The Preparation and Properties of Vapor-Grown $In_{1-x}Ga_xP$

C. J. NUESE, D. RICHMAN, AND R. B. CLOUGH

$In_{1-x}Ga_xP$ has been prepared over the entire alloy system by an epitaxial vapor-phase growth technique. The energy gap dependence on alloy composition for these layers has been determined by optical absorption, Schottky-barrier photoresponse, and electroluminescence measurements. These measurements indicate a nonlinear dependence of the (direct) conduction band minimum on $In_{1-x}Ga_xP$ composition, and a direct-indirect energy gap crossover at 2.20 ev and 70 pct GaP at room temperature. Zinc-diffused *p-n* junctions have been formed in the $In_{1-x}Ga_xP$ layers, and have been found to be reasonably well-behaved in regard to their I-V and C-V characteristics, and their photoresponse. The electroluminescent emission spectra contain a narrow high-energy near-bandgap peak, but are frequently dominated by low-energy impurity peaks. For indirect-bandgap alloys, impurity peaks lie approximately 0.25 and 0.5 ev less than bandgap. A third peak is found at an energy of 1.30 to 1.35 ev independent of composition, for $x > 0.4$.

REPORTS that the energy band structure of $In_{1-x}Ga_xP$ is direct to energies as high as 2.20 ev make this material particularly attractive for electroluminescent applications, spontaneous and coherent, over a large portion of the visible spectrum. However, difficulties in material preparation have hampered a detailed investigation of this alloy system, and only in recent years have single crystals of $In_{1-x}Ga_xP$ been prepared. In addition, the energy gap dependence on alloy composition has been reported to be quite different by different researchers, Hilsum and Porteous[1] and Rodot *et al.*[2] reporting a linear dependence of the direct conduction band minimum on composition, and Lorenz and Onton[3] reporting a significant deviation from linearity.

In the present paper we describe the preparation of single-crystal $In_{1-x}Ga_xP$ layers over the entire alloy system by an epitaxial vapor-phase growth technique. These layers have been evaluated electrically and optically to determine their energy gap dependence on alloy composition. In addition, *p-n* junctions have been formed in the $In_{1-x}Ga_xP$ layers in order to evaluate the quality of the junctions and the electroluminescent potential of the vapor-grown material. Details of the crystal growth, material characterization, and junction evaluation are discussed in the sections below.

MATERIAL PREPARATION AND CHARACTERIZATION

The apparatus used to prepare the $In_{1-x}Ga_xP$ alloys used here is a modified version of that described by Tietjen and Amick,[4] and is shown schematically in Fig. 1. The principal modification is the use of separate quartz tubes for the metal sources. In addition, the source zone has been doubled in length. These changes allow independent control of the temperature and the HCl concentrations at each metal source. The substrates used in this work were ⟨100⟩-oriented GaAs, which were chemically polished with bromine-methanol and Karo's acid prior to insertion into the growth system. The hydrogen carrier gas was palladium-diffused to remove contaminants. The metals, HCl, and phosphine gas (diluted to 5 to 10 pct in H_2) were the purest commercially available, and were used without further purification. The detailed experimental procedures and apparatus used here are closely similar to those previously reported,[4] and will not be repeated.

We have investigated the influence of the source, mixing, and deposition zone temperature on the alloy composition. Only the temperature of the deposition zone was found to strongly affect the alloy composition. With all the other variables constant, a decrease in the deposition temperature causes a decrease in the amount of gallium in the $In_{1-x}Ga_xP$ alloy, as shown in Fig. 2. We should mention, however, that varying the deposition temperature over the range shown in Fig. 2 significantly alters the surface appearance of the epitaxial layers, and is therefore not a practical method for controlling the $In_{1-x}Ga_xP$ alloy composition. For most of the work reported here, the deposition zone was held at 750°C, while the gallium and indium sources were maintained at 850° and 950°C, respectively. For these conditions, growth rates between 12 and 25μ per hr were typically found. The epitaxial layers were generally 25 to 100μ thick.

