

LIQUID PHASE EPITAXIAL GROWTH OF $\text{Ga}_x\text{In}_{1-x}\text{P}$

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Abstract

Single crystal epitaxial layers of $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloys have been grown by the steady-state liquid phase epitaxial growth technique on (111)B GaAs substrates. The crystal growth process has been studied in detail and the resultant epitaxial layers have been characterized with respect to their structural, electrical and optical properties. Epitaxial layers of good structural quality could be grown only in the composition range $x = 0.48$ to 0.53 , where the lattice parameter is close to that of the GaAs substrate. The band gap of these crystals was in the range $1.86 - 1.92$ eV as determined by optical absorption and photoluminescence measurements.

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Introduction

The search for material from which high efficiency visible light-emitting diodes can be fabricated has led to recent activity in the GaP-InP alloy system. Hilsum [1] first suggested this system as an alternative to the GaAs-GaP alloys. Archer [2] has predicted that brightness as high as 2400 f1/Acm² may be possible for yellow-green Ga_xIn_{1-x}P diodes. Burnham et al. [19] have also observed that in homogeneous, structurally sound Ga_xIn_{1-x}P, the photoluminescence (PL) output is comparable to that of GaAs and better than that of most high quality GaAs_{1-x}P_x. They conclude [20] that the material gives every indication of being an important LED and laser material.

The activity in Ga_xIn_{1-x}P has included determining the compositional dependence of the physical properties such as band gap [3-18] and luminescence, [4-20] phase diagram studies, [21-28] and device properties [5,7,15,29-32]. Many of these papers contain relatively little information about the methods used to fabricate single crystals for the properties measurements and it is clear that in many cases the crystals were inhomogeneous platelets or epitaxial layers with a large number of defects, or crystals cut from inhomogeneous polycrystalline boules. The only work in which the crystal growth process was treated in detail are the papers by Nuese et al. [15] on vapor phase epitaxial growth and Laugier and Chevallier [33] on the bulk growth of homogeneous polycrystalline samples. The literature cited contains several inconsistencies related to miscibility and the composition dependence of band gap, which are probably due in part to the poor quality of crystals used, so there is a need for further work on the growth of homogeneous, pure, structurally perfect single crystals. This paper will describe in detail the growth of Ga_xIn_{1-x}P crystals by steady-state liquid phase epitaxial growth (SSLPE) and some properties of the resultant crystals, with emphasis on homogeneity and crystalline perfection.

Experimental Procedure

The crystals of Ga_xIn_{1-x}P were grown by the SSLPE technique described by Stringfellow and Greene for the growth of InAs_{1-x}Sb_x [36]. This crystal growth technique is designed to grow homogeneous crystals in systems where the solid composition is strongly dependent on growth temperature. A schematic illustration of the crystal growth apparatus is shown in Fig. 1. The main feature is a temperature gradient of 1 - 30°C/in maintained between the source wafer and substrate which generates a composition gradient in the melt and acts as the driving force for crystal growth. This allows the substrate to be held at a constant temperature during the growth to maintain a constant solid composition, in contrast with other growth techniques where epitaxial layers or platelets of Ga_xIn_{1-x}P were grown by continuous cooling of the melt resulting in crystals containing large composition gradients [3, 14, 25-32]. The crystal growth takes place in a high purity graphite crucible which may be rotated to allow the substrate to be immersed in and removed from the melt. The crucible is enclosed in a fused silica tube in an ambient of purified H₂. The choice of an appropriate substrate

is a problem in the $\text{Ga}_x\text{In}_{1-x}\text{P}$ system. GaP has been used for the successful growth of alloys with $x > 0.8$ [8,9], but not in the composition range of interest near the direct-indirect band gap crossover; i.e., from $x = 0.5$ to $x = 0.7$. Neither GaP ($a_0 = 5.45\text{\AA}$) nor InP ($a_0 = 5.87\text{\AA}$) are adequate in this composition range because of the large lattice parameter mismatch; however, the lattice parameter of GaAs ($a_0 = 5.65\text{\AA}$) matches that of $\text{Ga}_x\text{In}_{1-x}\text{P}$ with $x = 0.52$ at 298°K and since the thermal expansion coefficient of the alloy is less than that of the GaAs, the matching composition is $x = 0.51$ at the growth temperature (800°C) [37]. Hence, GaAs was used for the substrate in experiments described in this paper.

The liquid compositions to be used for the growth of $\text{Ga}_x\text{In}_{1-x}\text{P}$ crystals were obtained from the calculated phase diagram illustrated in Fig. 2, which also contains experimental data points obtained during crystal growth experiments as described below. The growth temperatures were chosen to be as high as possible with the constraint that the phosphorus pressure be low enough so the phosphorus loss would not cause excessive shift of melt composition during growth.

