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MOCVD Growth and Characterization of AlGaInP Materials by a New Pre-Cracking Technique for PH_3

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We have demonstrated the MOCVD growth of AlGaInP under low pressure using a self-cracking system (SCS) for the group V hydride (PH_3). In the case of InGaP growth, the incorporation efficiency of In atoms for SCS method is higher than that for conventional method. For AlInP growth, however, its efficiency did not depend on growth methods and also growth temperatures. The peak position of the photoluminescence spectrum at 77K for AlGaInP is 0.59µm. The typical carrier concentration and Hall mobility at 300K for AlGaInP and InGaP are $5\times10^{10}cm^{-3}$, $700cm^2/v\cdot sec$ and $5\times10^{10}cm^{-3}$, $1400cm^2/v\cdot sec$. These results indicate that SCS-grown epitaxial layers are electrically of good quality.

§1. Introduction

The AlGaInP/GaAs system is currently of great interest because its system is one of the most possible candidates for the material of visible semiconductor laser, which is useful in a high density optical information processing system. AlGaInP has a largest band-gap energy in Ⅲ-V compound semiconductors with direct transition and also can be completely lattice-matched to GaAs. AlGaInP materials, however, have a crucial problem which is the large segregation of Al under a near thermally equilibrium growth such as liquid phase epitaxy (LPE), indicating that it is difficult to control the Al composition precisely.[1] Therefore, AlGaInP systems were successfully grown by molecular beam epitaxy (MBE)[2] and metalorganic chemical vapor deposition (MOCVD)[3,4] methods far from equilibrium method. DH layer was grown on GaAs substrate and laser action was observed. The lasing wavelength was 0.683µm for MOCVD[5] and 0.66µm for MBE.[2]

In MOCVD growth using PH_3 as a source of P atoms, PH_3 should be pre-cracked, especially under low pressure, in order to increase the incorpo-

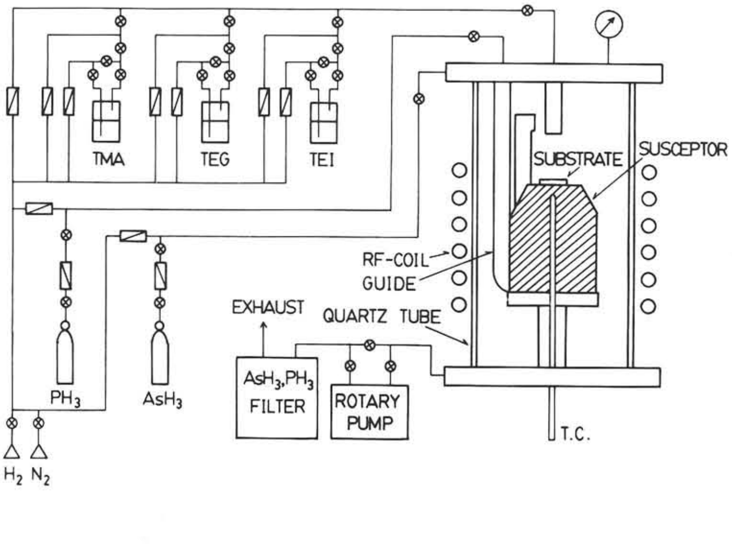

Fig.1. Schematic diagram of the total MOCVD system, including the main chamber with the pre-cracking system for PH_3.

ration efficiency of P and In atoms and avoid the formation of nonvolatile compounds. So far two methods of PH_3 pre-cracking were proposed for the growth of InGaAsP systems. One was to use additional furnace proposed by Duchemin et al.$^{6)}$ and the other the self-cracking system (SCS) proposed by Ogura et al.$^{7,8)}$

In this report, we present MOCVD growth of AlGaInP using a self-cracking system for cracking PH_3. Incorporation efficiency of In and P atoms when using SCS method are discussed. Optical and electrical properties of undoped InGaP, and AlGaInP are also presented.