As expected, the ratio of HCl flow over the two metal sources is of primary importance in establishing the

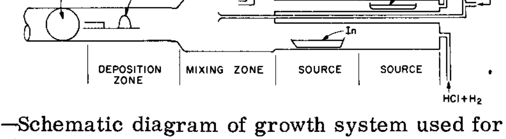

Fig. 1—Schematic diagram of growth system used for vapor-phase deposition of $In_{1-x}Ga_xP$.

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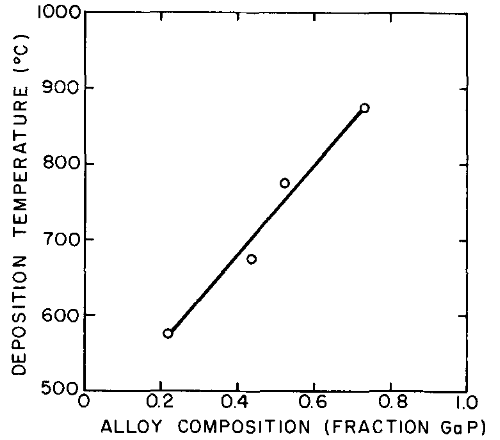

Fig. 2—$In_{1-x}Ga_xP$ alloy composition vs deposition temperature. All other growth parameters were held constant.

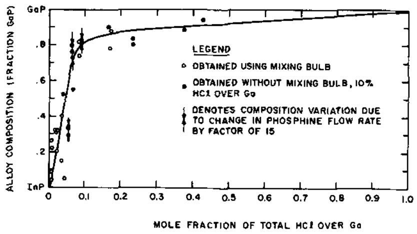

Fig. 3—$In_{1-x}Ga_xP$ alloy composition vs the fraction of the total HCl flow over the gallium source. Composition variations produced by changing the phosphine flow rate and by eliminating the use of a mixing bulb (for diluting the HCl) are also shown.

composition of the alloy, as shown in Fig. 3. Note here the rapid change in alloy composition for small changes in the HCl ratio. This behavior is not unexpected considering the greater relative stability of InCl to GaCl in the temperature range of this work. The rapid variation of composition with HCl ratio, however, makes the precise control of the gas flows particularly important for achieving homogeneous alloy compositions. For this reason, a mixing bulb was sometimes used to dilute the HCl with hydrogen in order to more accurately control the HCl concentrations over the metal sources. In later experiments, a diluted source tank of HCl (10 pct) was used. Note also in Fig. 3 that the $In_{1-x}Ga_xP$ alloy composition is only weakly affected by relatively large changes in the phosphine concentration.

One factor affecting the quality of the alloy layers is the lack of a suitable substrate for all compositions of $In_{1-x}Ga_xP$. The lattice constant of the GaAs substrate matches that of the $In_{1-x}Ga_xP$ epitaxial layer only for a composition, $x = 0.51$. In addition to the lattice constant mismatch, differences in thermal expansion coefficients between the epitaxy and the substrate will introduce strain, and possibly defects, into the alloy layer. We have seen evidence for this in the form of bowing of the epitaxy-substrate composite after removal of the wafer from the growth system, the direction of the bow being concave toward the substrate. Removal of the substrate from the epitaxial layer in some cases has also resulted in severe cracking of the epitaxial layer along (110) crystal planes. These conditions undoubtedly contribute to the low electroluminescence efficiencies obtained for these alloys.

Table I. Room Temperature Hall Mobilities and Carrier Concentrations for $In_{1-x}Ga_xP$

x	Electron Concentration, cm^{-3}	Mobility, sq cm v-sec
0.57	5×10^{17}	600
0.65	5×10^{16}	500
0.75	1×10^{17}	92

In spite of the warpage and cracking difficulties, it was possible to remove several n-type $In_{1-x}Ga_xP$ layers from their substrate in sufficient size to prepare Hall measurement samples. The results of Hall measurements on three such samples with alloy composition, x, equal to 0.57, 0.65, and 0.75 are shown in Table I. The relatively high mobilities for the samples with $x = 0.57$ and $x = 0.65$ suggest that the conduction band structure in these alloys is direct. Conversely, the relatively low mobility for the sample with $x = 0.75$ suggests an indirect conduction band. It should be noted, however, that the reduced mobility shown in Table I for $x = 0.75$ is not conclusive evidence for indirect-bandgap material, since the high density of states for the indirect conduction band minima could lead to reduced mobilities even though the zone center minimum could be lowest in energy.