A typical growth cycle will now be outlined. The (111)B GaAs substrate is prepared by lapping to remove saw damage, and then chemically polishing with 4% Br in methyl alcohol. The melt is prepared by weighting appropriate amounts of 6 g's In* and semiconductor grade InP and GaP platelets into the crucible. The GaP weight is less than the amount required to saturate the melt at the growth temperature. The system is appropriately purged and heated to the growth temperature for 20 minutes during which time the platelets completely dissolve in the melt. The GaP source chip, which is maintained at the liquidus temperature on the low temperature side of the crucible, is then rotated into the melt where it remains for one hour after which it is removed from the melt and the crucible cooled. (An experimental liquidus point can be obtained at this point, if desired, by determining the weight of GaP dissolved from the source chip and correcting for the amount of P loss to the vapor phase.) The crystal growth continues by loading the GaAs substrate and the GaP source in the appropriate positions, purging, and heating the crucible to 5-10° above the liquidus temperature of the melt to dissolve all $\text{Ga}_x\text{In}_{1-x}\text{P}$ platelets. The system is then cooled to the growth temperature and the substrate and source rotated into the melt to initiate crystal growth. After the growth is completed, the substrate and source are removed from the melt and the system is cooled to room temperature. The time-temperature sequence is illustrated in Figure 3.

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Experimental Results

Crystal Growth

The effects of several important variables on the growth process were investigated. First, it was established that proper substrate preparation is important. Controlled crystal growth could not take place on surfaces that were improperly prepared or which had been attacked by the vapor phase prior to insertion into the melt. It was found that the elimination of air leaks in the system was necessary to prevent such attack.

The degree of undercooling of the melt prior to insertion of the GaAs substrate was determined to be one of the critical crystal growth parameters. A melt on the liquidus line will not dissolve (Ga,In)P of the equilibrium composition, but it will dissolve GaAs, which is not in equilibrium with the melt. Thus, if GaAs is introduced into a saturated melt, the growth of (Ga,In)P and dissolution of GaAs will occur simultaneously, resulting in a GaAs/Ga_xIn_{1-x}P interface containing melt inclusions as illustrated in Fig. 4a-b. To obtain a good interface it is necessary to supercool the melt 5-10°C prior to introduction of the GaAs, then the Ga_xIn_{1-x}P rapidly covers the GaAs surface with no dissolution of the GaAs. Figures 4c-e illustrate cleaved sections of typical crystals grown in this way showing perfect interfaces with no melt inclusions. Too much supercooling may also be detrimental. Homogeneous nucleation of platelets in the melt is found to occur at supercooling of ~15° at 800-900°C, which of course removes the supersaturation.

Crystal growth experiments were performed at 800, 900 and 950°C. At 900 and 950°C a partial pressure of PH₃ was maintained over the melt to prevent phosphorus loss during crystal growth. The degree of control of the PH₃ necessary to avoid loss of phosphorus and prevent the growth of solid on the melt surface was difficult to achieve and, since the undercooling of the melt prior to crystal growth is such a critical parameter, controlled, reproducible growth at 900 and 950°C was impossible. Most of the crystals were grown at 800°C, where the phosphorus loss was small, without the PH₃ overpressure.

Crystal Characterization

Composition was determined using Debye-Scherrer X-ray powder diffraction patterns to obtain a_0 and determining composition from Vegard's Law which has been found to hold for the GaP-InP alloy system in the composition range considered here.(9,34)

Epitaxial crystals of Ga_xIn_{1-x}P were grown over the composition range $x = 0.31$ to $x = 0.78$. Back reflection Laué X-ray patterns indicated that the layers were single crystal. Even though crystals were grown over this range, close inspection revealed that only layers with x between 0.48 and 0.53 had high quality surface morphology, inclusion-free substrate/epitaxial layer interface and high crystalline

perfection free of inclusions and low angle grain boundaries, with dislocation densities less than 10^7 cm^{-2} . All of these characteristics degraded rapidly with $x < 0.48$ and $x > 0.53$. This phenomenon was studied in detail and is the subject of a separate paper [38]. Photographs of typically good epitaxial layers with $x = 0.51$ are presented in Fig. 5(b-d).

The homogeneity of the grown layers was studied in three ways.

(1) Samples of the $\text{Ga}_x\text{In}_{1-x}\text{P}$ layers were removed from the GaAs substrate and Debye-Scherrer X-ray powder diffraction patterns were obtained. For typical samples the $444 \text{ K}\alpha_1\text{-K}\alpha_2$ doublet is resolved and the line widths are typically similar to our measured values for pure GaAs. 2) The epitaxial layers were angle lapped at 1 and 2° and the PL spectrum was determined at several points corresponding to various depths in the epitaxial layer. The argon laser beam used to excite the PL was 40μ in diameter which corresponds to about 0.7μ and 1.4μ in depth, respectively. As seen in Fig. 6, the PL peak remains constant to within $x = \pm 0.003$. The PL was also found to be constant over the entire epitaxial area. The PL was examined under a microscope at $200\times$ in an attempt to observe evidence of phase separation or other microscopic inhomogeneity. The PL appeared to have a uniform color over the entire epitaxial layer. However, nonepitaxial platelets which grow at 800°C on the surface and around the edge were found to have a different composition and, therefore, a different color. This phenomenon is caused by the perturbation of the equilibrium composition of the solid by the strain energy and interfacial energy in the epitaxial layer and is described more fully in Reference [38]. 3) Electron microprobe scans were made for Ga, In, As and P along cleaved (110) sections of the epitaxial layers. The value of x was taken to be $I_{\text{Ga}}/(I_{\text{In}} + I_{\text{Ga}})K$ with K determined arbitrarily to give $x = 0.5$ in the center of the epitaxial layer. This should not be taken as the true composition of the epitaxial layer. X_{As} was taken as the intensity of the As characteristic emission over that in pure GaAs. As seen in Fig. 7, the concentrations of all four elements appear to change from GaAs to $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ over a distance of 2-3 microns and then remain constant throughout the remainder of the layer. The spot size of the microprobe is ~ 1 micron, but the resolution is less because the penetration depth of 25 KeV electrons is about 2.8μ in $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ [39], thus the area from which the characteristic X-rays are generated may be 3μ in diameter. The results of the three methods of analysis taken together indicate that the epitaxial layers are homogeneous and that the composition changes from GaAs to $\text{Ga}_x\text{In}_{1-x}\text{P}$ within a distance of less than 1μ .