§2. Experimental

Our growth system in this study is shown schematically in Fig.1. It is composed of a vertical quartz reactor 55mm in inner diameter which contains a graphite susceptor heated inductively at 250KHz. Trimethylaluminum (TMA), Triethylgallium (TEG), Triethylindium (TEI) and PH_3 are used as source materials, H_2 as a carrier gas. PH_3 diluted to 5% in H_2 gas are passed through a U-shaped line located near the rf-heated susceptor, before being introduced into the reactor, resulting in PH_3 pre-cracking. This system is essentially similar to our reported system for the horizontal reactor tube which is named self-cracking system (SCS).$^{7)}$ TMA, TEG and TEI are directly introduced into a cylindrical guide, which are transported by H_2 gas passing through a bubbler kept at 20°C for TMA, 3°C for TEG and 45°C for TEI. A rotary pump is used for the low-pressure growth.

Typical growth conditions for InGaP, AlInP, and AlGaInP are summarized in Table 1. The substrates used in this study were (100) GaAs supplied by Sumitomo Electric Ind. Co., Ltd.. These substrates, 10mmx10mm in size, were etched in a $5H_2SO_4:H_2O_2:H_2O$ solution for 2 min before epitaxial growth. Until the growth temperature was attained, AsH_3 was introduced into the reactor in order to avoid the thermal damage of the substrate surface. Then the AsH_3 flow was switched to a PH_3 flow and epitaxial growth was initiated. The surface morphologies of these alloys were mirror-like. The growth rates for AlGaInP quaternary alloys were 0.05µm/min, independent of the compositions.

Table 1. Typical growth conditions for InGaP, AlGaInP and AlInP.

	InGaP	AℓGaInP	AℓInP
·Growth temperature (℃)	650	750	750
·Reactor pressure (Torr)	100	100	100
·Flow rate (cc/min)			
H_2 into TMA (20 ℃)	–	3	3
H_2 into TEG (3 ℃)	50	50	–
H_2 into TEI (45 ℃)	100	127	100
PH_3	15	15	15
Total H_2	5600	5700	5600

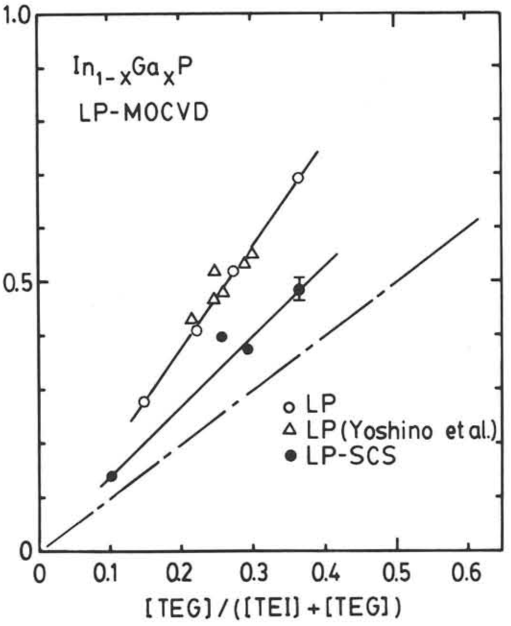

Fig.2. The relations between Ga composition x and (TEG)/[(TEI)+(TEG)] for $In_{1-x}Ga_xP$. Open circles (○) and filled circles (●) are for LP and LP-SCS, respectively. Triangles (△) are calculated from a previous work reported by Yoshino et al.$^{9)}$

§3. Results and Discussion

The solid-vapor distribution relations for $In_{1-x}Ga_xP$ and $Al_xIn_{1-x}P$ are shown in Fig.2 and Fig.3, respectively. In Fig.2, our results are in good agreement with those of Yoshino et al.$^{9)}$ The incorporation efficiency of In atoms for LP-SCS which means SCS under low pressure is higher than that for LP which means the conventional low pressure system. An additional advantage for this SCS is the reduction of the PH_3 concentration needed for epitaxial growth. Actually, even a concentration corresponding to only 30% of that needed for the LP method without PH_3 cracking, was

