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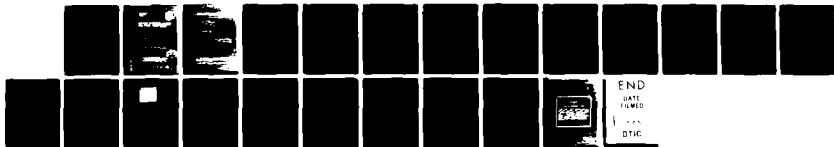
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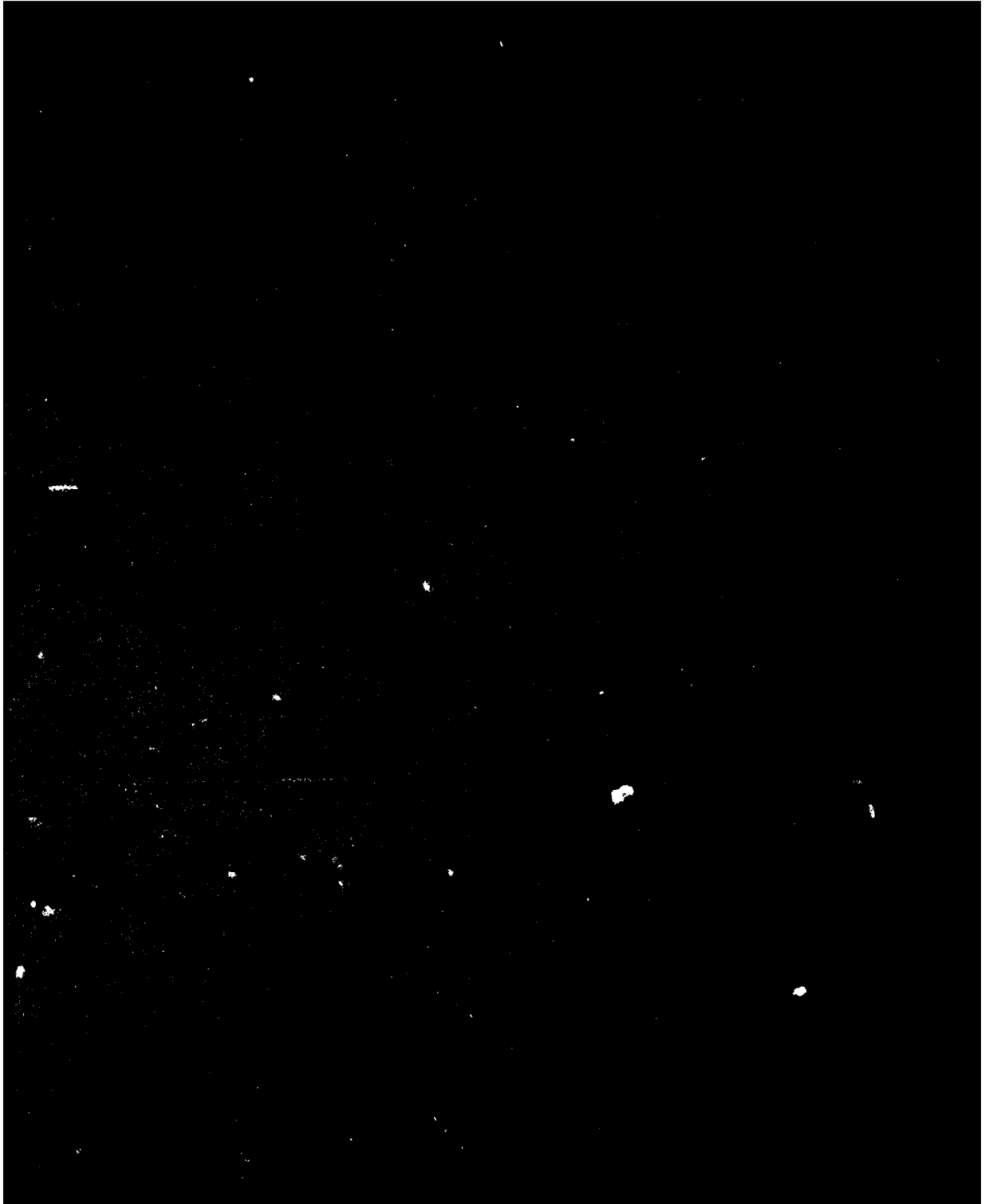
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A procedure was devised for the growing of high purity InP by the vapor phase epitaxy (VPE)-hydride method. A continuous in situ etch with HCl of the InP substrate and the epitaxial layer under growth was developed in the VPE-hydride reactor. A study of the effect of the continuous in situ etch of HCl on the growth rates and properties of epitaxial layers prepared by the vapor phase epitaxy-hydride technique is reported. Growth rates were determined as a function of the following variables: HCl flow rates in the mixing and source zones, PH ₃ flow rates, and mixing zone temperatures. Epitaxial		