There is disagreement in the literature about the composition dependence of the band gap in the $\text{Ga}_x\text{In}_{1-x}\text{P}$ system. We have made several types of measurements directed at clarifying the situation. The PL and lattice parameter were measured on samples of various compositions. The composition was determined from X-ray measurements using Vegard's law which has been found to be accurate in the range of interest [9,34]. The results are presented in Fig. 8 along with a curve of the form

$$E_g = a + b x + c x^2$$

with $a = 1.35$ eV (the band gap of InP [40], $a + b + c = 2.78$ eV (the direct band gap of GaP [41]) and c determined to give the least squares fit to our data, yielding $c = 0.70$, in agreement with the value predicted by Van Vechten and Bergstresser [42]. A summary of the sources of data from the literature is presented in Table II. The curve agrees with the results of Lorenz et al. [8, 9] and Nuese et al. [15]. In order to be certain that the PL was not due to traps 100-200 meV deep as suggested by Mabbitt [13], the PL was measured at temperatures between 77 and 450°K. The peak shifted exactly as the band gap is known to change with temperature and there was no evidence of a higher energy peak at higher temperatures where the deep centers would be expected to empty leaving only band-to-band recombination. Optical absorption, PL and X-ray powder analysis were also performed on several samples of material. The PL and optical absorption give the same energy gap and the data agree with that of Lorenz et al. [8, 9]. The optical absorption data are plotted in Fig. 9. The shape of the band edge is similar to Onton and Lorenz's [9] for $x = 0.64$ and is less steep than that for pure InP.

The electrical properties of $\text{Ga}_x\text{In}_{1-x}\text{P}$ layers with x near 0.51, grown at 800°C without intentional doping, were determined by three techniques. Carrier concentration was obtained from C-V measurements on Au Schottky barriers and p-n junction diodes made in the material. The carrier concentration, type and mobility were also determined from Hall effect and conductivity measurements obtained on samples grown on semi-insulating GaAs substrates. The samples chosen for fabrication of Hall bars had high crystalline perfection without melt inclusions or low angle grain boundaries, since the high imperfection density present in some samples would be expected to affect the measured mobility.

The free electron concentrations and mobilities at 300 and 77°K for several samples are tabulated in Table I. The carrier concentration was found to vary between 10^{17} and 10^{18} cm^{-3} for material grown in high purity graphite crucibles. The rather high impurity concentration is believed to be S from the graphite crucible. GaP grown under the same conditions showed high S concentration from 4.2°K PL studies. The S was eliminated by growing in BN crucibles which gave $n < 5 \times 10^{15}$ cm^{-3} . The mobility values, ranging up to 1362 cm^2/Vs at 300°K, are somewhat larger than the values of 600 cm^2/Vs obtained by Nuese et al. [5] for (Ga,In)P grown by the vapor phase technique on GaAs substrates. The mobilities are somewhat lower than obtained in InP doped in the high 10^{17} cm^{-3} range. Roder et al. [43] obtained mobilities of 2000 cm^2/Vs at 300°K and Clarke et al. [44] obtained 1250 at 300°K and 1770 at 77°K. Rode [45] calculated a mobility of 2200 at 1×10^{18} cm^{-3} with no compensation. The effective mass of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ has been calculated to be $0.095 m_e$ compared to 0.072 for InP [46]. Thus for a combination of polar optical and ionized impurity scattering the room temperature mobility would be expected [47, 48] to be $(0.072/0.095)^{3/2} \times 2200 = 1450$ cm^2/Vs in good agreement with our experimental results.

