Acknowledgment

The authors would like to thank Dr. P. Zanzucchi and W. Frenchu for their IR absorption measurements.

Manuscript submitted June 6, 1986; revised manuscript received Aug. 26, 1986.

RCA Laboratories assisted in meeting the publication costs of this article.

REFERENCES

1. J. E. Lawrence and H. R. Huff, in "VLSI Electronics Microstructure Science," Vol. 5, N. C. Einspurich, Editor, p. 55, Academic Press, New York (1982).
2. L. Jastrzebski, *IEEE Trans. Electron Devices*, **ED-29,** 475 (1982).
3. L. Jastrzebski, R. Soydan, B. Goldsmith, and J. T. McGinn, *This Journal*, **131,** 2944 (1984).
4. J. Dishman, S. E. Hasaka, R. B. Marcus, D. P. Murarka, and T. T. Sheng, *J. Appl. Phys.*, **50,** 2689 (1979).
5. S. P. Murarka, T. Seidel, J. Dalton, J. Dishman, and M. Reed, *This Journal*, **127,** 716 (1980).
6. L. Jastrzebski, R. Soydan, J. T. McGinn, N. Armour, R. Kleppinger, M. Blumenfeld, G. Gillespie, B. Goldsmith, W. N. Henry, and S. Vecrumba, in "Reduced Temperature Processing for VLSI," A. Reif and G. R. Srinivasan, Editors, p. 405, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1986).
7. L. Jastrzebski, P. A. Levine, W. A. Fischer, A. D. Cope, E. D. Savoye, and W. N. Henry, *This Journal*, **128,** 885 (1981).
8. M. Suezawa, K. Sumino, and I. Yonenaga, *Phys. Status Solidi A*, **51,** 217 (1979).
9. D. Thebault and L. Jastrzebski, *RCA Rev.*, **41,** 592 (1980).
10. L. Jastrzebski, G. W. Cullen, W. N. Henry, and S. Vecrumba, Paper 418 presented at The Electrochemical Society Meeting, Las Vegas, NV, Oct. 13-18, 1985.
11. K. Sumino, in "Semiconductor Silicon 1981," H. R. Huff, R. J. Kriegler, and Y. Takeishi, Editors, p. 208, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1981).
12. Y. Kondo, in "Semiconductor Silicon 1981," H. R. Huff, R. J. Kriegler, and Y. Takeishi, Editors, p. 220, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1981).
13. T. Abe, K. Kikuchi, S. Shirai, and S. Muraoka, in "Semiconductor Silicon 1981," H. R. Huff, R. J. Kriegler, and Y. Takeishi, Editors, p. 54, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1981).
14. K. Sumino, I. Yomegawa, M. Imai, and T. Abe, *J. Appl. Phys.*, **54,** 5016 (1983).
15. T. Abe, T. Masui, H. Haraota, and J. Chikawa, in "VLSI Science and Technology/1985," W. M. Bullis and S. Broydo, Editors, p. 543, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1985).
16. K. Sumino, I. Yomegawa, M. Imai, and T. Abe, *J. Appl. Phys.*, **54,** 5016 (1983); Y. Tokumaru, H. Okushi, T. Masui, and T. Abe, *Jpn. J. Appl. Phys.*, **21,** L443 (1982).
17. H. J. Stein, *Appl. Phys. Lett.*, **43,** 296 (1983).
18. H. J. Stein, in "Thirteenth International Conference on Defects in Semiconductors," L. C. Kimerling and J. M. Parsey, Jr., Editors, p. 839, The Metallurgical Society of American Institute of Mining, Metallurgical and Petroleum Engineers, Warrendale, PA (1985).
19. A. R. Kirkpatrick, *et al., IEEE Trans. Electron Devices*, **ED-24,** 429 (1977).
20. C. Nauka, M. Gorsky, J. Lagowski, and H. C. Gatos, *J. Appl. Phys.*, In print; Presented at the Electronic Materials Conference, Boulder, CO, June 1985.

The Effect of PH_3 Pyrolysis on the Morphology and Growth Rate of InP Grown by Hydride Vapor Phase Epitaxy

R. F. Karlicek, Jr., D. Mitcham, J. C. Ginocchio, and B. Hammarlund[1]

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

ABSTRACT

The incomplete pyrolysis of PH_3 is shown to have a significant effect on the growth rate and morphology of InP grown by hydride vapor phase epitaxy. Using ultraviolet absorption spectroscopy to determine the extent of PH_3 pyrolysis, the growth rate of InP is shown to increase with decreasing PH_3 pyrolysis. Incomplete PH_3 pyrolysis is also shown to dramatically increase the formation of growth hillocks on <100> InP epitaxial layers. The use of various metal catalysts to expedite PH_3 pyrolysis to eliminate hillock formation during InP growth is described, and a qualitative model of PH_3 induced hillock growth is presented.