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InP structures with good morphology were obtained when the continuous HCl etch was varied between 0.8 and 1.5 cc/min. The average values (77 K) of the carrier concentrations and mobilities were $1.3 \times 10^{15} \text{ cm}^{-3}$ and $23,000 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$, respectively. The study indicates that the continuous in situ HCl etch improves the quality of the epitaxial InP layers.

sq cm/V/sec

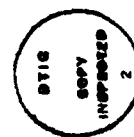
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Preface

During the course of this study, the authors have received assistance from many others. Therefore, they wish to thank John K. Kennedy for his advice and encouragement. They also express gratitude to the following people for assistance in this project: John J. Fitzgerald (Auger analysis); Joseph A. Adamski (bulk InP preparation); Robert M. Hilton (single crystal InP preparation); Jane A. Horrigan (X-ray analysis); and Joseph R. Weiner (substrate polishing). The authors also thank William D. Potter for his help and advice.



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High Purity InP Grown by the Vapor Phase Epitaxy-Hydride Method

I. INTRODUCTION

Considerable research is currently being devoted to the preparation of InP and InGaAsP for the fabrication of double-heterostructure lasers and light-emitting diodes.^{1,2} These materials are prepared primarily either by the vapor phase or the liquid phase epitaxial technique. Olsen and Zamerowski³ have published an excellent review paper on the vapor phase epitaxial (VPE)-hydride technique for the preparation of InP and the quaternary alloys (In,Ga) (As,P). These studies and investigations⁴ carried out at this laboratory indicate that the production of good

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1. Chen, P. C., Yu, K. L., Margalit, S., and Yariv, A. (1981) Embedded epitaxial growth of low-threshold GaInAsP/InP injection lasers, Appl. Phys. Lett. **38**:301.
2. Olsen, G. H., Zamerowski, T. J., and Digiuseppe, N. J. (1980) 1.5-1.7 μm V.P.E. InGaAsP/InP C.W. Lasers, Electron. Lett. **16**:516.
3. Olsen, G. H., and Zamerowski, T. J. (1980) Crystal Growth and Properties of Binary, Ternary and Quaternary (In,Ga) (As,P) Alloys Grown by the Hydride Vapor Phase Epitaxy Technique, in Progress in Crystal Growth and Characterization, Vol. II, Pergamon Press Ltd., London, pp. 309-375.
4. Anderson, T. (1980) Influence of Reaction Variables on the Electrical Properties of Homoepitaxial InP in the Hydride System, USAF Summer Faculty Research Program, Research Reports Vol. I, W.D. Peele and R.K. Kopka, Ed., SCEE Press.

morphological, epitaxial InP is difficult. The defects originate from a number of sources, for example, dislocations in the substrates, inappropriate epitaxial growth conditions, and impurities.

The present study was initiated to improve the morphology of InP epitaxial layers. This paper is a report of an investigation of the effect of a continuous etch on the epitaxial layer during growth. Thermodynamic considerations dictate that this etch will promote crystalline growth with fewer defects. The etch, hydrogen chloride, was added directly to the mixing zone of the VPE-hydride reactor. The hydrogen chloride etch has the capability to remove impurities and unstable species that give rise to defects. This role of HCl in the deposition zone may be the factor responsible for the lower carrier concentrations and higher mobilities⁵ obtained with the epitaxial InP layers grown by the VPE-chloride method. Growth rates and morphological character of the epitaxial layers were studied as functions of temperature, amount of hydrogen chloride in the mixing zone, and flow rates of phosphine and source HCl (this being the HCl which reacts with the elemental indium source to form InCl). Epitaxial layers with good morphology were observed when hydrogen chloride was added to the mixing zone at low flow rates.

