^{-3}$  atm of the InCl partial pressure, the composition reached a constant value of about 0.5. This composition hardly changed, even for a further increase in the InCl partial

pressure. The growth thickness was found to be approximately 2.8 Å/cycle under above growth conditions.

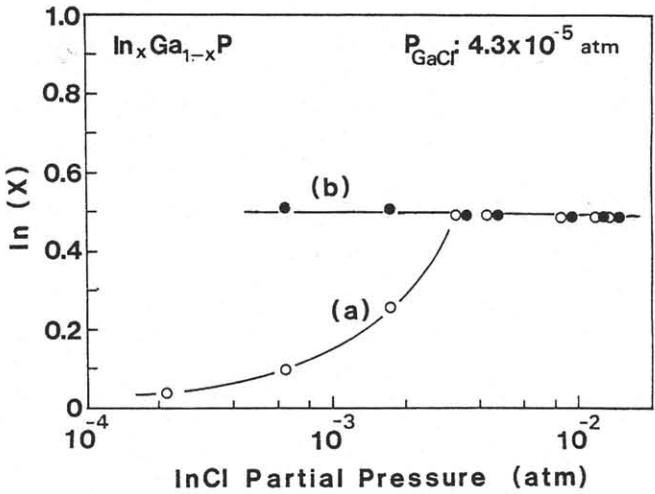


Fig. 2 In content as a function of InCl partial pressure. (a) Data from X-ray diffraction measurements, (b) Data from photoluminescence measurements at 77 K.

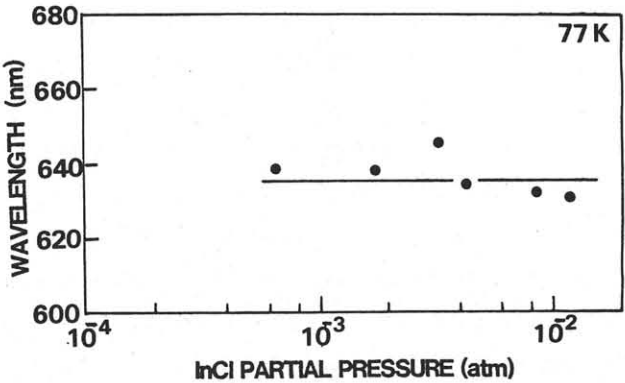


Fig.3 InCl partial pressure dependence of photoluminescence peak wavelength at 77K.

Figure 3 shows the InCl partial pressure dependence of the photoluminescence peak wavelength of above samples measured at 77 K. The peak wavelengths were found to be insensitive to the InCl partial pressure. These values nearly correspond to the bandgap energy of  $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ . The minimum FWHM value was 21 meV, which was obtained from a sample grown at  $P(\text{InCl}) = 4.2 \times 10^{-3}$  atm and was as narrow as that for VPE-InGaP grown at 700  $^\circ\text{C}$ . In the conventional hydride VPE,

the grown surface became very rough, when the growth temperature was decreased to 550 °C, as has been reported elsewhere<sup>5)</sup>, probably due to the existence of the miscibility gap. However, in ALE, featureless mirror surfaces were obtained, even at the growth temperature of 450 °C. The present method was compared with another ALE method growing (In,Ga)P, as described previously. The 77 K photoluminescence spectra from two samples by different ALE methods are shown in Fig. 4. The growth temperature was 400 °C. The photoluminescence spectrum, with double weak and broad peaks, was observed from an (In,Ga)P sample, while the (InP)(GaP) sample revealed a strong and narrow single peak. The authors consider that these results support the alternate growth of InP and GaP layers in the present method.

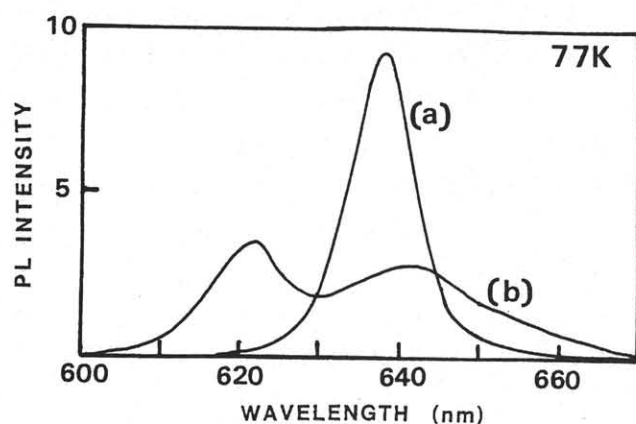


Fig.4 77 K photoluminescence spectra from two kinds of ALE-InGaP layers, (a) by (InP)(GaP) growth mode, and (b) by (In,Ga)P growth mode.