Hydride vapor phase epitaxy (VPE) is an important technique for the growth of InP and lattice matched alloys in the system $In_xGa_{1-x}As_yP_{1-y}$ (1). The technique derives its name from the use of the hydrides AsH_3 and PH_3 as sources for the group V elements in these materials. While both hydrides are unstable at temperatures typically used for hydride VPE, PH_3 pyrolysis is much slower than AsH_3 pyrolysis (2), suggesting that PH_3, as well as its pyrolysis products P_2 and P_4, can be present at sufficiently high concentrations in the growth region of the reactor to participate in the growth process.

Thermal decomposition of PH_3 under VPE growth conditions has not been studied in detail in the recent literature. Spectroscopic (2) and mass spectrometric (3) investigations suggest that PH_3 pyrolysis is usually incomplete, but the effect of unpyrolyzed PH_3 on the growth of InP has not been reported. Early studies (4, 5) of PH_3 pyrolysis kinetics show that pyrolysis occurs heterogeneously (*i.e.*, at surfaces), and that the absolute rate of decomposition is dependent upon the type and prior history of the surface involved.

This report discusses the effect of PH_3 pyrolysis on the growth rate and morphology of InP epitaxial layers. Using ultraviolet (UV) absorption spectroscopy (6) to determine the concentrations of PH_3, P_2, and P_4 *in situ* just prior to layer growth, reduced PH_3 pyrolysis is shown to increase the InP growth rate and reduce the quality of the surface morphology of <100> InP epitaxial layers. More specifically, the incomplete pyrolysis of PH_3 results in extensive hillock formation on <100> InP epitaxial layers. By using various metal catalysts, the pyrolysis of PH_3 can be expedited to the thermodynamic limit, allowing routine growth of hillock-free InP layers.

The effect of PH_3 on the InP growth rate is qualitatively explained in terms of the thermodynamics of growth from PH_3, P_2, or P_4 species. A simple model is also presented for the growth of hillocks caused by PH_3, and is supported with some general observations about hillock growth on <100> InP epitaxial layers. The possible ramifications of incomplete PH_3 pyrolysis on repro-

---

[1] Present address: Institute of Microwave Technology, Stockholm, Sweden.

ducible growth of InP and related quaternary compounds are also discussed.

Experimental

Studies of the effect of PH_3 decomposition on InP growth were conducted in two different reactor systems. The hydride VPE reactor used for UV *in situ* monitoring of PH_3 pyrolysis has been described elsewhere (6). The flows of all input gases were selected using electronic mass flow controllers from mixtures of 5% HCl/H_2 and 2% PH_3/H_2. The reactor design permitted the variation of the extent of PH_3 pyrolysis without altering $In_{(l)}$ source conditions by using the arrangement shown in Fig. 1. In order to expedite PH_3 pyrolysis, catalysts fabricated from W, Mo, or Ta wire were placed in the center of PH_3 source tube. Specific amounts of PH_3 decomposition could be selected by controlling the relative amounts of input PH_3 flowing around or through the catalyst. The degree of pyrolysis was determined from UV optical absorption measurements at 185, 203, and 230 nm using previously reported absorption data for PH_3, P_2, and P_4 at these wavelengths (6). These measurements were made prior to the addition of InCl to the growth region because strong absorption by InCl below 200 nm precluded detection of PH_3 and P_2 during growth. The addition of InCl to the growth region was assumed not to influence the extent of PH_3 pyrolysis.

All growth experiments were performed on <100> InP LEC substrates which were hand polished just prior to growth with a 1% Br-methanol solution. Samples were then placed in the reactor and inserted to the growth position with PH_3 flowing at the conditions selected for that growth experiment. After determining the extent of PH_3 pyrolysis during the preheat period (~5 min), the substrate was etched by combining a small flow of HCl with the PH_3 used for preservation. The growth was initiated by passing HCl through the $In_{(l)}$ source region. The total flow rate in this reactor was 2100 sccm with input HCl and PH_3 partial pressures of 3.9×10^{-3} and 2.7×10^{-3} atm, respectively. The InP growth temperature was 700°C. For most runs, no evidence of extraneous deposition of InP on the reactor walls (determined optically) was observed.