In situ noncontinuous etching of substrates has been studied extensively in the preparation of GaAs⁶⁻⁹ and InP^{10, 11} by the VPE-chloride technique.^{6-9, 10, 11} This preliminary etching ensured a clean and damage-free substrate prior to epitaxial growth. The HCl used in these in situ etching processes is generated from the reaction of the group VB trichloride with hydrogen. Chevrier et al¹⁰ have found that the smoothness of the InP epitaxial layer correlated well with the morphology of the substrate etched in situ with PCl_3 and H_2 .

2. EXPERIMENTAL PROCEDURES

The epitaxial growth studies of InP were conducted with a VPE-hydride quartz reactor similar to that used by Tietjen and Amick (Figure 1).¹² The reactor has three temperature zones: source, mixing, and deposition. These zones are heated by "clamshell" resistance heating units. Flow rates were regulated by mass flow controllers (Tylan). The reactant gases used in the synthesis of the epitaxial InP were of the highest purity obtainable: phosphine, supplied as a 5 percent mixture in hydrogen from MG Scientific, Kearny, New Jersey, with purity of PH_3 and hydrogen 99.998 percent and 99.999 percent, respectively; the carrier gas, hydrogen, supplied by American Industrial and Medical Products, Auburn, Massachusetts, with 99.999 percent purity, and further purified by a hydrogen purifier (Palladium

(Due to the large number of references cited above, they will not be listed here. See References, page 19.)

Diffusion Process-Engelhard); hydrogen chloride from Precision Gas Products, Inc., Rahway, New Jersey, with 99.995 percent purity; and indium from the Indium Corporation of America, with purity 99.999 percent.

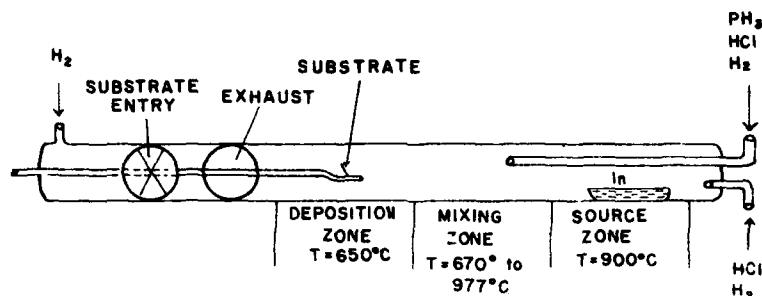


Figure 1. Vapor Phase Epitaxy (VPE) Reactor for the Preparation of Epitaxial InP by the Hydride Method

Epitaxial growth was studied at various flow rates and temperatures, in order to determine conditions for optimum morphology. The source and deposition temperatures were maintained at 900° and 650°C, respectively. The mixing temperature was varied from 670° to 977°C. Hydrogen chloride, introduced to the mixing zone by means of the PH_3/H_2 inlet, varied in flow rate from 0 to 2.0 cc/min. The PH_3 flow rate varied from 2.7 to 15.9 cc/min and the source HCl flow rate changed from 2.3 to 6.9 cc/min. The carrier hydrogen flow rate was either 1684 or 2390 cc/min. Time duration for epitaxial growth was 45 min, with growth rate determined from the surface area of the substrate, mass of deposit, and density of InP.

