# Control of Order Parameter during Growth of In<sub>0.5</sub>Ga<sub>0.5</sub>P/GaAs Heterostructures by GSMBE Using Tertiarybutylphosphine (TBP)

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#### **1.Introduction**

The  $In_{0.5}Ga_{0.5}P/GaAs$  heterostructure is an excellent material system for advanced high frequency devices such as HBTs and HEMTs with high performance and high reliability. However, InGaP prepared by MOVPE using phosphine, which is currently the standard growth technique, is known to show a strong tendency of natural ordering of group III atoms. This causes significant changes of fundamental properties such as bandgap and band offsets [1]. Thus, control of ordering during growth is important for reproducible fabrication of devices. It also provides an attractive chance for band engineering.

In this paper, we report on the first investigation of order parameter control during growth of InGaP/GaAs (001) heterointerface by gas-source molecular beam epitaxy (GSMBE) using tertiarybutylphosphine (TBP) which is much less toxic than phosphine.

#### 2.Experimental

The flow rate ( $F_{TBP}$ ) and the cracking temperature of TBP used as the phosphorus source were 2-8 sccm and 800°C, respectively. Conventional metallic sources were used for supply of In, Ga, and As beams. Elemental Si was used for n-type doping. The growth temperature was varied from 450°C to 580°C. For heterostructure formation, a thick GaAs buffer layer was grown on the (001) n<sup>+</sup>-GaAs substrate, first, and then an InGaP layer was grown on top. Simultaneous growth on the (001) and (113)A substrates, put side by side, was made in some cases for the purpose of comparison. Grown samples were characterized by in-situ XPS, PL and C-V measurements.

#### **3.Results and Discussion**

# 3.1 Optimization of growth conditions for formation of defect-free InGaP/GaAs heterointerfaces

For meaningful control of ordering at heterointerfaces, grown interfaces should be free of interface defects over wide range of growth conditions. However, our previous study [2] has indicated a strong tendency that a particular type of interface defects having a PL transition energy near 1.7 eV are formed at small values of  $F_{TBP}$ , as shown in the **Fig.1(a)**. In this study, this difficulty has been removed by controlling the surface reconstruction pattern of GaAs prior to growth of InGaP. Namely, previous growth has always done on c(4x4)-reconstructed GaAs surface. It has been found, however, that interface defects can be suppressed as shown in **Fig.1 (b)** for a wide range of  $F_{TBP}$  values by growing on a (2x4)-reconstructed GaAs surface which was obtained by controlling the residual As pressure in the MBE chamber at the growth temperature of InGaP.

From PL measurements, it has been also found that the optimum growth temperature to obtain a high and narrow PL peak changes with  $F_{TBP}$  as summarized in Fig.2.

## 3.2 Control of ordering in InGaP by TBP flow rate

Examples of PL spectra obtained on InGaP/GaAs samples simultaneously grown on GaAs(001) and (113)A substrates are shown in **Fig.3** for various values of  $F_{\text{TBP}}$ . Since it is known [3] that InGaP grown on GaAs(113)A surface is always almost completely disordered, PL peak energy shifts seen on (001) samples in **Fig.3** are due, no to change of alloy composition, but to that of ordering. XRD measurements also confirmed very small deviations of the alloy composition. The order parameter,  $\eta$  defined by

$$\begin{split} \eta &= (\ E_{PL}(d) - E_{PL})/ \ (E_{PL}(d) - E_{PL}(o)) \ (1) \\ \text{is often used as a measure of ordering. Here, } E_{PL} \ \text{is PL} \\ \text{energy, and o and d refer to ordered and disordered limits,} \\ \text{respectively. The value of } \eta \ \text{determined using past PL data} \\ \text{changed in our case from 0.1 to 0.3 by changing } F_{TBP} \ \text{from} \\ \text{2 to 8sccm, causing the band gap energy change of 40 meV.} \end{split}$$

### 3.3 Band offsets and sheet carrier density of 2DEG

The valence band offset,  $\Delta E_v$ , was measured by in-situ XPS measurements on thin InGaP layers grown on GaAs. An example is shown in Figs.4 (a) and (b). The measured values were in the range of 0.28 - 0.30 eV, being independent of  $\eta$ . This is similar to the case of MOVPE growth, although some theoretical calculation [4] has predicted its change. Thus, the observed band gap energy change of 40 meV caused that of the conduction band offset,  $\Delta E_c$ , in our samples.

An example of measured C-V carrier profile is shown in **Fig.5** (a), indicating existence of 2DEG. The measured sheet carrier density,  $n_s$ , is plotted in **Fig.5** (b) as a function of  $\eta$ . As seen in **Fig.5** (b),  $n_s$  changes sharply with  $\eta$ , and this is due to change in  $\Delta E_c$  in agreement with the simple approximate formula, relating  $n_s$  to  $\Delta E_c$  [5]. Thus, control of order parameter is possible and important in GSMBE growth of  $In_{0.5}Ga_{0.5}P/GaAs$  heterostructure using TBP.

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Fig.1. PL spectra of InGaP/GaAs heterostructures. InGaP were grown on (a)GaAs c(4x4) and (b)GaAs (2x4) surfaces.



Fig.2. PL peak intensity and FWHM of InGaP layers vs growth temperature at  $F_{TBP}$ =4 and 8sccm.



Fig.3. PL spectra of single InGaP layers grown on GaAs(001) and (113)A substrates at  $F_{TBP}=2$ , 6 and 8sccm.



Fig.4. (a) As3d and P2p XPS spectra from InGaP/GaAs heterostructure and (b) band line up ( $F_{TBP}$ =8sccm).



Fig.5. (a) Example of carrier profile in InGaP/GaAs heterostructure and (b)  $n_s$ -F<sub>TBP</sub> plot.