Discussion

The results of the present work on the growth of $Ga_xIn_{1-x}P$ crystals are important in clearing up several important uncertainties about the GaP-InP system. First, Mabbitt [24] has suggested that his results indicated the presence of a miscibility gap in the system at temperatures below $900^\circ C$, based on the appearance of two phases in the epitaxial layers grown on GaP substrates. We have observed that the composition of the epitaxial layer may be different than that of the platelets grown simultaneously from the same melt at the same temperature [38]. This inhomogeneity is due to the effect of strain and mismatch dislocations on the total free energy of the epitaxial layer, which perturbs the composition toward that which produces no lattice parameter mismatch with the substrate [38], and is not associated with a miscibility gap. The epitaxial layers themselves are single phase and homogeneous for $x = 0.31$ to 0.78 , grown at $800^\circ C$. This, however, doesn't prove that there is no miscibility gap because the mismatch energy makes this a nonequilibrium situation. The fact that homogeneous platelets could be grown does indicate that $T_c < 800^\circ C$. The critical temperature can be calculated from the Ga-In-P phase diagram and would be predicted to be $727^\circ C$ from the work of Stringfellow [23] and was calculated to be $577^\circ C$ by Foster and Woods [49]. Foster [49] has also suggested that even though there may not be a miscibility gap at growth temperatures, the tendency to phase separation due to the large positive InP-GaP interaction parameter may cause clustering which makes the material inherently unsuitable for the fabrication of LED's. Such clustering will surely exist to some extent on a submicroscopic scale, but we can observe no microscopic effects in PL. And since we observed the PL intensity to be greater than comparably doped Ga(As,P) used for the fabrication of LED's, the clustering does not seem to have a deleterious effect on luminescence efficiency.

Another important uncertainty is related to the composition dependence of the band gap of $Ga_xIn_{1-x}P$. There are two important features of this uncertainty, 1) the band gap at $x = 0.51$ where the best crystals of $Ga_xIn_{1-x}P$ may be grown and, 2) the value of the energy gap and composition of the direct/indirect crossover. Our results indicate that $Ga_{0.51}In_{0.49}P$ has a band gap of 1.903 eV and the crossover is at $x = 0.69$ and $E_g = 2.18$ eV.

A third important aspect of the crystal growth reported is that under the growth conditions used, $Ga_xIn_{1-x}P$ layers with x outside the range $0.48 - 0.53$ are difficult to grow and are characterized by structural defects such as melt inclusions and dislocation densities greater than $10^7/cm^2$.

One would conclude that LPE $Ga_xIn_{1-x}P$ grown on GaAs substrates will be suitable for high efficiency LED's only near $x = 0.51$ and $h\nu = 1.9$ eV. It is likely that efficient non-red LED's could be fabricated in material grown on special substrates of alloys such as Ga(As,P) with matching lattice parameters, or by tapering the composition from $x = 0.51$ to the final composition over several microns.

Summary

The liquid phase epitaxial growth of $\text{Ga}_x\text{In}_{1-x}\text{P}$ crystals has been investigated. It was found that uniform layers with high structural quality and excellent morphology may be grown on GaAs substrates only in the range $x = 0.48 - 0.53$ such that the lattice parameter is approximately equal to the lattice parameter of GaAs. The band gap of such crystals was determined from PL and optical absorption to be in the range 1.86 - 1.92 in agreement with the results of Lorenz et al. [8,9] and Nuese et al. [15]. The epitaxial layers typically contained electron concentrations in the range $10^{17} - 10^{18} \text{cm}^{-3}$ with mobilities of up to $1362 \text{cm}^2/\text{Vs}$ at 300°K and 77°K .

The results clearly indicate that at 800°C there is no miscibility gap in the GaP-InP system and there is no evidence of microscopic inhomogeneity due to clustering.

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TABLE I

Electrical Properties of $\text{Ga}_x\text{In}_{1-x}\text{P}$

$h\nu$ (PL at 300°K)	n_{300}	μ_{300}	n_{77}	μ_{77}
1.92	5.76×10^{17}	882	-	-
1.891	4.20×10^{17}	1362	2×10^{17}	1347
1.907	8.06×10^{17}	1045	7.60×10^{17}	1036
1.883	9.25×10^{17}	769	9.05×10^{17}	763
1.899	7.33×10^{17}	1304	7.37×10^{17}	1310
2.26 (GaP)	2.56×10^{16}	138	9.78×10^{12}	1025

TABLE II

Summary of references dealing with the composition dependence of band gap in $\text{Ga}_x\text{In}_{1-x}\text{P}$

Symbol	Reference	Method of Determining	
		Band Gap	Composition
●	8,9	CL, PL, abs.	X-ray, microprobe
⊙	4	Abs.	X-ray
I	3	Abs.	Chemical analysis, X-ray
X Direct } ⊗ Indirect }	12	PL excitation at 88°K extrapolated to 300°K	X-ray
▲ 6 9's In } Δ 5 9's In }	13	CL	Microprobe
■ Direct } ▣ Indirect }	5	Pressure dependence of EL	Microprobe
■ } ▣ }	14	Abs. PL	Microprobe
▽	16	Abs. visual CL	Microprobe
⊙	17	PL at 4.2°K extrapolated to 300°K	X-ray
●	15	Abs. EL, Schottky barriers	X-ray
⬡	6	Thermoreflectance	X-ray
◇ } ◆ }	Present work	PL Abs.	X-ray X-ray
⊖	50	Intraconduction band abs.	
⊖	51, 52	Photoemission, Pressure dependence of transport properties	