The substrates were obtained from a liquid encapsulated Czochralski (LEC) grown iron-doped InP boule. Slices of the boule were cut 3° off the (100) plane towards the (111) plane and polished on an Electropolisher (Sylvania Company) with Pellon PAN-W pads (J.I. Morris Company, Southbridge, Massachusetts), using a 0.5 to 1.0 percent bromine-isopropyl alcohol solution. The substrates were degreased by treatment with toluene, 1, 1, 1, -trichloroethane, and acetone; they were etched for 5 min in Caro's acid ($1 \text{ water} + 1 \text{ H}_2\text{O}_2 + 5 \text{ H}_2\text{SO}_4$). Having been washed with water, the substrates were further etched for 2 min in a 0.3 percent Br_2 -methanol solution and washed with methanol. This was followed by another 5-min Caro's acid etch. The substrates were washed with water and then with methanol; they were blow-dried with nitrogen.

Carrier concentration and mobilities were obtained from resistivity and Hall measurements at 77 K by the van der Pauw technique.¹³ A permanent magnet provided a field of 4.0 kG for the Hall measurements. Auger electron spectrographs of the epitaxial InP layers and InP substrates were obtained with a Perkin-Elmer Auger Spectrometer.

3. RESULTS AND DISCUSSIONS

The objectives of the present study are: (1) to study the growth rates of InP epitaxial layers at low flow rates of gaseous reactants in the presence of a continuous etch; and (2) to determine the growth conditions in the presence of the continuous etch that produce good morphological InP layers. The differences in the growth rates observed in this study are assumed to be due to reaction limitations, as opposed to either mass-transport or mass-transfer limitations.³

3.1 Growth Rates and Morphology

Figure 2 shows the effect on the growth rate of InP caused by the addition of HCl to the mixing zone. The presence of 1.5 cc/min HCl in the mixing zone decreases the growth rate of the epitaxial InP. The slopes of the lines obtained when InP growth rate is plotted against flow rate of source HCl are 0.4 $\mu\text{m}/\text{cc}$ HCl in the absence of a continuous etch and 0.1 $\mu\text{m}/\text{cc}$ HCl in the presence of the 1.5 cc/min flow rate of HCl in the mixing zone. The linear increase in growth rate beyond the 1:1 ratio of PH_3/HCl indicates the nonstoichiometry of the reaction in this region. These results indicate that an efficient etching reaction is taking place during the growth of InP with HCl in the mixing zone. The flow rate of source HCl was not increased beyond values greater than 6.9 cc/min, since at this flow rate polycrystalline layers of InP were obtained.

Figure 3 shows the effect of increasing the PH_3 flow rate on the growth rate of InP in the presence and absence of HCl in the mixing zone. The limitation of growth rate occurs at approximately the same value of the PH_3 flow rate in the presence or absence of the continuous etch. The growth rate with 1.5 cc/min HCl in the mixing zone is about one-half of that obtained without the continuous etch. The results show that no decrease in growth rate of InP is observed at the higher flow rate values of the group VB compound as has been found for InP in the

13. van der Pauw, L.J. (1958) A method of measuring specific resistivity and Hall effect of discs of arbitrary shape, Philips Res. Repts. 13:1.

In- PCl_3 - H_2 system.¹⁴ These results indicate that no competitive adsorption processes exist between indium and phosphorus atoms in the kinetic control region of the hydride technique. Shaw¹⁵ has discussed this mechanism for the Ga/HCl/As/ H_2 system. In addition, these results indicate that for the chloride system, the tailing off in the growth rate of InP with increasing PCl_3 flow rate may be caused by in situ HCl etching of the InP.