In addition to undoped layers, which were usually found to be n-type in the 10^{16} electrons per cu cm range, $In_{1-x}Ga_xP$ layers also were prepared with heavy n- and p-type doping by introducing gaseous H_2Se and zinc (in a hydrogen carrier) into the growth chamber. P-n junction structures also were prepared entirely from the vapor-phase growth; however, their diode characteristics were usually somewhat inferior to those of zinc-diffused $In_{1-x}Ga_xP$ diodes, as discussed further below.

ENERGY BANDGAP DETERMINATION

The alloy composition of each of a series of $In_{1-x}Ga_xP$ epitaxial layers was determined by measuring the lattice constant by the Debye-Scherrer X-ray technique, and by assuming Vegard's relationship between lattice constant and alloy composition. One of three different techniques was then used to determine the energy gap of each layer at room temperature.

First, for several n-type vapor-grown layers, it was possible to chemically remove the GaAs substrate from the $In_{1-x}Ga_xP$ epitaxial layer, thereby facilitating bulk optical absorption measurements on a Cary Model 14 double-beam spectrophotometer. In these measurements, the dependence of the absorption coefficient on the photon energy was assumed to be of the form[5]

$$\alpha = K(h\nu - E_g)^m \ . \qquad [1]$$

For indirect-bandgap alloys, m was found to be about 2; however, because of the steepness of the absorption edge, we could only ascertain that the proper value of m lies between 1/2 and 1 for the direct-bandgap alloys. For such direct-bandgap material, the extrapolated energy-gap values determined by employing either $m = 1/2$ or $m = 1$ lie within the energy range covered by the physical size of the data points (circles) in Fig. 4, below.

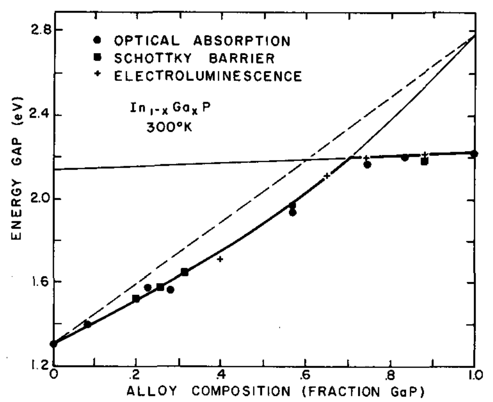

Fig. 4—Energy gap at 300°K vs $In_{1-x}Ga_xP$ alloy composition. Direct-indirect transition occurs at 2.20 ev and 70 pct GaP.

Photoresponse measurements of Schottky-barrier diodes formed by evaporating a thin layer of gold onto n-type $In_{1-x}Ga_xP$ layers were also used for energy gap determination. This technique has been successfully applied to the $GaAs_{1-x}P_x$ alloy system[6] and to AlAs and AlSb[7] by Mead and Spitzer. The technique assumes that the magnitude of the photoresponse is proportional to the absorption coefficient, and the relationship of Eq. [1] is used for either direct- or indirect-bandgap material. The accuracy of the photoresponse and absorption data is estimated to be within 0.04 ev. Photoresponse curves were also generally attained for zinc-diffused p-n junctions in $In_{1-x}Ga_xP$, as discussed in the next section. However, the photoresponse of a p-n junction can not be used for precise energy gap measurements since its shape depends strongly on minority carrier diffusion lengths, bulk absorption coefficients, and junction depth.

Finally, the high-energy peak of the electroluminescent spectra was also used as an approximation to the energy gap, although it is recognized that this peak could well arise from transitions involving extrinsic states slightly removed from the band edges in energy. In addition, strong absorption of the high-energy emission edge could also shift the observed emission peak to lower values.