Some InP growth runs were performed in an unmonitored VPE single barrel reactor similar to that designed by Johnston and Strege.[2] The reactor was used to grow n-p-n InP structures used in the fabrication of V-groove lasers (7) and permitted growth on two substrates simultaneously. This facilitated comparison of substrate preparation techniques on the growth of hillocks on <100> InP surfaces. For most experiments, final surface preparation consisted of a sequential degreasing in boiling chloroethane, acetone, and methanol followed by a 3 min dip in H_2SO_4:H_2O_2:H_2O in the ratio 5:1:1.

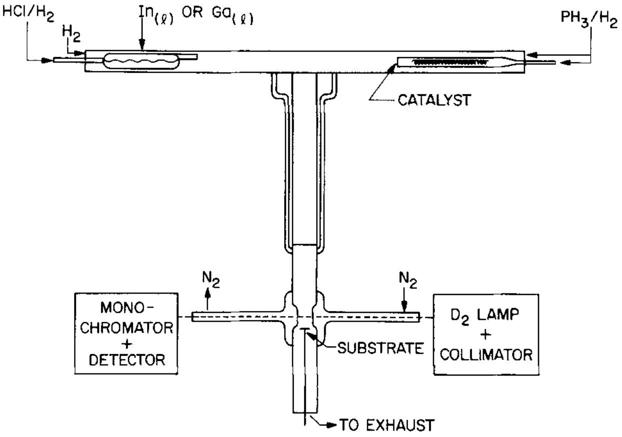

Fig. 1. Schematic of the optically monitored VPE reactor used to study variations in PH_3 decomposition and their effect on InP epitaxial growth.

The growth sequence in this reactor consisted of a 5 min preheat in a PH_3/H_2 ambient, an *in situ* etch using HCl and PH_3, and the growth of n-p-n junctions using H_2S and elemental zinc as the n- and p-type dopants, respectively. The total flow rate was 6450 sccm with typical input HCl and PH_3 partial pressures of 1.5×10^{-3} and 3.8×10^{-3} atm, respectively. The InP growth temperature was 695°C. The growth runs were performed both with and without a W catalyst in the input PH_3 source region. While the extent of pyrolysis could not be measured in this reactor, increased pyrolysis efficiency was inferred from the substantial increase in white P_4 in the reactor exhaust line whenever the pyrolysis catalyst was in use.

Results and Discussion

Initial efforts to grow InP in the unmonitored reactor system invariably produced epitaxial layers with extensive hillock formation. Some general observations regarding hillock growth on <100> InP which led to the consideration of incomplete PH_3 pyrolysis as a possible cause of hillock formation are described. This is followed by spectroscopic monitoring results which conclusively show the correlation of InP growth rate and hillock formation to the extent of PH_3 pyrolysis. An evaluation of various metal catalysts for expediting PH_3 pyrolysis is also discussed. Finally, the observed correlation between InP growth rate and PH_3 pyrolysis is explained using a simple thermodynamic model, and a mechanism for PH_3 induced hillock formation is presented.

Observations regarding hillock formation.—Initial experiments on InP growth in which no effort was made to increase PH_3 pyrolysis yielded InP epilayers containing a high density of hillocks (from 1 to ~100/cm²). Occasionally, very broad (100 μm diam), low (1-2 μm high) hillocks (referred to as mounds) were observed instead of, or in addition to, hillocks. In most cases, the hillock density varied with position on the wafer surface and was reproducible from run to run for the same reactor operating conditions (saturation, flow rate, and temperature). The planar growth rate (determined from a stained cross section between hillocks) was usually the same for high and low hillock density regions of the same wafer. Variations in the III/V ratio between 0.4 and 1.3 (with $P_{PH_3} + P_{InCl}$ = constant) did not significantly affect the hillock density. The regions of high hillock density could be moved to a different portion of the wafer by changing the position of the sample in the growth zone (*i.e.*, the distance from the $InCl/PH_3$ mixing baffle), or by changing the relative flow rates in the reactor source regions under conditions of constant saturation and total flow rate in the growth region.

These observations suggest that hillock formation is correlated to variations in gas phase stoichiometry across the wafer surface. Such variation could be caused by local variations in the III/V ratio due to poor mixing of $InCl/H_2$ and PH_3 (P_2, P_4)/H_2 gas streams from the reactor source region, but this explanation is not consistent with the observation of a uniform planar growth rate across the sample independent of the local hillock density.