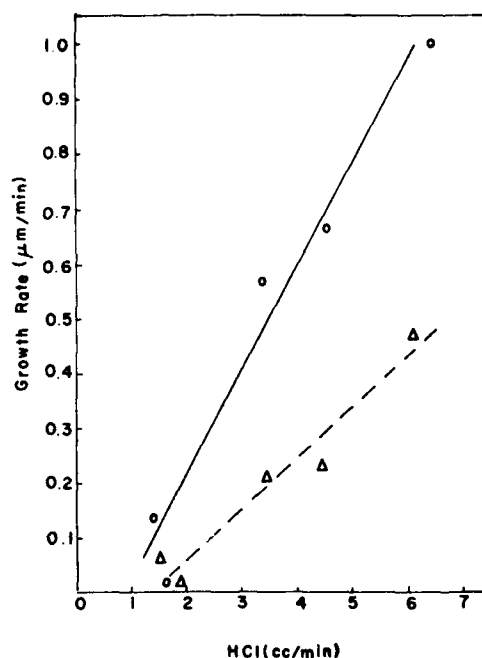


Figure 2. Growth Rate of Epitaxial InP as a Function of Source HCl Flow Rate With and Without HCl in PH_3 Inlet:
 Δ --- Δ , 1.5 sccm HCl in PH_3 inlet;
 O — O , No HCl; $\text{PH}_3 = 3.1$ sccm;
 H_2 (PH_3) = 842 sccm;
 H_2 (HCl) source = 842 sccm. Substrate temp. = 650°C ; source temp. = 900°C ; mixing temp. = 950°C

14. Mizuno, O. (1975) Vapor growth of InP, J. Appl. Phys. (Japan) 14:451.
15. Shaw, D.W. (1970) Epitaxial GaAs kinetic studies: (001) orientation, J. Electrochem. Soc. 117:683.

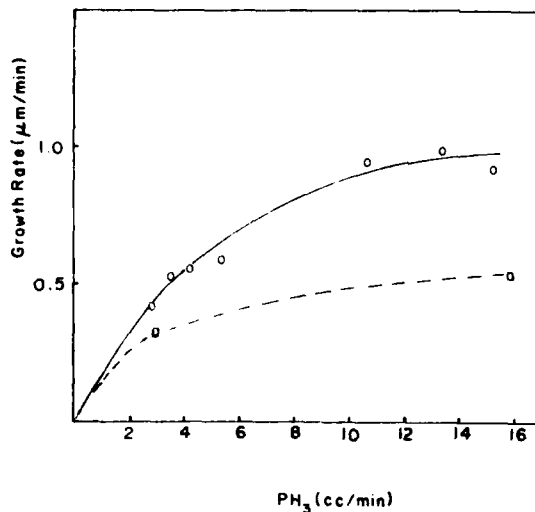


Figure 3. Growth Rate of Epitaxial InP as a Function of Phosphine Flow Rate With and Without HCl in PH₃ Inlet: O—O, No HCl; □---□, 1.5 sccm HCl (PH₃), Source HCl = 5.3 sccm; H₂ (PH₃) = 842 sccm; H₂ (HCl source) = 842 sccm. Substrate temp = 650°C; source temp. = 900°C; mixing temp = 950°C

The study of InP growth rate as a function of the flow rates of HCl in the mixing zone was studied at two PH₃ flow rates: 3.1 cc/min and 15.9 cc/min. The results of the study are presented in Figure 4. The curves were dramatically different than expected with maximum rates in the vicinity of 0.8 cc/min of HCl in the mixing zone. The maximum growth rates for the 3.1 cc/min and 15.9 cc/min PH₃ flow rates are approximately 0.7 μm/min and 1.8 μm/min, respectively. A possible explanation for this unexpected growth at these intermediate HCl values has been suggested from the GaAs studies of Shaw.¹⁶ With HCl in the mixing zones, impurities at critical sites are removed; otherwise growth would be hindered. Shaw¹⁶ indicated that the slow growth on the (111) B plane is the result of impurities at critical sites. The epitaxial growth at flow rate values of HCl (mixing zone) equal to or greater than the maximum would be expected to display less defects with smoother surfaces. At flow rate values greater than 1.8 cc/min of HCl (mixing zone), only the etching reaction is observed. Microscopic studies of the epitaxial layers grown with HCl (mixing zone) flow rates between 0.8 and 1.8 cc/min and at

16. Shaw, D.W. (1968) Influence of substrate temperature on GaAs epitaxial deposition rates, J. Electrochem. Soc. 115:405.

a PH_3 flow rate value of 15.9 cc/min demonstrated better morphology than those grown with flow rates of mixing zone HCl below 0.8 cc/min. At 3.1 cc/min PH_3 flow rate, InP layers with good morphology were obtained with 1.3 cc/min and 1.5 cc/min HCl flow rates in the mixing zone. Figure 5 shows typical morphological characteristics of the epitaxial layer grown at a 1.3 cc/min HCl flow rate in the mixing zone with the phosphine flow rate at 3.1 cc/min.