The dependence of the energy bandgap at room temperature on $In_{1-x}Ga_xP$ alloy composition, as determined by the three measurements described above, is presented in Fig. 4. For consistency, absorption data taken with InP and GaP are also included as the terminal points of Fig. 4. The values obtained for these end points agree with the literature values (2.26 ev for GaP,[8,9] 1.30 ev for InP) within the accuracy of our measurements. The primary feature of Fig. 4 is the clear deviation of the Γ (direct) conduction band minimum from a linear dependence on alloy composition. The curvature of the Γ minimum in Fig. 4 generally confirms the cathodoluminescent measurements of Lorenz and Onton[3] on bulk $In_{1-x}Ga_xP$ prepared by a modified Bridgeman growth technique, but differs from the linear energy gap dependence first observed by Hilsum and Porteous[1] on platelets grown from solution, and later confirmed by Rodot *et al.*[2]

From Fig. 4, the direct-indirect energy gap crossover occurs at 2.20 ev for an alloy consisting of 70 pct GaP. This composition at the crossover is reasonably close to that determined by Lorenz and Onton[3] (74 pct GaP), but somewhat higher than that determined by Hilsum and Porteous[1] and by Rodot *et al.*[2] (60 pct GaP). A crossover near 60 pct GaP has also been suggested by the photoluminescence measurements of Williams *et al.*[10] and White *et al.*[11] (60 ± 5 pct GaP) and by pressure experiments with $In_{1-x}Ga_xP$ diodes by Hakki *et al.*[12] (63 pct GaP).

It is conceivable that the deviations from linearity observed by some workers, but not by others, is a result of internal crystal strain, which under certain circumstances or at some alloy compositions, could shrink the effective energy gap. In this regard, the vapor-grown $In_{1-x}Ga_xP$ layers prepared epitaxially in our research are thought to be significantly strained, as evidenced by a bowing which is frequently observed on the epitaxy-substrate composite following growth. In addition, the X-ray diffraction patterns observed for the $In_{1-x}Ga_xP$ layers were usually somewhat broadened at intermediate compositions, but sharp near the indium-rich and gallium-rich terminal compositions. Such behavior could be caused by strain or by slight inhomogeneities in the alloy composition. Either of these effects could cause the bandgap curve to deviate from linearity.

The data for the (direct) conduction band minimum in Fig. 4 extrapolates roughly to an energy value of 2.78 ev in GaP, consistent with Zallen and Paul's determination of the Γ minimum in GaP from high-pressure experiments.[13] The data for the indirect minima in $In_{1-x}Ga_xP$ extrapolate to an energy value of 2.15 ev for the indirect subsidiary minima in InP. Calculations[14] and recent experimental observations[15] suggest that these minima lie about 0.90 ev above the direct conduction band minimum, or at approximately 2.20 ev. The direct nature of the $In_{1-x}Ga_xP$ band structure to energies as high as 2.20 ev illustrates the potential of this alloy system for electroluminescent applications through most of the visible portion of the spectrum.

P-N JUNCTIONS

As mentioned previously, p-n junctions have been formed in epitaxial layers of $In_{1-x}Ga_xP$ both by changing extrinsic dopants (selenium and zinc) during vapor-phase growth, and by a subsequent diffusion of zinc into n-type layers of $In_{1-x}Ga_xP$. In general, the junctions formed by zinc diffusion were found to be of somewhat higher quality than the vapor-grown junctions for reasons which are not yet clear.

The zinc diffusions were carried out in an evacuated (10^{-6} torr) quartz ampoule which contained sufficient elemental phosphorus to provide 1 atm pressure of P_4 at the specific diffusion temperature used, typically 750°C. The surface appearance of the $In_{1-x}Ga_xP$ layers was not perceptibly affected by the diffusion process.