Experiments performed to examine the effect of surface preparation on hillock formation showed that Br-methanol and degreasing/etching surface preparation techniques are essentially equivalent with regard to hillock density and InP planar growth rate. This equivalence is probably due to the use of an *in situ* etch step just prior to layer growth for both types of substrate preparation. Regions of contamination apparently caused by the tweezers used to load the wafers were occasionally observed to cause small regions of high hillock density near the wafer edge, but no other surface preparation effects could be found to correlate to the occurrence or density of hillocks.

The growth of n-p-n InP structures was useful for determining the point during growth at which hillock growth started or stopped. Figure 2 shows two hillocks with the corresponding stained cross sections showing

---

[2] This reactor is described in Ref. (1).

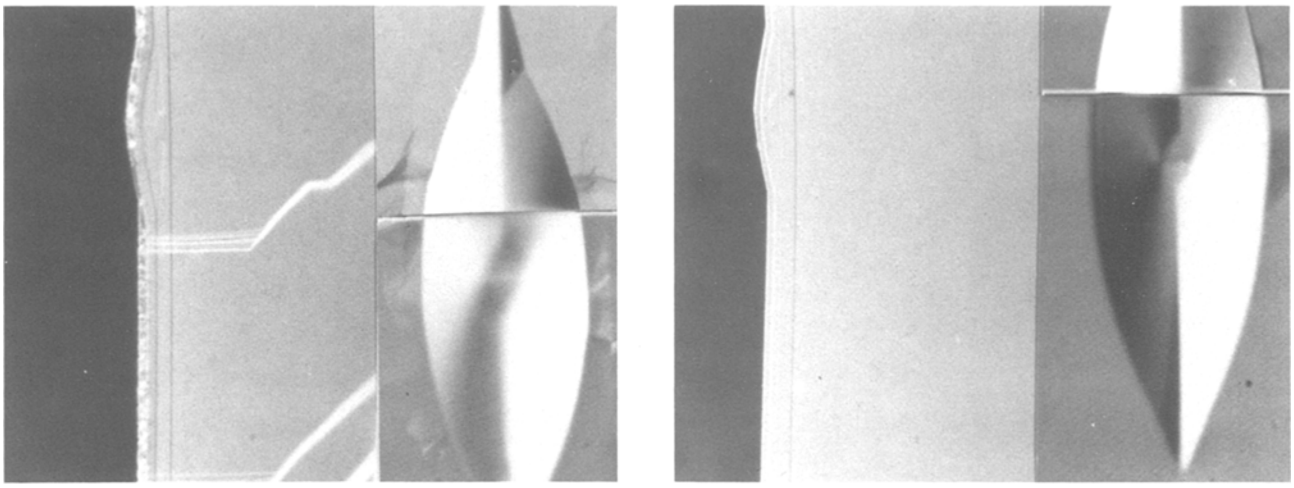

Fig. 2. Normarski contrast micrographs of hillocks formed during the growth of n-p-n InP epitaxial layers. The top view and cleaved/stained edge view are shown for two hillocks formed at different times during epilayer growth: (a, left) during the n-buffer layer; and (b, right) during the p-InP layer.

the n-p-n structure at the hillock sites. Both hillocks are of comparable size and on the same wafer. Figure 2a shows a hillock which grew during the first-to-grow n-InP layer, and is covered uniformly by the growth of subsequent p- and n-layers, while the hillock cross section shown in Fig. 2b reveals hillock formation initiated during the p-InP layer growth. Hillocks formed during the growth of the final n-InP layer were also observed. This shows that hillock growth can be initiated during epi layer growth and need not start at the VPE-substrate interface.

The uniform InP coverage of the hillocks shown in Fig. 2 by InP epi layers of different doping shows that hillocks, once started, do not continue to grow for the rest of the growth run. This is consistent with the mechanism proposed by Joyce and Mullin (8) for GaAs chloride VPE in which hillock growth is initiated by the condensation of Ga droplets on the surface, forming hillocks via vapor-liquid-solid (v-l-s) (9) growth. The same mechanism has also been used to explain hillock growth observed in InP chloride VPE (10). In this mechanism, the hillock size would be determined by the size of the metal droplet on the surface, and hillock growth would cease once the free metal on the surface is consumed. Uniform layer growth covering the hillock, as observed in Fig. 2, would continue after hillock growth.