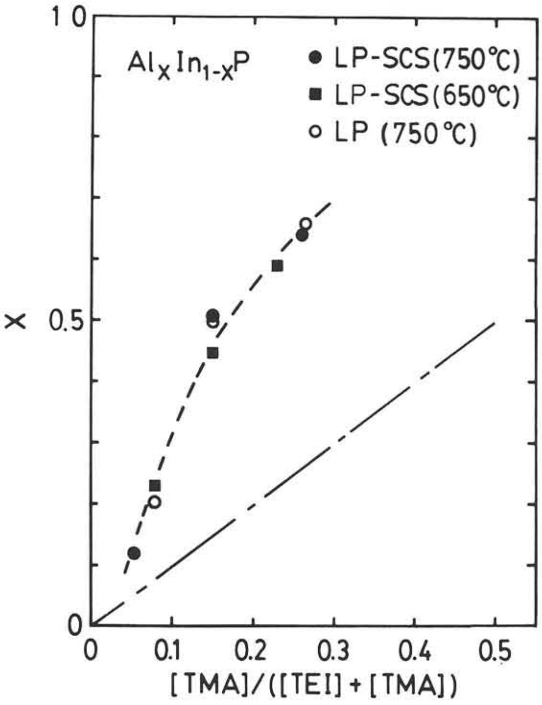

Fig.3. The relation between Al compositions x and (TMA)/[(TEI)+(TMA)]. Filled circles (●) filled squares (■) and open circles (○) are for the LP-SCS method at 750°C, the LP-SCS method at 650°C and the LP method at 750°C, respectively.

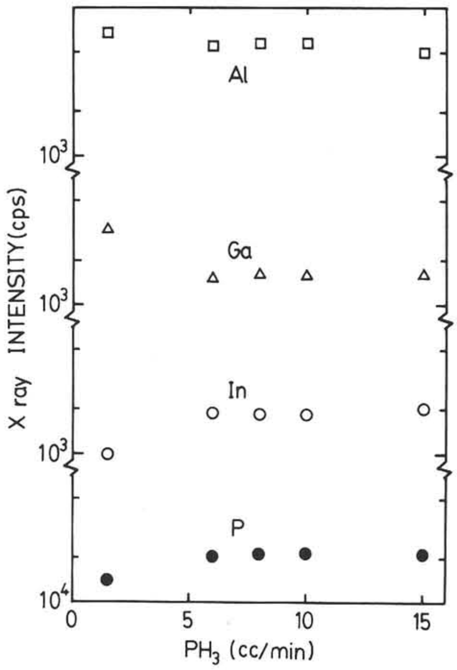

Fig.4. The relation between X-ray intensity of $(Al_xGa_{1-x})_yIn_{1-y}P$ alloy elements and PH_3 flow rate. Open squares (□), open triangles (△), open circles (○) and filled circles (●) are for Al, Ga, In and P composition, respectively.

sufficient for obtaining good epitaxial films. For Al_xIn_{1-x}-P, on the other hand, the incorporation efficiency of In atoms does not depend on growth methods or growth temperatures, though it seems that our construction (SCS) is essentially more effective for the cracking of the group V hydrides as growth temperature is higher. This physical mechanism is not clear yet. It is probably caused by large segregation of Al.

Figure 4 and Fig.5 show the relation between X-ray intensity of AlGaInP quaternary alloy elements and PH_3 flow rate, and growth temperature, respectively, which were evaluated using an electron probe X-ray microanalyzer (EPMA). Alloy compositions x, y were calculated from EPMA results. These compositions are independent of PH_3 flow rate in the range between 5cc/min and 15cc/min and also growth temperature in the range between 650°C and 775°C.