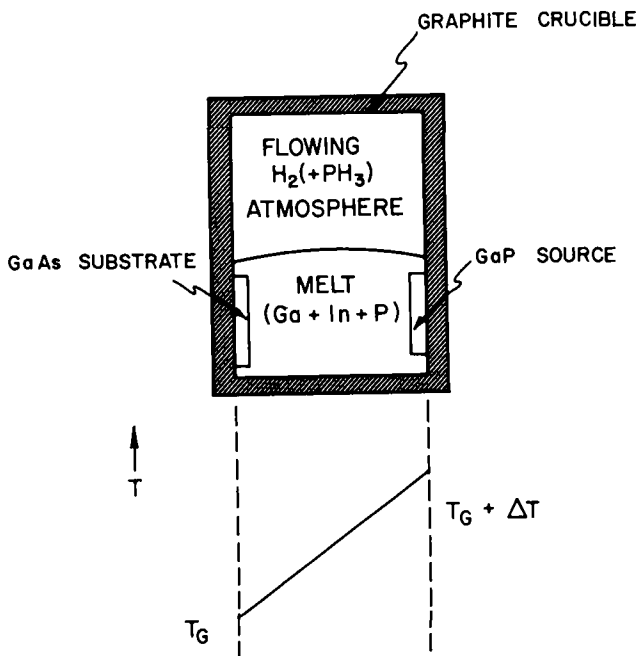


Figure 1. Schematic illustration of SSLPE crystal growth technique used for the growth of $Ga_x In_{1-x} P$ on GaAs substrates.

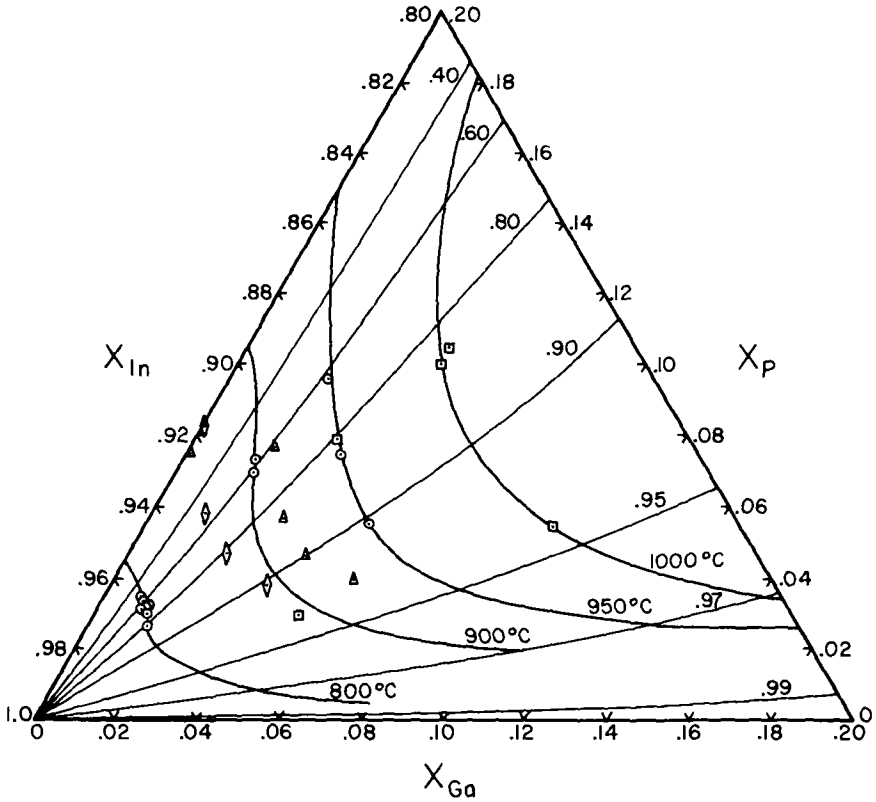


Figure 2. In rich corner of the Ga-In-P Phase Diagram. Liquidus lines are calculated [23]. Data points were obtained from the work of Panish [21] \square , Hakkı [25] \diamond (850°C), Kajiyama [26] \triangle (900°C), present work O.