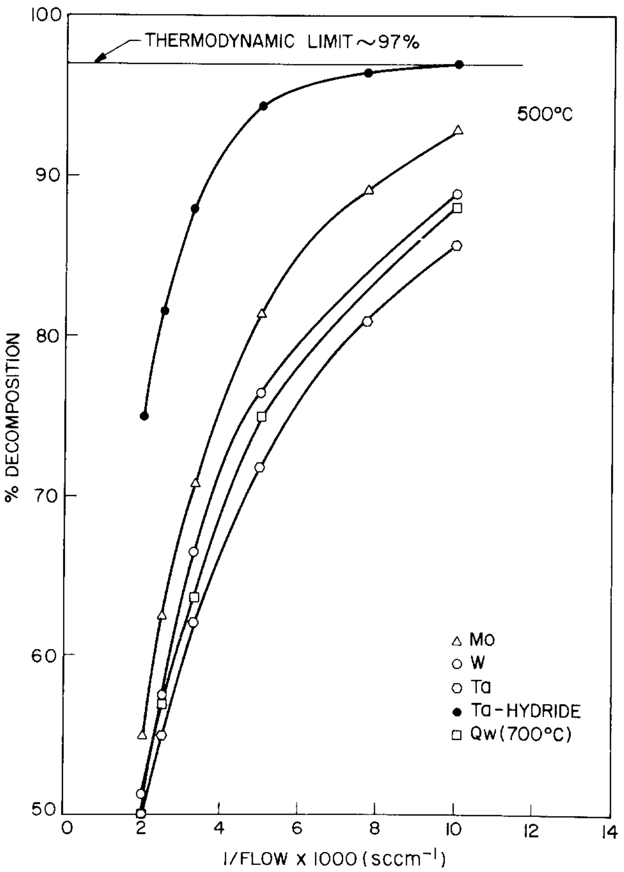

Fig. 3. A comparison of the relative rates of PH_3 pyrolysis for W, Mo, Ta, and Ta_xH catalysts at 500°C. The rate measured for quartz wool at 700°C with ~5 times the available surface area is shown for comparison.

PH_3 pyrolysis and InP growth.—Catalytically expedited PH_3 pyrolysis.—In order to study the effect of PH_3 pyrolysis on InP growth spectroscopically, it was necessary to expedite the pyrolysis catalytically. Preliminary optical measurements without a catalyst in the PH_3 source region revealed that PH_3 pyrolysis reached only 80% of the thermodynamic limit (~96-98%), and that the exact amount of pyrolysis obtained depended markedly on the prior thermal history of the reactor. The catalytic behavior of W and Mo (5) was studied previously, but not under conditions typically encountered in hydride VPE. The catalytic activity of Ta was also studied on the basis of its use as a pyrolysis catalyst in molecular beam epitaxy (MBE) (11). A comparison of the extent of PH_3 pyrolysis at 500°C as a function of the PH_3 residence time in the catalyst tube (expressed as the inverse of the flow rate) for the various metals is shown in Fig. 3. This lower temperature was selected to illustrate variations in the catalytic activity of various metals over a wide range of PH_3 residence times. Data for quartz wool at 700°C is also shown. The quartz wool surface area was about 5 times larger than used for the metal catalysts tested, demonstrating the high catalytic activity of the metal relative to SiO_2 for the pyrolysis of PH_3.

Two curves for Ta are shown in Fig. 3. It was observed that after heating Ta to ~700°C in H_2, the catalytic activity was significantly higher. Unlike W or Mo, Ta is known to form a hydride under these conditions (12). Examination of the Ta following the pyrolysis experiments revealed that the Ta wire initially present had crumbled into small pieces of what was assumed to be TaH_x ($x < 0.5$). It was not possible to determine if the increase in catalytic activity was due to the formation of the hydride, the increase in the available surface area due to hydride formation, or some combination of the two. Although Ta exhibits the highest catalytic activity for PH_3 pyrolysis, the powdering after hydride formation made it difficult to prevent Ta from getting blown out of the catalyst tube. For the InP growth experiments discussed below, W was used as a catalyst.

In all measurements, the PH_3 decomposition kinetics were found to be first order in P_{PH_3} (*e.g.*, the rate of pyrolysis is proportional to the PH_3 concentration), in agreement with previous studies (4, 5). This suggests that the use of a catalyst might be avoided by using larger values of input P_{PH_3} at lower flow rates (but constant total flow in the growth region). While the use of higher values of P_{PH_3} at proportionally lower input flow rates produces the same phosphorus mole fraction in the growth region, the faster decomposition rate at higher input P_{PH_3} values, as well as the longer residence time in the reactor source region may permit pyrolysis to the thermodynamic limit without the use of a catalyst.