Photoluminescence spectra for $(Al_xGa_{1-x})_y$-$In_{1-y}P$ ($x \sim 0.3$, $y \sim 0.5$) and $In_{1-x}Ga_xP$ ($x \sim 0.5$) are shown in Fig.6. The half width and the peak wavelength at 77K are 80meV, 0.65μm for InGaP and 150

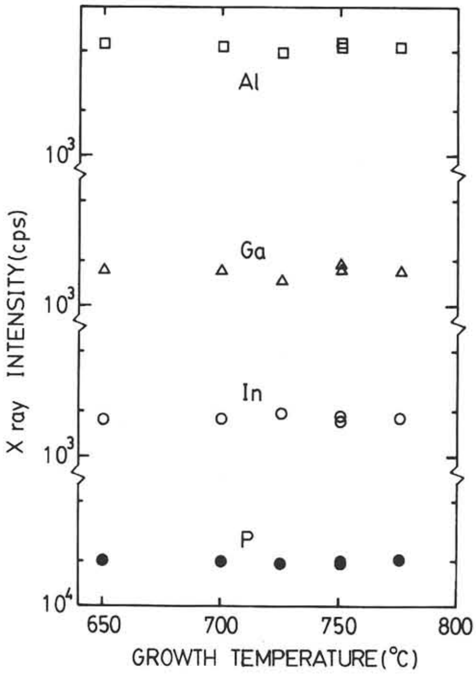

Fig.5. The relation between X-ray intensity of $(Al_xGa_{1-x})_yIn_{1-y}P$ alloy elements and growth temperature. Various symbols are already identified in the caption of Fig.4.

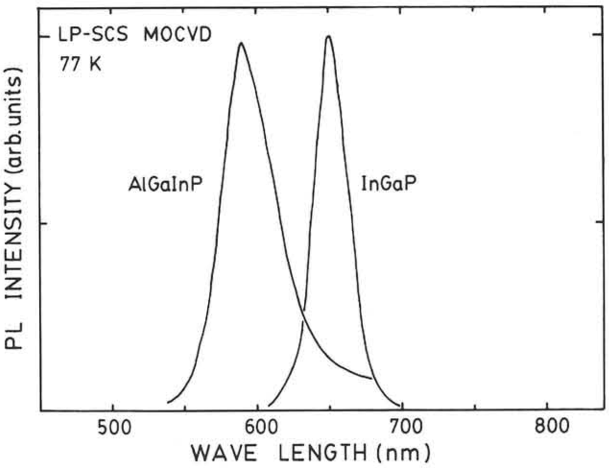

Fig.6. PL spectra for $(Al_xGa_{1-x})_yIn_{1-y}P$ (x∿0.3, y∿0.5) and $In_{1-x}Ga_xP$ (x∿0.5) almost lattice-matched to GaAs ($\Delta a/a \leq 10^{-3}$).

meV, 0.59μm for AlGaInP, respectively. These PL spectra were obtained using a 5145A Ar laser focused on the surface of an AlInP/AlGaInP/AlInP double heterostructure sample for AlGaInP and single layer for InGaP.

Electrical properties were also evaluated by Hall measurements for highly-resistive samples. The resistivity of undoped films grown on semi-insulation GaAs ($\geq 10^7 \Omega\cdot cm$) were $\sim 10^5 \Omega\cdot cm$. Carrier concentration and Hall mobility of AlGaInP were obtained for the first time. Typical carrier concentration and Hall mobility were $5 \times 10^{10} cm^{-3}$, 1400 $cm^2/v\cdot sec$ for InGaP and $5 \times 10^{10} cm^{-3}$, $700 cm^2/v\cdot sec$ for AlGaInP.

§4. Summary

We have successfully grown AlGaInP materials by MOCVD using a self-cracking system for PH_3. In the case of InGaP, the incorporation efficiency of In atoms for LP-SCS is higher than that for LP. For AlInP, however, its efficiency did not depend on growth temperatures or growth methods. The compositions x, y of AlGaInP are independent of PH_3 flow rates and growth temperatures in the particular range. We have found that these AlGaInP films obtained are electrically of good quality.

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