Contacts to the uppermost p-type layer of $In_{1-x}Ga_xP$ were made by evaporating Ag-Mn dots[16] and sintering at 600° to 700°C in H_2. Au-Sn was used to contact either the n-type GaAs substrate or the n-type layer of $In_{1-x}Ga_xP$ in cases where the epitaxial layer was thick enough (> 75μ) to remove the substrate. Removal of the GaAs from the $In_{1-x}Ga_xP$ was accomplished by immersing the wafer in an acid solution of 4 HNO_3 : 1 HF, which does not etch $In_{1-x}Ga_xP$ alloys containing a significant fraction of GaP.

The room-temperature I-V characteristics of p-n

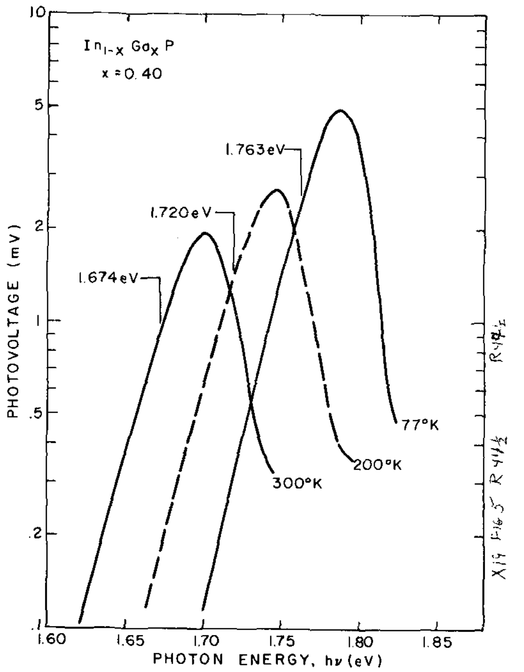

Fig. 5—Photovoltage response of an $In_{0.60}Ga_{0.40}P$ p-n junction at T = 77°, 200°, and 300°K.

junctions formed by zinc diffusion into n-type $In_{1-x}Ga_xP$ were generally found to be well-behaved, with forward voltage saturation beginning at approximately 1.5 v, as expected for the relatively large energy gaps of these alloys. Reverse breakdown voltages for such diodes were in the range of 5 to 20 v, depending on the donor concentration in the n-type layer prior to diffusion. In general, at decreasing temperatures between 300° and 77°K carrier freeze-out frequently (but not always) occurred, as observed in the form of a significant increase in the series resistance of the forward I-V characteristics. Despite the effect of carrier freeze-out on impurity or defect states, the p-n junctions formed in the epitaxial layers of $In_{1-x}Ga_xP$ were reasonably well-behaved in several other respects, as described further below.

A photoresponse was detected for all of the $In_{1-x}Ga_xP$ junctions examined, with the low-energy intercept of the spectral response occurring at approximately the bandgap energy of the $In_{1-x}Ga_xP$ alloy. In addition, the photoresponse was found to shift with temperature in a fashion appropriate for the change in the semiconductor energy gap with temperature, as shown in Fig. 5 for an $In_{0.60}Ga_{0.40}P$ p-n junction. Here, for temperatures between 200° and 300°K, the half-amplitude point of the photoresponse shifts with a temperature dependence of about 4.6×10^{-4} ev per °K, in excellent agreement with the temperature dependence of the direct conduction band minimum in InP.[17] The sharp fall-off on the high-energy side of the photoresponse curves in Fig. 5 is due primarily to the strong absorption of the high-energy illumination in the region between the crystal surface and the p-n junction, and was much more gradual for the Schottky barrier diodes (used in the energy gap determination of Fig. 4), where most of the incident radiation reaches the depletion region of the barrier. The decrease in the magnitude of the photoresponse with increasing temperature in Fig. 5 is probably due to larger absorption losses at room temperature, which prevent much of the radiation from reaching the vicinity of the junction.

