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The Preparation and Properties of Vapor-Deposited Epitaxial $\text{InAs}_{1-x}\text{P}_x$ Using Arsine and Phosphine

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ABSTRACT

Single crystalline $\text{InAs}_{1-x}\text{P}_x$ layers have been prepared by a vapor-phase growth technique previously used to prepare very high-quality $\text{GaAs}_{1-x}\text{P}_x$. These $\text{InAs}_{1-x}\text{P}_x$ alloys exhibit electron mobilities equivalent to the highest yet reported for this system. Extensive electron mobility data is reported for the alloys at 77°K. At this temperature, a mobility value of 120,000 $\text{cm}^2/\text{v-sec}$ was measured for InAs, which is slightly higher than previously reported. Vegard's law is obeyed over the entire composition range. Both n- and p-type doping has been achieved during vapor growth to provide a broad range of electrical resistivities and p-n junctions.

$\text{InAs}_{1-x}\text{P}_x$ alloys have a broad range of band gaps and electron mobilities. Consequently, they have potential advantage for a number of device applications. These include infrared emitting (1) and detecting devices, utilizing their low energy band gaps, and devices operating at high frequencies, which can take advantage of their high mobilities. Although results (2-5) have been reported pertaining to improving the preparation and properties of melt-grown crystals, very little work has involved the vapor-phase growth of these alloys.

Recently, a vapor phase growth method (6) has been described for the growth of $\text{GaAs}_{1-x}\text{P}_x$ alloys, and the high purity, homogeneity, and crystalline perfection of the crystals prepared by this technique has been demonstrated. With this growth method, Ga is transported as its subchloride via a reaction with HCl gas, and AsH_3 and PH_3 serve as the sources of the group V elements. As a logical extension of this growth technique, a simple substitution of In for the Ga has permitted the preparation of $\text{InAs}_{1-x}\text{P}_x$ single crystals having very good electrical properties and crystallinity. In addition, both n- and p-type doping has been achieved, and multilayer structures have been prepared.

Experimental

Apparatus and materials.—The apparatus, shown schematically in Fig. 1, is essentially identical to that described previously (6) with the exception that the source Ga is replaced by In. It consists principally of a straight tube through which the pertinent vapors pass. A large bore stopcock separates the growth region from a forechamber which may be purged independently to facilitate insertion and withdrawal of the specimens without contaminating the system. HCl gas, AsH_3 , PH_3 , and H_2Se (which serves as the n-type dopant source) are all monitored into the apparatus by precision valves and flowmeters. P-type doping is achieved by vaporizing metallic Zn in a heated side-arm and transporting the vapors into the deposition zone with H_2 carrier gas.

With the exception of the use of In,¹ and $\langle 100 \rangle$ -oriented InAs single crystalline substrates,² the ma-

terials employed in this study are as described previously (6). The InAs substrates were mechanically polished to a flat, mirror-smooth finish, and then chemically polished in a solution of 2% by volume of bromine in methanol. Typical substrate dimensions were about 2 cm^2 in area and 0.5 mm thick.

Procedure.—The growth procedure also closely follows that described previously (6). Freshly etched substrates are inserted in the growth chamber and heated in hydrogen at a rate of about 20°C/min. When the substrate temperature reaches 600°C, the AsH_3 flow is started in order to provide an arsenic atmosphere to stabilize the substrate surface. When the final operating temperatures are reached, the HCl flow over the In is started and the epitaxial deposition of InAs occurs. The flow of PH_3 is then initiated and slowly increased to produce a final gas phase mixture of AsH_3 and PH_3 appropriate to the desired alloy composition. The dependence of the alloy composition on the concentration of PH_3 in the AsH_3 - PH_3 mixture is presented in Fig. 2. By slowly increasing the PH_3 flow, a region is introduced which is graded in composition from InAs at the substrate to the selected alloy composition. This graded region, which has been as thick as 50 μ for phosphorus-rich alloys, is included to minimize strain arising from