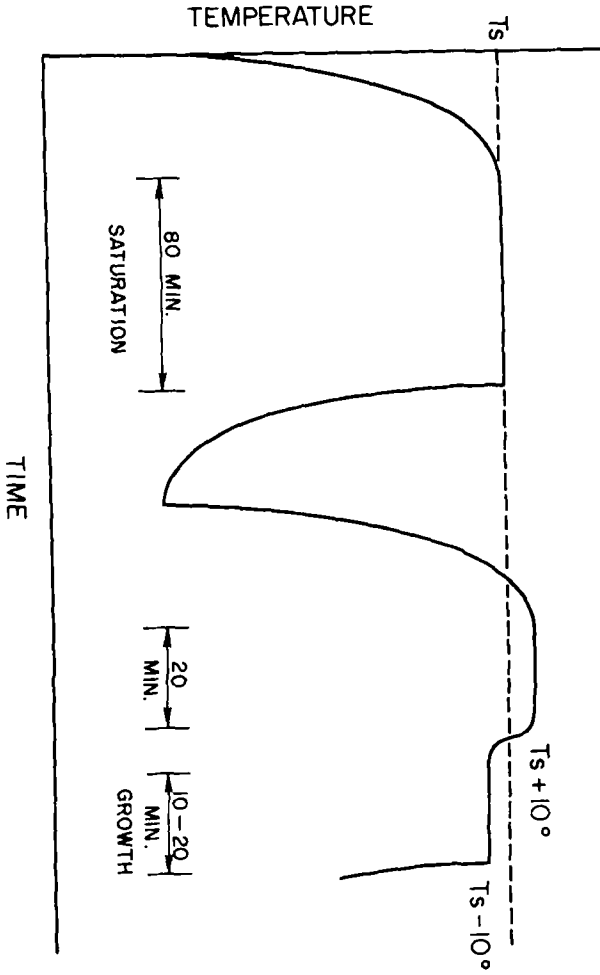


Figure 3. Time temperature cycle for typical $Ga_xIn_{1-x}P$ growth runs.

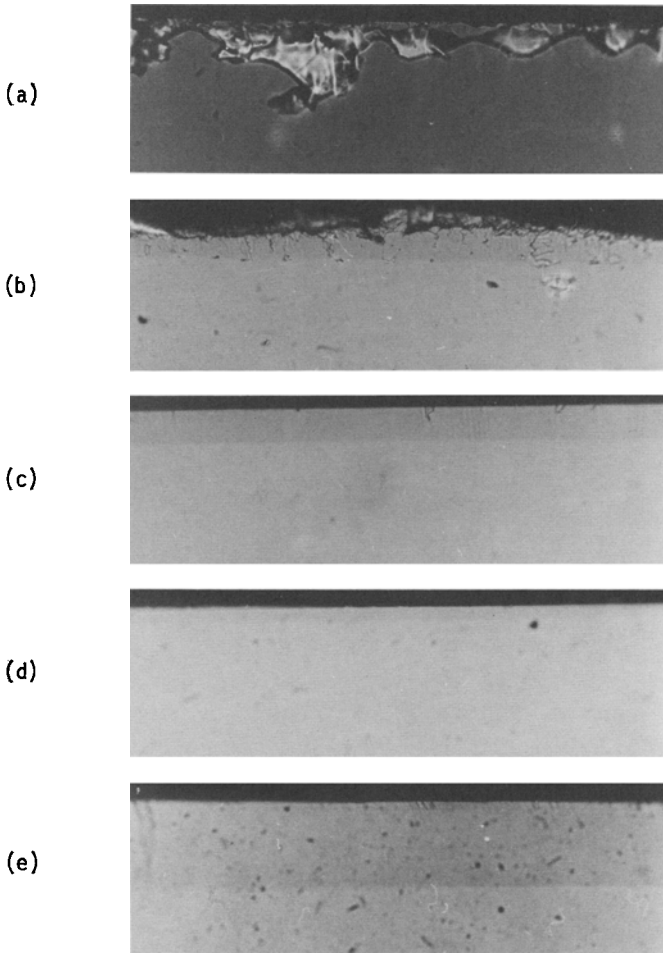
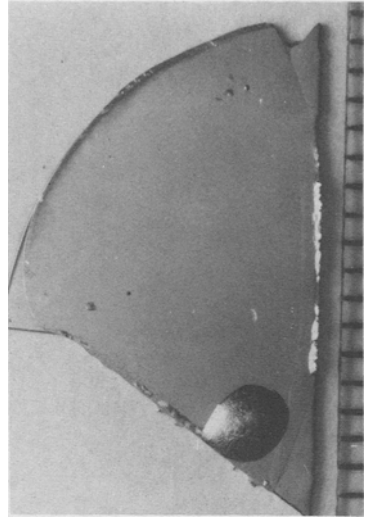


Figure 4. Cleaved sections of $\text{Ga}_x\text{In}_{1-x}\text{P}$ epitaxial layers with $x \approx 0.5$.

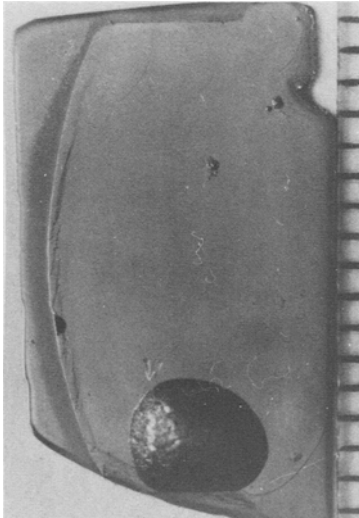
- a. Typical layer with GaAs rotated into slightly unsaturated melt.
- b. Typical layer growth with no undercooling of the melt.
- c-e. Typical layers grown with undercooling of 10°C .