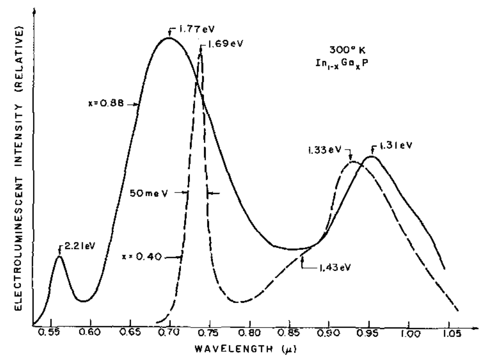

Fig. 6—Room-temperature emission spectra of $In_{1-x}Ga_xP$ electroluminescent diodes with x = 0.40 and x = 0.88. Spectra are not corrected for Sl photomultiplier response. $J \approx 50$ amp per sq cm.

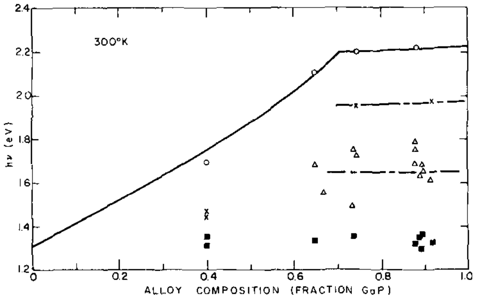

Fig. 7—Near-bandgap and impurity peaks in $In_{1-x}Ga_xP$ electroluminescent diodes, $x \geq 0.4$. T = 300°K.

Finally, from one layer which was thick enough for Hall sample preparation, the carrier concentration determined from C-V measurements of the p-n junction could be compared with that determined from Hall measurement. From the slope of the $1/C^2$ vs V characteristics, an electron concentration of 2.4×10^{17} cm^{-3} was obtained, in good agreement with a value of 1.4×10^{17} cm^{-3} from the Hall measurement.

ELECTROLUMINESCENCE

The electroluminescent spectra of the $In_{1-x}Ga_xP$ p-n junctions were usually dominated by low-energy impurity peaks, as shown in Fig. 6. Here, the room-temperature spectra of typical p-n junctions are illustrated for alloys with x = 0.40 and x = 0.88. In both spectra, a narrow near-bandgap peak is observed at the shorter wavelengths (high energy) as well as two impurity peaks at longer wavelengths. An impurity peak at 1.31 to 1.33 ev is present in both spectra, and was also found in junctions prepared over a wide range of $In_{1-x}Ga_xP$ alloy compositions. Emission at 1.30 to 1.35 ev has also been observed in our vapor-grown $GaAs_{1-x}P_x$ and AlAs,[18] however, the origin of the recombination center is not known.

The peak at 1.77 ev for $In_{0.12}Ga_{0.88}P$ lies approximately 0.5 ev below the bandgap energy, and is similar to the 1.78 ev peak that provides the red emission in GaP. Since the 1.78 ev GaP peak is known to result from zinc to oxygen transitions,[19] and since oxygen was in fact detected in our vapor-grown layers by spark source mass spectrographic analysis, we can ascribe the 1.77 ev peak in Fig. 6 to zinc to oxygen transitions in $In_{1-x}Ga_xP$.

The spectrum of the $In_{0.6}Ga_{0.4}P$ sample also illustrates a shoulder at 1.43 ev, which is about 0.25 ev less than bandgap. The origin of this center has not yet been identified.

In general, over a wide range of indirect-bandgap alloy compositions, low-energy impurity peaks are observed at energies approximately 0.25 and 0.5 ev less than bandgap, as shown in Fig. 7. The invariant energy of these peaks with alloy composition is consistent with the similarly weak energy gap dependence for the alloy system with $x > 0.7$. The third impurity peak at 1.30 to 1.35 ev appears to be independent of alloy composition for $x > 0.4$, although further data is required to determine the nature of this peak for indium-rich alloys. For all of the electroluminescent junctions studied here, the donor concentrations were in a range of 2×10^{17} to 2×10^{18} cm^{-3}, therefore the possible influence of donor concentration on the impurity peaks was not established.