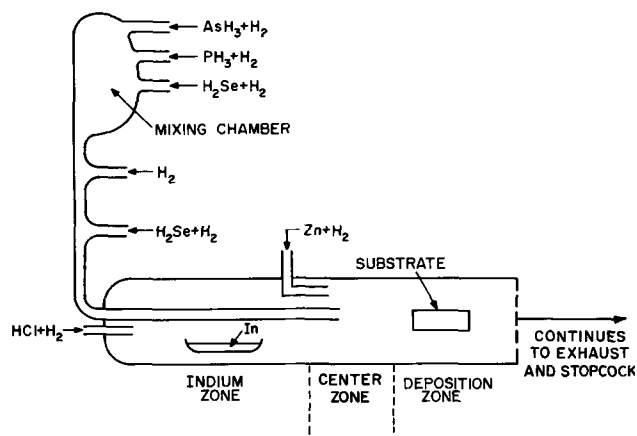


Fig. 1. Schematic representation of vapor deposition apparatus

¹ Purchased from Cominco American, Inc., Spokane, Washington (manufacturer's reported purity is 99.9999%).

² Purchased from Monsanto Company, St. Louis, Missouri.

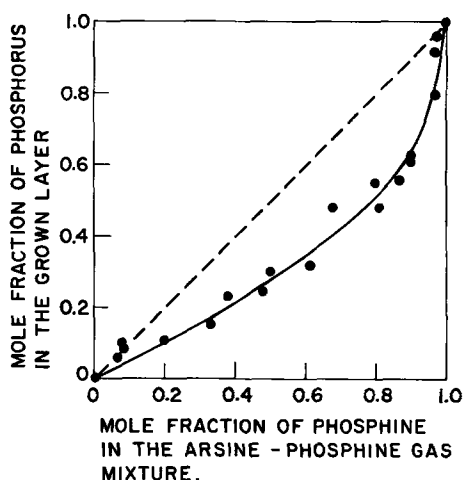


Fig. 2. Dependence of alloy composition on concentration of PH_3 in the AsH_3 - PH_3 gas mixture.

differences between the lattice constants of the substrate and the final alloy layer.

The sum of the flow rates of pure AsH_3 and PH_3 are in the range of 20-60 cm^3/min . The HCl flow rate is about 5 cm^3/min , and between 1 and 2 l/min of hydrogen is used as a carrier. With these flow rates, with a substrate temperature in the range of 675°-725°C, a center zone temperature of 950°-975°C, and an indium zone temperature of between 850° and 950°C, growth rates in the range of $\frac{1}{4}$ to $\frac{1}{2}$ μ/min are obtained under steady-state conditions. Typical thicknesses for the constant composition region of these deposits have been between 50 and 150 μ .

Results and Discussion

Crystallinity and growth morphology.—X-ray analysis by the Debye-Scherrer technique indicates that these layers are single phase, cubic, solid solutions, and show no detectable range of composition. In addition, Laue back-reflection analysis reveals that the layers are epitaxial. The lattice constant is presented as a function of alloy composition in Fig. 3, which demonstrates that Vegard's law of solid solutions is obeyed in this system. This result is in general agreement with those of Folberth (2), and Koster and Ulrich (7). The compositions were determined by chemical analysis (8) with an accuracy of $\pm 0.5\%$.

Although no detailed evaluation of the crystalline perfection of these layers was carried out, examina-

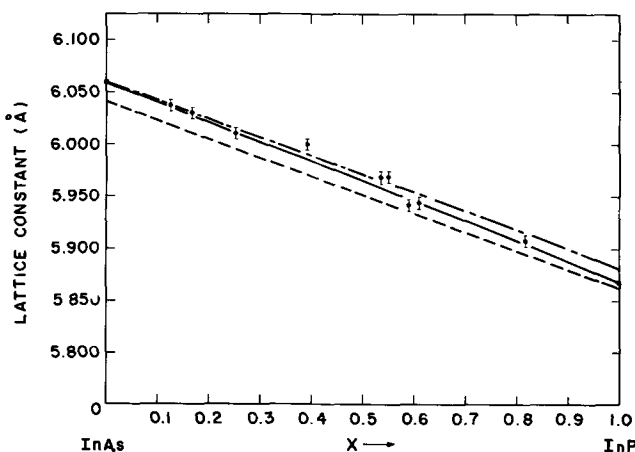


Fig. 3. Dependence of lattice constant on alloy composition in the system $\text{InAs}_{1-x}\text{P}_x$. The dependence observed by Folberth (2) and Koster and Ulrich (7) is also included: - - - Folberth; - · - Koster and Ulrich; — this paper.

tion by optical microscopy revealed that macroscopic surface imperfections, such as hillocks, were prevalent only in phosphorus-rich alloys. For alloys containing less than 50% InP , surfaces are obtained which show virtually no gross structure, and to the unaided eye appear to be mirror-smooth.