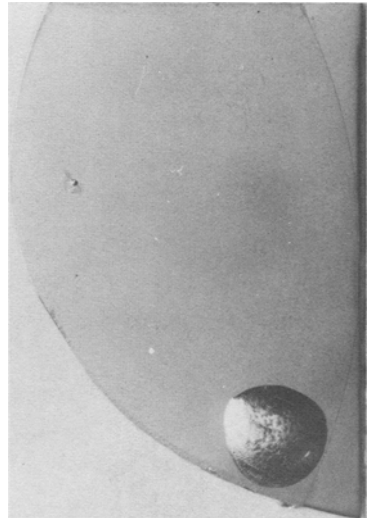
(a)



(b)



(c)



(d)

Figure 5. Photographs of typical good Ga_xIn_{1-x}P crystals with $x \approx 0.5$. These samples correspond to cleaved sections shown in Figures 4 b-e). The poor morphology associated with insufficient undercooling is evident in a).

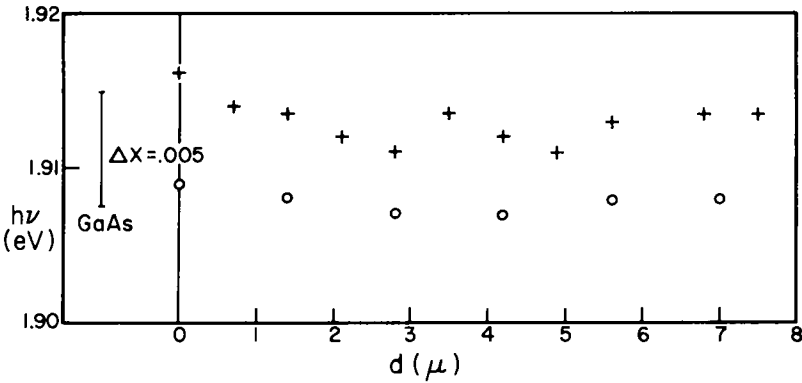


Figure 6. Photoluminescence measured on angle lapped $\text{Ga}_x\text{In}_{1-x}\text{P}$ samples. The laser spot was 40μ in diameter and PL was measured every 40μ along the surface. The two samples, GH77 (+) and GH66 (o) were angle lapped at 1° and 2° respectively from the (111) growth plane.

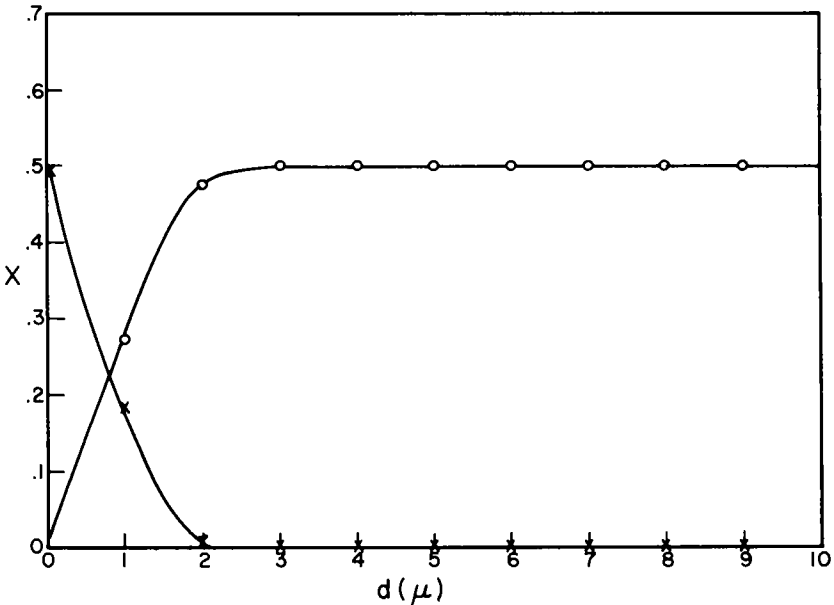


Figure 7. Results of microprobe scan in (111) direction across cleaved (110) section of $\text{Ga}_x\text{In}_{1-x}\text{P}$ sample. x is represented as a dot (•) and $1-x$ is represented as a cross (x).