The fact that the recombination mechanisms of the near-bandgap and the low-energy peaks differ was confirmed by examining the spectral intensities of the various peaks as a function of the applied forward bias. In all cases, the current dependence was significantly stronger for the near-bandgap recombination than for the impurity recombination, suggesting a higher-order recombination process for the near-bandgap peak. Similar observations have been reported for a variety of III-V compounds, and have been previously explained by Mayburg and Black.[20] The fact that two of the high-energy spectral peaks lie very close to the semiconductor energy gap at alloy compositions close to GaP may be consistent with the near-bandgap exciton recombination reported for the green emission in GaP at room temperature.[21]

Although impurity peaks have indeed been typically large in the $In_{1-x}Ga_xP$ layers prepared to date, the fact that this is not fundamental to vapor-grown $In_{1-x}Ga_xP$ is illustrated in the spectra of an $In_{0.35}Ga_{0.65}P$ *p-n* junction shown in Fig. 8. Here, the magnitude of the impurity peaks are no more than 10 pct that of the near-bandgap peak, even though this particular alloy is very close to the direct-indirect energy gap transition. The crystalline perfection of the layer in which this junction was formed was superior to most others similarly examined in regard to surface smoothness and freedom from warping. The external quantum efficiency of the diode whose spectrum is shown in Fig. 8 was 2×10^{-6} at room temperature. In general, the total electroluminescent efficiencies of the $In_{1-x}Ga_xP$ diodes examined here ($x \geq 0.4$) were in the range of 10^{-5} to 10^{-6} at 300°K and 10^{-3} to 10^{-4} at 77°K for current densities on the order of 1 to 10 amp per sq cm.

CONCLUSIONS

Single-crystal epitaxial layers of $In_{1-x}Ga_xP$ can be prepared across the entire alloy series by the vapor-phase growth technique described in this paper. The principal growth parameter for controlling the alloy composition of the $In_{1-x}Ga_xP$ layers is the relative flow rate of HCl over the gallium and indium sources.

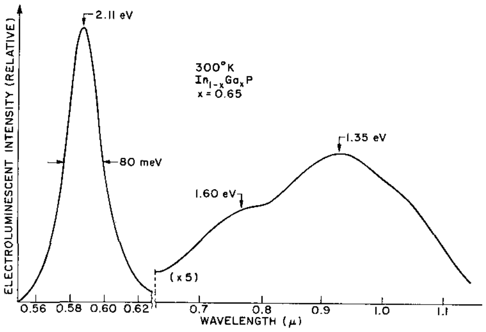

Fig. 8—Electroluminescent emission spectrum of $In_{0.35}Ga_{0.65}P$ zinc-diffused *p-n* junction at room temperature. Spectrum is not corrected for Sl photomultiplier response. $J \approx 10$ amp per sq cm.

Because of the high relative stability of the InCl as compared to that of GaCl at typical growth temperatures, much larger HCl flow rates are required over the indium than over the gallium in order to prepare intermediate $In_{1-x}Ga_xP$ alloy compositions.

The dependence of the direct conduction band minimum on $In_{1-x}Ga_xP$ alloy composition is nonlinear, with the direct-indirect crossover in the energy gap occurring at 70 pct GaP and 2.20 ev. This nonlinear dependence is in reasonable agreement with the measurements of Lorenz and Onton, but differs significantly from the linear bandgap dependence determined by Hilsum and Porteous and by Rodot *et al.*

P-n junctions formed by diffusing zinc into *n*-type $In_{1-x}Ga_xP$ layers behave reasonably well in regard to their I-V and C-V characteristics, and their junction photoresponse. However, the electroluminescent spectra of the diodes are generally dominated by low-energy impurity peaks, which are probably caused either by contamination or by strain-induced lattice defects. Three main impurity peaks are frequently observed in the room-temperature spectra of gallium-rich $In_{1-x}Ga_xP$ alloys, one about 0.25 ev below bandgap, another 0.5 ev below bandgap, and a third at about 1.30 to 1.35 ev for $x > 0.4$. Electroluminescent efficiencies in this compositional range are on the order of 10^{-5} to 10^{-6} at room temperature and 10^{-3} to 10^{-4} at 77°K.

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