Electrical properties.—The epitaxial layers were examined by Hall coefficient and resistivity measurements using a technique (6) which permits these measurements to be made on layers as thin as 50 μ . Typical electron carrier concentrations for undoped alloys are in the range of 5×10^{15} to $1 \times 10^{16}/\text{cm}^3$. The electron mobilities are presented as a function of alloy composition in Fig. 4 and 5 for room temperature and 77°K, respectively. The data of other workers (3, 5, 9-11), and the results of a theoretical analysis of Ehrenreich (12) based on polar scattering alone, are included for comparison. In general, the mobility values at room temperature are good. In addition, these data corroborate Ehrenreich's contention that alloy scattering is not dominant in this alloy system, at room temperature. The relatively low mobility values obtained for alloy compositions approaching InP are attributed to strain arising from lattice and thermal-expansion differences between the InAs substrate and the alloy layer. It is anticipated that further compositional grading can alleviate this problem.

The data presented in Fig. 5 are the most extensive data reported for 77°K for this alloy system and compare favorably with the best previously reported mobility values. The mobility value of 120,000 $\text{cm}^2/\text{v-sec}$ for InAs is to be compared to the best previously reported value of 112,000 $\text{cm}^2/\text{v-sec}$ (9). However, the value of 18,000 $\text{cm}^2/\text{v-sec}$ for InP is somewhat lower than the best reported value of 23,400 $\text{cm}^2/\text{v-sec}$ (10).

Doping.—Doping of InAs has been investigated using H_2Se gas as a source of Se for n-type doping, and zinc for p-type doping. Electron concentrations as high as $3 \times 10^{19}/\text{cm}^3$ were achieved and in general these crystals exhibit mobilities comparable to the best reported in the literature for untreated samples (11, 13). For example, at carrier concentrations of 1×10^{18} and 3×10^{19}

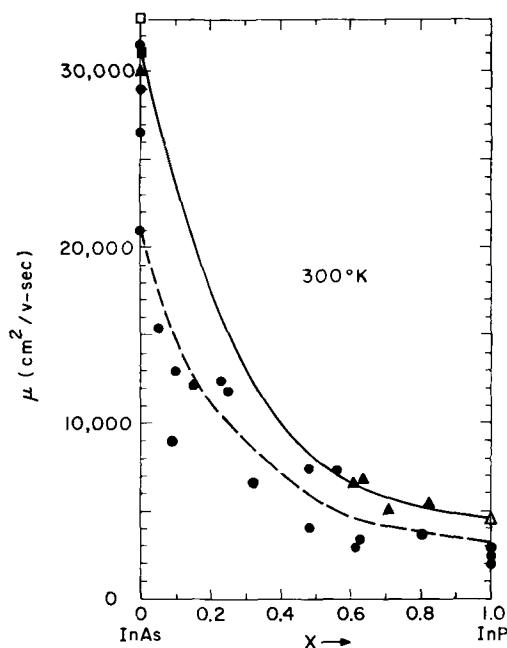


Fig. 4. Dependence of electron mobility on alloy composition in the system $\text{InAs}_{1-x}\text{P}_x$ at room temperature. The experimental results of other workers and a theoretical analysis of Ehrenreich (12) are also included: - - - Weiss (3); \blacktriangle Winkler, et al. (5); \blacksquare Cronin and Borello (9); \triangle Glicksman and Weiser (10); \square Hilsum and Rose-Innes (11); — Ehrenreich; \bullet this paper.