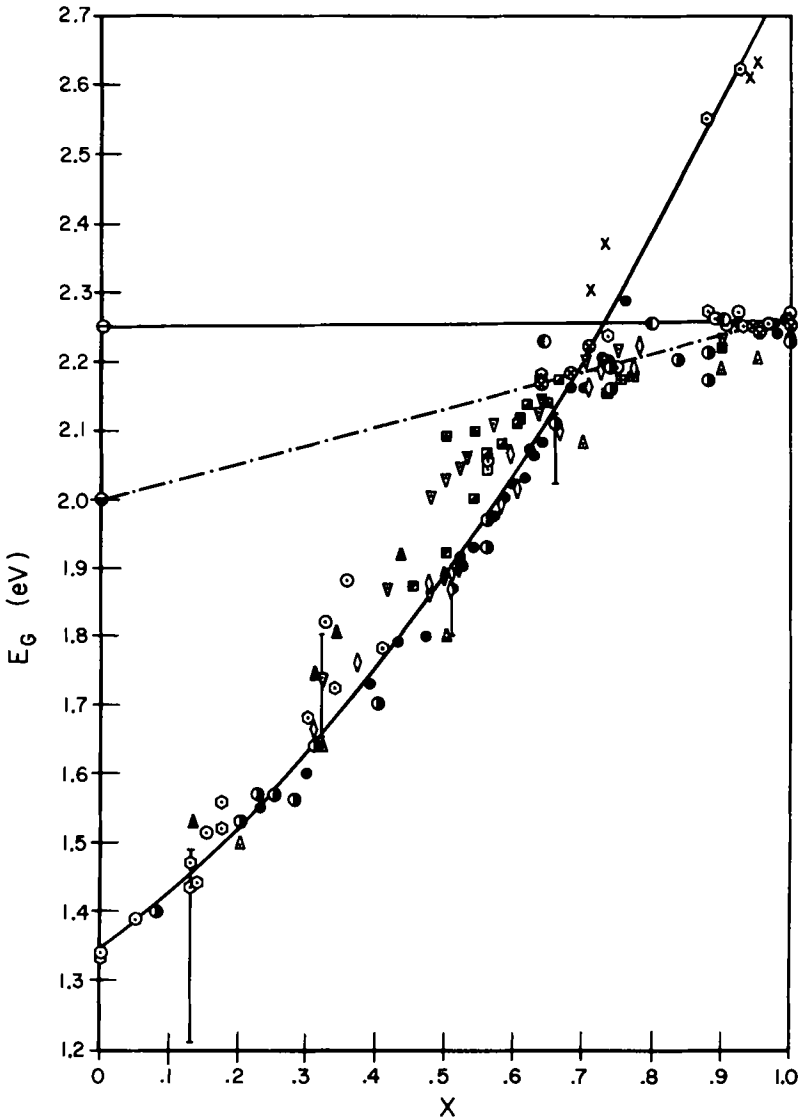


Figure 8. Bandgap versus composition for $Ga_xIn_{1-x}P$. This figure includes our results, identified as \diamond and \blacklozenge , as well as other published results identified in Table II. The least squares fit to our data is represented by the solid line described by the equation:

$$E_G = 1.35 + 0.73x + 0.70x^2$$

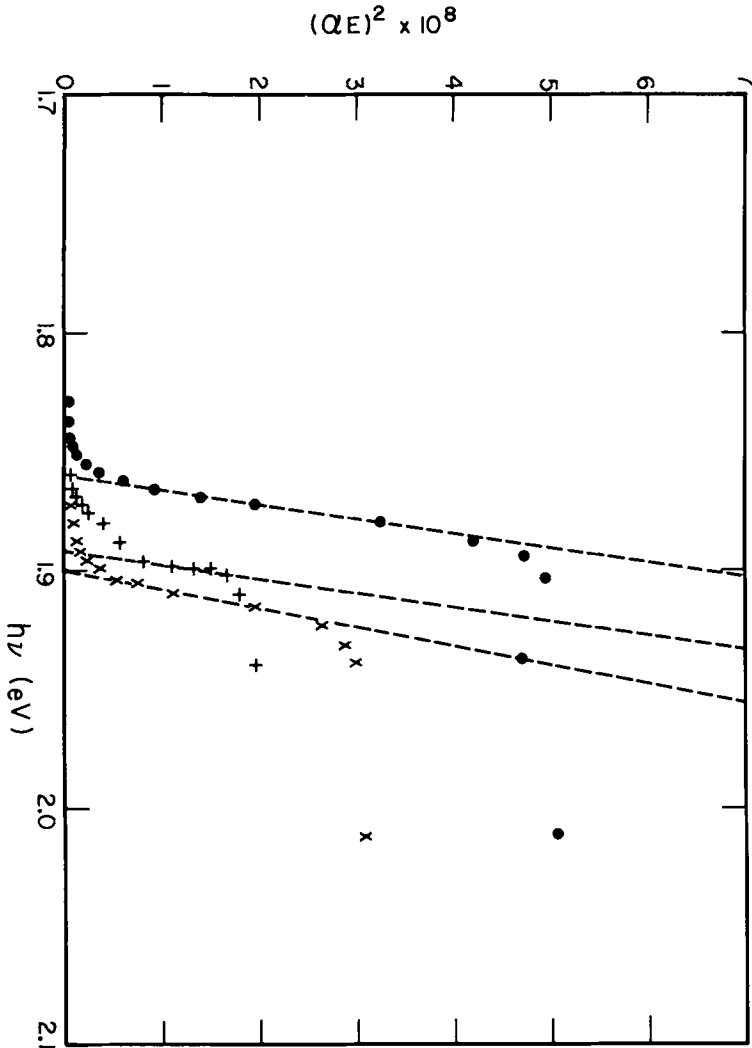


Figure 9. Optical absorption coefficient plotted as $(\alpha E)^2$ versus $h\nu$ for three samples of $\text{GaIn}_{1-x}\text{P}$. The PL peaks for the samples were 1.865 (●), 1.886 (+) and 1.92 (x).