Effect of PH_3 pyrolysis on InP hillock growth.—The first set of experiments designed to study the effect of PH_3 pyrolysis on hillock formation was conducted in the unmonitored VPE reactor. Variations of the source temperature between 640° and 850°C were found to have no pronounced effect on either the hillock density or the InP growth rate (8-14 μm/h depending on gas phase saturation). The reactor design employed a narrow (0.7 cm id) PH_3 inlet tube in this region of the furnace, and large variations in the extent of PH_3 pyrolysis for this range of source temperatures were not expected because of the short PH_3 residence time (<0.5s) in the PH_3 inlet tube. By increasing the temperature of the reactor mixing zone to ~1100°C to increase PH_3 pyrolysis, hillock-free surfaces and an InP growth rate of ~4 μm/h were obtained. The growth rate was reduced from that obtained without the high temperature mixing zone for equivalent gas phase saturation. Although hillock-free growth was obtained initially, the formation of hillocks began to occur after several runs, accompanied by an increase in the InP growth rate, suggesting a gradual reduction in the catalytic activity of the reactor walls for PH_3 pyrolysis. Similar aging effects were reported for PH_3 pyrolysis in a quartz vessel by Hinshelwood and Topley (4).

Subsequent experiments employing a tungsten wire catalyst yielded essentially hillock-free wafers at an InP growth rate of ~5 μm/h. The gradual increase with increasing number of runs in both hillock density and growth rate using the tungsten catalyst for PH_3 pyrolysis was not observed. Measurement of the background carrier concentration for nominally undoped InP layers grown with the tungsten catalyst gave values of $n_D - n_A$ comparable to those obtained in the absence of the catalyst ($5\text{-}9 \times 10^{15}$ cm^{-3}).

For InP growth experiments in the monitored reactor, the relationship between InP growth rate, surface morphology, and the extent of PH_3 pyrolysis could be quantified, as shown for three consecutive growth runs in Table I. When PH_3 pyrolysis was at the thermodynamic limit, the surface morphology was quite good and almost always free of growth hillocks. As the extent of pyrolysis was reduced slightly hillock growth was rather severe (~1000 hillocks/cm^2). The growth rates, also shown in Table I, corroborate the general trends observed for InP growth in the unmonitored VPE reactor system.

The effect of incomplete PH_3 pyrolysis on the growth rate of InP may be explained by examining the relative equilibrium constants governing the deposition of InP from PH_3, P_2, and P_4 as shown in Table II (13). Since the growth of InP is far more favorable using PH_3 than either P_2 or P_4, it may be reasonable to expect a higher growth rate when PH_3 decomposition is incomplete. Since kinetic factors influencing the growth of InP from PH_3, P_2, and P_4 are not known, a more detailed thermodynamic treatment is not warranted.

The mechanism of PH_3 induced hillock formation.—Any mechanism of hillock growth caused by incomplete PH_3 pyrolysis must rely on a detailed understanding of the InP growth process at a molecular level. While little is known about the details of InP growth at the surface/vapor interface, the growth of GaAs by VPE has been extensively studied (14-16). In the following discussion, a four-step mechanism is proposed for the growth of hillocks on <100> InP surfaces due to incomplete PH_3 pyrolysis, with support drawn from the details of the GaAs growth process as well as observations of hillock growth on InP.

Table I. The dependence of hillock density and growth rate on the extent of PH_3 pyrolysis for three consecutive InP growth runs. The extent of PH_3 pyrolysis was determined using *in situ* UV absorption spectroscopy as described in Ref. (6)

PH_3 decomposition (%)	Growth rate (μm/h)	Hillock density (cm^{-2})
70.2	15.8	9200
86.7	13.0	1000
97.9	9.0	0

Table II. Chemical equilibrium constants for the deposition of InP from the reaction of InCl with PH_3 P_2, and P_4

Reaction	K_{eq}[a] (700°C)
$InCl + PH_3 \rightarrow InP + HCl + H_2$	163
$InCl + \frac{1}{2}P_2 + \frac{1}{2}H_2 \rightarrow InP + HCl$	2.74
$InCl + \frac{1}{4}P_4 + \frac{1}{2}H_2 \rightarrow InP + HCl$	0.238

[a] Calculated from data in Ref. (13).