By using photoluminescence peak values in Fig. 3 and a proposed equation by Stringfellow for the relationship between the composition and the photoluminescence peak wavelength, the In compositions were calculated, as shown in Fig. 2. It is clearly seen that there is a great discrepancy in the region below  $3 \times 10^{-3}$  atm between the In composition obtained from X-ray diffraction measurements and that obtained from

photoluminescence measurements. To investigate this reason, samples grown at  $P(\text{InCl}) = 6.4 \times 10^{-4}$  atm and  $4.2 \times 10^{-3}$  atm were chemically etched by conc.  $\text{HNO}_3$  for 20 seconds. The normal InGaP layer should not be etched by the  $\text{HNO}_3$  solution. No distinct change was observed for the surface of the sample grown at higher InCl partial pressure, while the sample grown at lower InCl partial pressure was partly attacked by the solution. By the cathodeluminescence measurements at 77 K, very luminous stripes and dark stripes appeared alternately. These results indicate that  $\text{In}_x\text{Ga}_{1-x}\text{P}$ , having  $x \approx 0.5$  In composition, deposited locally on the substrate, while the remaining part resulted in Ga-rich composition having a large strain due to the lattice-mismatch to the GaAs substrate, when sufficient InCl partial pressure is not applied to the growth region. X-ray diffraction peaks observed are considered to correspond to such Ga-rich region.

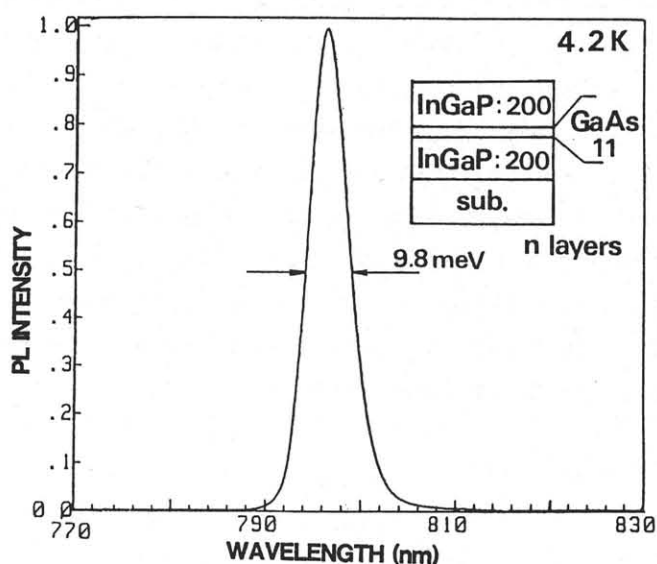


Fig. 5 Photoluminescence spectrum for an InGaP/GaAs/InGaP single quantum well with  $L_z = 11$  layers.

Using ALE-InGaP as a barrier, single quantum well (QW) structures of InGaP/GaAs, as shown in an insertion in Fig. 5, were fabricated at the growth temperature of

450 °C. The InCl partial pressure for growing InGaP was  $4.2 \times 10^{-3}$  atm. There were 200 InGaP layers for one side barrier. The GaAs well with 11 monolayers was also grown by ALE. The GaAs well thickness was confirmed by transmission electron microscopy (TEM) observation. Figure 5 shows a 4K photoluminescence spectrum. The 794 nm peak wavelength and the 9.8 meV narrow FWHM was obtained. Strong luminescence was also observed in 842 nm with the 33 meV FWHM at room temperature.

#### 4. CONCLUSION

Using the chloride ALE method, the InGaP growth was studied. InCl, PH<sub>3</sub> and GaCl source gases are supplied independently through three different chambers and the substrate surface was exposed to these gases alternately. Under sufficient InCl partial pressure conditions, it was found that the composition is insensitive to the partial pressure and that In<sub>x</sub>Ga<sub>1-x</sub>P having about x=0.5 composition can be grown. Using InGaP as a barrier, the authors fabricated single quantum well structures having ALE-GaAs as a well. Sufficiently narrow photoluminescence FWHM values, 9.8 meV at 4K and 33 meV at room temperature, were obtained. These results show the chloride ALE has a high potential for the growth of thin film heterostructures and its device applications.

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