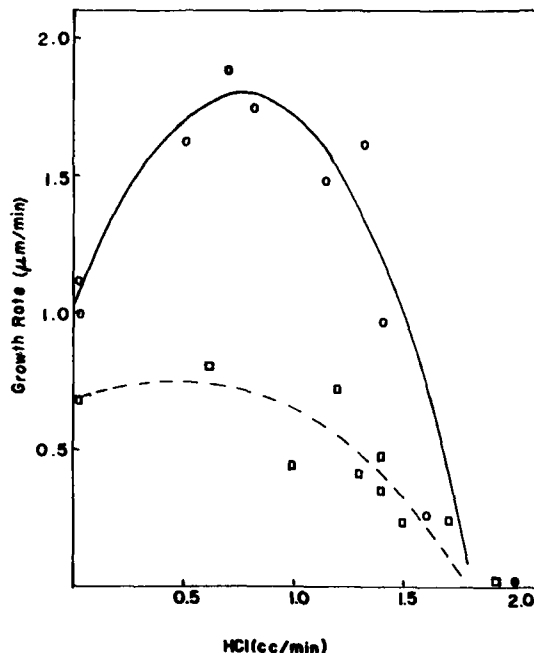


Figure 4. Growth Rate of Epitaxial InP as a Function of Hydrogen Chloride Flow Rate in the Mixing Zone at Two Phosphine Concentrations:
 O — O, $\text{PH}_3 = 15.9$ cc/min.
 □ --- □, $\text{PH}_3 = 3.1$ cc/min. HCl (Source flow rate, 5.3 cc/min; H_2 flow rates, 842 cc/min (HCl inlet) and 842 cc/min (PH_3 inlet). At 3.1 cc/min PH_3 , source temp., 900°C; mixing temp., 950°C; deposition temp., 650°C. At 15.9 cc/min PH_3 , source temp., 900°C; mixing temp., 900°C; deposition temp., 650°C



Figure 5. Nomarski Contrast Photomicrograph of a Surface of an Epitaxial InP Layer Grown With Continuous Etch of 1.3 cc/min HCl (128X)

— = 0.1 mm

The effect of the temperature of the mixing zone as a function of the flow rate of HCl (mixing zone) on InP growth rate is shown in Figure 6. The growth rate decreases with decreasing mixing zone temperature. At a flow rate value of 0.25 cc/min HCl in the mixing zone, the growth rate decreases from 0.7 $\mu\text{m}/\text{min}$ to 0.5 $\mu\text{m}/\text{min}$ to 0.2 $\mu\text{m}/\text{min}$, when the temperature is lowered from 950° to 900°C to 850°C. The growth curve obtained for the InP at a mixing zone temperature of 950°C is arced while those obtained at 900°C and 850°C are linear. This indicates that possibly a different mechanism for the growth-etch reactions is occurring at the higher temperature. The increased growth rate with increased mixing zone temperatures can be attributed to the higher percentages of P_4 and P_2 in the deposition zone. Indium phosphide decomposes to indium and phosphorus according to the following scheme:¹⁷



Therefore, an increase in either P_4 or P_2 will decrease the decomposition of InP in the deposition zone. Ban¹⁸ has measured the increase in the decomposition of

17. Ugal, Y. A., Bitvutskaya, L. A., and Gurza, L. F. (1966) Dependence of indium phosphide dissociation pressure, *Izv. Akad Nauk SSSR, Neorg. Mater.* 2:1944.

18. Ban, V. S., and Ettenberg, M. (1973) Mass spectrometric and thermodynamic studies of vapor-phase growth of $\text{In}_{(1-x)}\text{Ga}_x\text{P}$, *J. Phys. Chem. Solids* 34:1119.