The proposed hillock growth mechanism is shown schematically in Fig. 4a-d. In Fig. 4a, InCl is chemisorbed on the <100> InP surface, similar to that found for conventional GaAs growth (15). The continued growth requires the formation of atomic hydrogen for removal of chlorine as HCl, or the direct desorption of HCl by molecular H_2 as recently proposed (16). The removal of chlorine as HCl, which includes the step of atomic hydrogen formation, is generally regarded as the rate-limiting step in the GaAs growth process. In the case of incomplete PH_3 pyrolysis, atomic hydrogen can be supplied more rapidly from PH_3 decomposing at the growth surface than by dissociation of molecular H_2, and

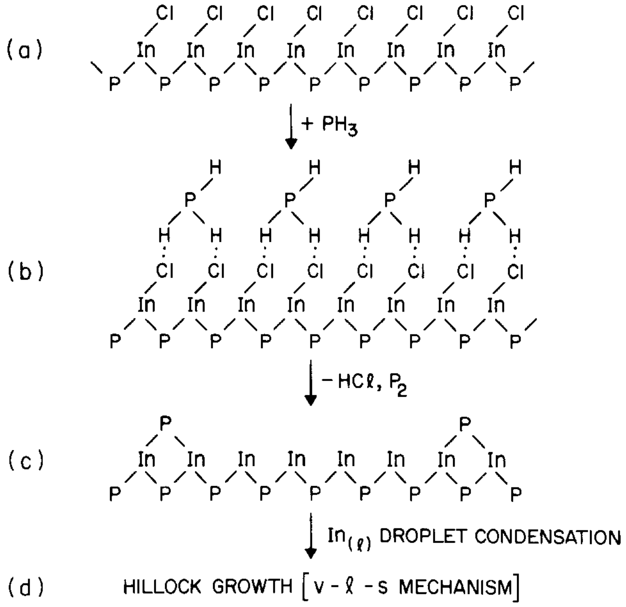

Fig. 4. Schematic diagram of the proposed mechanism of PH_3 induced hillock growth on <100> InP. (a) The initial growth surface is saturated with chemisorbed InCl by analogy to proposed mechanism for GaAs growth. (b) PH_3 pyrolyzes at the Cl-saturated surface, forming HCl, which desorbs to leave the In-rich region shown in (c), which subsequently condenses to form an $In_{(l)}$ droplet resulting in hillock formation (d).

can compete with the conventional growth mechanism postulated for GaAs. This is consistent with the proposed mechanism of growth rate enhancement for InP when PH_3 is added to a trichloride (PCl_3) reactor system (17). In Fig. 4b, excess PH_3 in the vapor reacts with adsorbed InCl at the InP surface to form HCl. While removal of adsorbed chlorine by PH_3 may proceed via an intermediate state such as that shown in Fig. 4b, it is only intended to show that adsorbed chlorine is removed by PH_3 pyrolysis at the growth interface at a rate faster than the addition of phosphorus atoms required for continued layer growth. This is particularly true if some of the phosphorus from PH_3 reacts to form P_2 and does not subsequently participate in the growth process. The resulting surface, shown in Fig. 4c, contains indium-rich regions which are assumed to be unstable with regard to hillock formation.

Consistent with a previously proposed mechanism of hillock growth on GaAs involving condensation of $Ga_{(l)}$ droplets at the surface (8), the indium-rich surface in Fig. 4c may nucleate $In_{(l)}$ droplet condensation from the gas phase via

$$InCl_{(g)} + \frac{1}{2}H_2 \rightarrow In_{(l)} + HCl_{(g)}$$

or by coalescing surface indium atoms, or both. Hillock growth proceeds until the available indium is consumed and the higher growth rate planes exposed when the hillock is nucleated are terminated by lower growth rate facets which appear as hillock growth proceeds. The indium-rich surface regions shown in Fig. 4c may also react with P_4 or P_2 to continue epitaxial growth, or readsorb HCl from the gas phase to form the original chlorine stabilized surface shown in Fig. 4a.

The proposed mechanism for hillock growth is consistent with generally accepted techniques used to reduce hillock formation. For InP growth, the addition of extra HCl has been found to reduce hillock formation on <100> growth surfaces (18). Additional HCl would suppress HCl desorption from the growth surface reducing the extent of indium-rich regions which may tend to form hillocks. Growth on nominally misoriented (2°-6° off of <100>) substrates has also been found to reduce the tendency for hillock formation in InP (19) as well as GaAs (20). Since growth on misoriented substrates results in a higher growth rate by providing a large number of kinetically favored step sites for layer growth, hillock growth is suppressed because the higher conventional growth rate would also reduce the extent of indium-rich surface regions available for hillock formation.