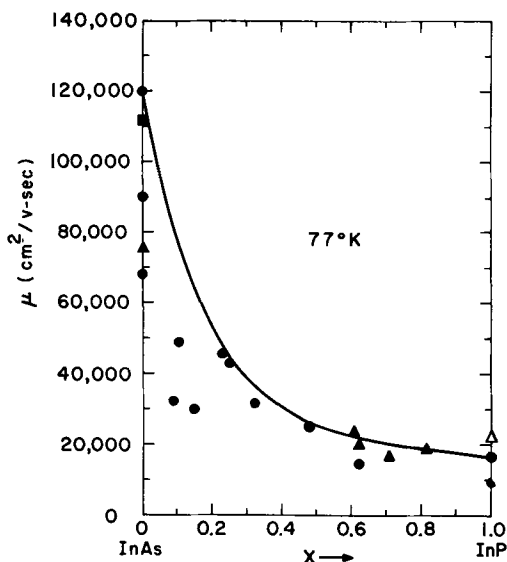


Fig. 5. Dependence of the electron mobility on alloy composition in the system $\text{InAs}_{1-x}\text{P}_x$ at 77°K . The experimental results of other workers are also included: \blacktriangle Winkler *et al.*; \blacksquare Cronin and Borello; \triangle Glicksman and Weiser; \square Hilsum and Rose-Innes; — this paper.

cm^{-3} the mobility values at room temperatures are 10,000 and 1,500 $\text{cm}^2/\text{v}\text{-sec}$, respectively. Thus, doping to these high donor concentrations does not degrade the material. With respect to hole concentrations, values in the range of 5×10^{17} to $1 \times 10^{19}/\text{cm}^3$ can be readily obtained, with mobilities of between 150 and 90 $\text{cm}^2/\text{v}\text{-sec}$ for this doping range. These compare with earlier reported values as high as 120 $\text{cm}^2/\text{v}\text{-sec}$ for hole concentrations of about $2 \times 10^{19}/\text{cm}^3$ (11).

Both n- and p-type doping were also demonstrated for some $\text{InAs}_{1-x}\text{P}_x$ alloys, and for InP, as characterized by point-contact breakdown and thermal probe measurements. In addition, multilayer structures involving both n- and p-type regions were prepared for selected alloy compositions.

Conclusions

The ability to prepare good-quality $\text{InAs}_{1-x}\text{P}_x$ alloys by a vapor-growth method previously used for the preparation of $\text{GaAs}_{1-x}\text{P}_x$ alloys has been demonstrated. Electron mobilities have been obtained for these $\text{InAs}_{1-x}\text{P}_x$ alloys which are comparable to the best previously reported values for melt-grown material. Both n- and p-type doping can be achieved over a broad resistivity range, and these doped layers can be incorporated in multilayer structures. Vegard's law of solid solutions was found to be obeyed in this alloy system.

Acknowledgments

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Oxygen Doping of Solution-Grown GaP

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ABSTRACT

The solubility of oxygen in Zn-doped, solution-grown GaP was determined from the degree of compensation of the Zn by the oxygen electrons. An oxygen content of $7 \times 10^{16} \text{ cm}^{-3}$ was obtained for crystals grown at 1144°C from Ga-GaP melts that were doped with 0.016 m/o (mole per cent) Ga_2O_3 . The solubility of Ga_2O_3 in Ga as a function of temperature was also determined, and a distribution coefficient for oxygen between the solid and liquid of 0.0055 was derived. The implications of these findings for the generation of red luminescence in GaP are discussed.

Visible luminescence of high efficiency can be achieved in GaP that is doped with Zn and oxygen (1-3). Emission is attributed in part to recombination of an electron bound to a neutral Zn-O complex with a hole on a distant Zn acceptor (4), and in part to an exciton bound to a Zn-O nearest neighbor pair (4, 5). At room temperature this emission is centered at about 7000\AA . In addition, there is an infrared band that can be resolved at low temperatures into a spectrum characteristic of ordinary pair emission between Zn and O on distant, randomly spaced sites (6). In

the last case the oxygen behaves as an isolated, very deep donor at about 0.9 eV below the conduction edge. For the nearest neighbor case, the donor energy is reduced by coulomb interaction to about 0.4 eV.

Zinc is a fairly shallow acceptor in GaP and has been reported at 0.03 eV (7) and, more recently, at about 0.06 eV (8, 9) above the valence band.

Studies of this luminescence in GaP have almost all employed GaP crystals that were obtained by precipitation from dilute Ga-GaP solutions. To a large extent this has been a matter of convenience. How-