PH_3 to P_4 and P_2 with increasing temperatures. Figure 6 shows that higher growth rates are attained at 950°C over a wider range of etchant HCl flow rate values than at 900°C and 850°C . This wider range of higher growth rates may also be attributed to the increase in P_4 and P_2 species which not only inhibit the decomposition of InP but also decrease the extent of the etching reaction:

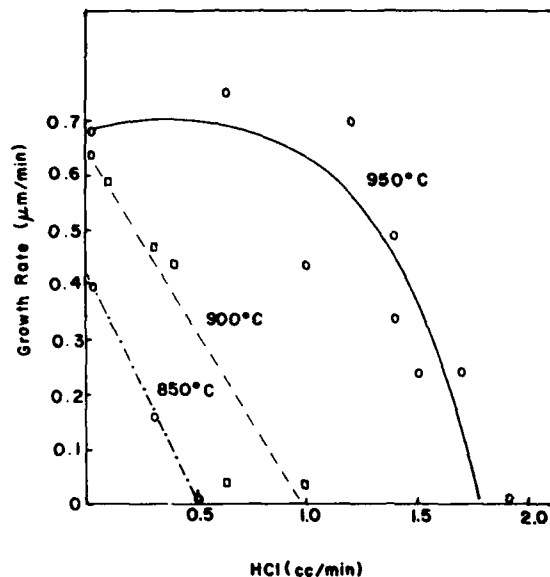
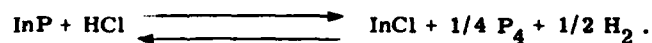


Figure 6. Effect of Mixing Temperature and HCl in Mixing Zone on Epitaxial Growth Rate of InP . HCl (source), 5.3 cc/min; PH_3 , 3.1 cc/min; H_2 842 cc/min (source HCl inlet), 842 cc/min (PH_3 inlet). Source temp., 900°C ; deposition temp., 650°C ; mixing temperatures, $\text{O} \text{---} \text{O}$, 950°C ; $\square \text{---} \square$, 900°C ; $\text{O} \text{---} \text{---} \text{O}$, 850°C

The extent of the inhibition of the growth of InP by the in situ HCl etch can readily be observed from measurements of the apparent activation energies. We use the term "apparent activation energy" because the change in the growth rate of InP is observed when the temperature of the mixing zone is varied, even though the temperature of the deposition (growth) zone remains unchanged. The effect of the

mixing zone temperature on the growth rate of InP in the presence and absence of HCl in the mixing zone is shown in Figure 7, where growth rate is plotted against the reciprocal of the absolute temperature. The etchant HCl flow rate is 0.5 cc/min. The apparent activation energies for the growth rate of InP in the presence and absence of HCl etch were calculated to be 154 kJ/mole and 11 kJ/mole, respectively. These values illustrate that competitive processes are occurring when HCl is added to the mixing zone. When etchant HCl is not present in the mixing zone, the morphological quality of the InP epitaxial layers have generally been poor. The low apparent activation energy allows for rapid, haphazard growth of InP. The addition of HCl to the mixing zone at a flow rate of 0.5 cc/min, however, increases the apparent activation energy by a factor of 14. As a result of this, the InP epitaxial layer grows more selectively and at a slower rate. This can account for the improved morphology of the InP epitaxial layer, when it is grown in the presence of the in situ HCl etch.

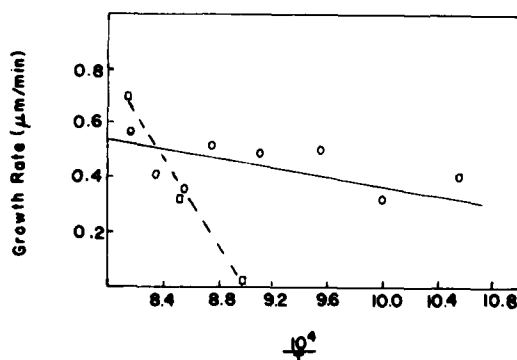


Figure 7. Effect of Mixing Temperature on Growth Rate of Epitaxial InP With and Without HCl in Mixing Zone: O — O, without HCl in mixing zone; □ --- □, 0.5 cc/min HCl in mixing zone. Source temp., 900°C; deposition temp., 650°C. Without HCl (mixing), source HCl, 5.3 cc/min; PH₃, 3.1 cc/min; H₂, 1.16 l/min (PH₃ inlet), 1.23 l/min source HCl inlet). With HCl (mixing), source HCl, 5.3 cc/min; PH₃, 3.1 cc/min; H₂, 842 cc/min (PH₃ inlet), 842 cc/min (source HCl inlet)