Conclusion

The effect of incomplete PH_3 pyrolysis on the morphology and growth rate of <100> InP epitaxial layers has been studied using *in situ* optical absorption spectroscopy to measure the extent of PH_3 pyrolysis in the reactor growth region. Increasing PH_3 decomposition was found to reduce the InP growth rate and improve the surface morphology. The most drastic effect of incomplete PH_3 pyrolysis was found to be the formation of hillock defects. The same correlation between InP growth rate, hillock formation, and PH_3 pyrolysis was also found for the growth of n-p-n InP structures in an unmonitored reactor. Hillocks grown on these structures were found to start at various points during epitaxy without correlation to various substrate preparation techniques.

Elimination of hillocks is favored by complete PH_3 pyrolysis, which requires the use of W, Mo, or Ta catalysts installed in the reactor source region. Without metallic catalysts, PH_3 pyrolysis was observed to depend upon the thermal history of the reactor, with pyrolysis gradually becoming less complete as the time spent by the reactor at normal operating temperatures increased. For undoped InP epilayers, the addition of the W catalyst was found to have no effect on the residual carrier concentration, and for n-p-n layers, no effect on device performance was observed. The effect of incomplete PH_3 pyrolysis on the InP growth rate can be qualitatively understood in terms of the relative thermodynamics of InP growth from PH_3, P_2, or P_4. Failure to attain equilibrium PH_3, P_2, and P_4 concentrations reproducibly introduces additional uncertainty in hydride VPE reactor operation, and should be avoided to obtain reproducible growth of InP and related quaternary alloys.

Acknowledgments

The authors would like to thank S. N. G. Chu for many helpful discussions and W. D. Johnston, Jr., for his advice and encouragement.

Manuscript submitted Aug. 1, 1986; revised manuscript received Sept. 2, 1986.

AT&T Bell Laboratories assisted in meeting the publication costs of this article.

REFERENCES

1. G. H. Olsen, in "GaInAsP Alloy Semiconductors," T. P. Pearsall, Editor, John Wiley and Sons, Inc., London (1982).
2. V. M. Donnelly and R. F. Karlicek, *J. Appl. Phys.*, **53,** 6399 (1982).
3. V. S. Ban, *This Journal*, **118,** 1473 (1971).
4. C. N. Hinshelwood and B. Topley, *J. Chem. Soc.*, **125,** 393 (1924).
5. H. W. Melville and H. L. Roxburgh, *ibid.*, **264,** 586 (1933).
6. R. F. Karlicek, Jr., B. Hammarlund, and J. Ginocchio, *J. Appl. Phys.*, **60,** 794 (1986).
7. D. P. Wilt, R. F. Karlicek, K. E. Strege, W. C. Dautremont-Smith, N. K. Dutta, E. J. Flynn, W. D. Johnston, Jr., and R. J. Nelson, *J. Appl. Phys.*, **56,** 710 (1984).
8. B. D. Joyce and J. B. Mullin, *Solid State Commun.*, **4,** 463 (1966).
9. R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.*, **4,** 89 (1964).
10. D. J. Aschen, D. A. Anderson, N. Apsley, and M. T. Emeny, *J. Cryst. Growth*, **60,** 225 (1982).
11. M. B. Panish and S. Sumski, *J. Appl. Phys.*, **55,** 3571 (1984).
12. K. M. Mackay, "Hydrogen Compounds of the Metallic Elements," pp. 80-83, E. and F. N. Spon, Ltd., London (1966).
13. D. W. Shaw, *J. Phys. Chem. Solids*, **36,** 111 (1975).
14. D. W. Shaw, *J. Cryst. Growth*, **31,** 130 (1975).
15. J. B. Theeten, L. Hollan, and R. Cadoret, "Crystal Growth and Materials," E. Kaldis and H. J. Scheel, Editors, Ch. I.6, North Holland Publishing Co., Amsterdam (1977).
16. W. Seifert, S. Schwetlick, J. Reinhold, and E. Butter, *J. Cryst. Growth*, **66,** 333 (1984).
17. I. H. Goodridge and N. B. Hasdell, in "GaAs and Related Compounds," B. deCremoux, Editor, p. 205, Institute of Physics Conference Series No. 74, London (1984).
18. T. E. Erstfeld and K. P. Quinland, *J. Electron. Mater.*, **11,** 647 (1982).
19. L. M. Zinkiewicz, T. J. Roth, B. J. Skromme, and G. E. Stillman, in "Gallium Arsenide and Related Compounds, 1980," pp. 19-28, Institute of Physics Conference Series No. 56, London (1980).
20. J. V. DiLorenzo, *J. Cryst. Growth*, **17,** 189 (1972).