One aspect of these reactions which has not received attention in this type of study is the variation of results observed. Fairhurst et al⁵ have suggested that

these reactions involve free radicals that participate in chain reactions. Surfaces are known to play an important role in these reactions¹⁹ and are probably the source of the variation. Various parameters, for example, temperature, moisture, gas flow and so on, can influence the surface of the reactor, consequently affecting the results. The results presented in this investigation are consistent for the variables studied with this reactor.

3.2 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) analyses were performed on the as-grown epitaxial InP layers and the InP substrates. For the epitaxial InP layers, the results showed significant intensities for surface oxygen and carbon indicative of surface contamination. Oxygen is completely absent at the 20 Å level while carbon disappears between 20 to 50 Å. The oxygen is probably present as InPO_4 , with smaller amounts²⁰ of In_2O_3 . Carbon may possibly arise from a hydrocarbon contamination.

The AES analyses of the InP substrates showed results similar to those of the epitaxial layers; however, there was also a small amount of nickel present on the surface, and the carbon is only present within 10 Å of the surface.

3.3 Electrical Properties of VPE-Hydride Grown InP

The electrical properties of three InP samples displaying good morphology are presented in Table 1. These results were calculated from the resistivity and Hall measurements obtained with the van der Pauw technique. The carrier concentration has been associated with silicon transported from the quartz reactor.²¹ These results compare favorably with those obtained by Hyder,²² and Olsen²³ with the $\text{PH}_3/\text{In}/\text{HCl}/\text{H}_2$ system. Based on the calculations of Walukiewicz et al.,²⁴ the data show that the compensation ratios at 77 K for the three samples, EQ-8, EQ-14, and EQ-52, are 0.5, 0.7 and 0.5, respectively. Very recently, however, Zinkiewicz et al.²⁵ have reported average mobilities of $36,000 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ (with a high of $56,100 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$) for InP grown with the VPE-hydride method, using very low H_2 carrier flow rates.

The present study shows that the use of a continuous HCl etch improves the electrical properties of the epitaxial InP layers grown by the VPE-hydride technique. At the present time, studies with the VPE-chloride method illustrate that this technique is capable of producing epitaxial InP with lower carrier concentrations and higher mobilities⁵ ($n = 10^{14} \text{ cm}^{-3}$ and $\mu = 100,000 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at 77 K).

(Due to the large number of references cited above, they will not be listed here. See References, page 19.)

Table 1. Electrical Properties of VPE-InP With Good Morphology

Run Number	Source HCl (sccm)	PH ₃ (sccm)	HCl in PH ₃ (sccm)	n (77 K) cm ⁻³	μ (77 K) cm ² V ⁻¹ sec ⁻¹
EQ-8	5.3	3.1	1.5	1.4×10^{15}	27,340
EQ-14	5.3	3.1	1.3	9.6×10^{14}	24,055
EQ-52	5.3	15.9	0.8	2.6×10^{15}	19,512

4. CONCLUSION

The effect of a continuous etch of HCl in the mixing zone of the VPE-hydride reactor on the morphology and electrical properties of epitaxial InP has been studied. Epitaxial InP layers were obtained with good morphology when the flow rate of the HCl in the mixing zone was in the range between 0.8 and 1.8 cc/min. The electrical properties of these InP structures proved to be comparable to those reported by others. These studies indicate that epitaxial layers of InP of good morphology can be obtained by using a continuous etch in the VPE-hydride reactor.

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3. Olsen, G.H., and Zamerowski, T.J. (1980) Crystal Growth and Properties of Binary, Ternary and Quaternary (In,Ga) (As,P) Alloys Grown by the Hydride Vapor Phase Epitaxy Technique, in Progress in Crystal Growth and Characterization, Vol. II, Pergamon Press Ltd., London, pp. 309-375.
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