Composition dependence of the band gaps of In1-xGaxAs1-yPy quaternary solids lattice matched on InP substrates

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Composition dependence of the band gaps of $In_{1-x}Ga_xAs_{1-y}P_y$ quaternary solids lattice matched on InP substrates

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The In-Ga-As-P quaternary phase diagram required for the growth of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ layers on InP substrates has been determined experimentally at 650°C. The liquidus isotherms were obtained by the seed-dissolution technique. The solidus isotherms were determined by electron-microprobe analysis performed on surfaces of quaternary epitaxial layers grown on Sn-doped InP (111)*B* substrates from quaternary saturated melts. Lattice constants of layers were measured by an x-ray-diffraction technique. The liquid-phase-epitaxy growth conditions of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ ($0 \le x \le 0.47$, $0 \le y \le 1.0$) layers on InP were found from the results of the phase diagram and lattice constant measurements. Lattice-matched layers with various band gaps (from 1.34 to 0.74 eV at room temperature) were grown by using these conditions. Band gaps of the layers were determined by photoluminescence measurements at 300 and 77 K. The band gap at each temperature was found to be linearly dependent on alloy-composition parameters x and y and can be expressed as a function of composition by $E_g = 1.35 - 1.30x$ at 300 K and $E_g = 1.41 - 1.30x$ at 77 K. The energy shift between the two band gaps was constant all over the composition and was equal to 0.06 eV.

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I. INTRODUCTION

The room-temperature (RT) band gap of the $In_{1-x}Ga_xAs_{1-y}P_y$ quaternary alloy lattice matched to InP can vary from 1.34 eV (0.92 μm)[1,2] to 0.74 eV (1.68 μm)[3] or to 0.75 eV (1.65 μm)[4]. Therefore, the In-Ga-As-P quaternary system is becoming increasingly important for the fabrication of optical sources and detectors designed for longer wavelengths than 0.9 μm. Many reports on the heterojunction lasers[5–14] and light-emitting diodes (LED's)[15–19] prepared from $In_{1-x}Ga_xAs_{1-y}P_y$ alloys have been made since Bogatov *et al.*[5] reported the pulsed 77 K operation of InGaAsP/InP double-heterostructure diode lasers emitting at 1.02 μm. The quaternary photocathodes[20–22] and photodiodes[23] were also reported.

In order to fabricate these optical devices by liquid-phase-epitaxial (LPE) growth, it is necessary to determine the In-Ga-As-P phase diagram and to know the growth conditions for close lattice matching to InP. Antypas *et al.*[24,25] reported this phase diagram first. We also presented the phase diagram and growth conditions which supplied sufficient information required for the growth of lattice-matched quaternary layers giving emission in the wavelength range from 0.92 to 1.36 μm.[26] However, there are no phase diagrams which describe the whole compositional range of quaternary alloys lattice matched to InP. As regards the growth conditions (i.e., compositions of melts and starting growth temperatures), many reports[8,13,18,27–31] have been made. Some authors[3,18,32] also reported the growth conditions for lattice-matched InGaAs, which was one of the end points of the quaternary system. All of these authors except Sankaran *et al.*[30] and us,[26] however, determined the growth conditions by using supersaturated solutions, and these conditions were not under equilibrium. P concentrations in quaternary melts were shown only in a few reports.[13,18,26,29]

Accurate information on composition dependence of the band gap of the quaternary alloy is also required for the design of the devices. Moon *et al.*[33] calculated the relation between band gap and composition by interpolating the ternary data into the quaternary region. Pearsall *et al.*[16] reported that the band gap of any lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ could be roughly estimated by assuming a linear relation between band gap and alloy composition x. Systematic experimental results have not been presented until now.

In this paper, the experimentally determined In-Ga-As-P phase diagram and LPE growth conditions which gave enough information to grow lattice-matched layers with various compositions or wavelengths (from 0.92 to 1.65 μm) are described systematically. The growth was performed by using saturated rather than supersaturated solutions at the starting growth temperatures. P concentrations in the solutions are also shown clearly. Moreover, we have experimentally determined the composition dependence of the band gap of the exactly lattice-matched quaternary alloy at 300 and 77 K.

II. EXPERIMENTS AND RESULTS

A. Quaternary phase diagram

1. Liquidus determination

The 650 °C liquidus isotherms were determined by the seed-dissolution technique.[34–36] A ternary undersaturated In + Ga + As solution was saturated with P at 650 °c by bringing the melt into contact with an InP seed. The As concentration in the ternary solution was always below the solubility limit at 650 °C. The solution and the seed were kept in contact at the temperature for 1 h. The P solubility was calculated from the weight loss of the seed after removal of the solution. The ternary undersaturated solution was made from In, InAs, and GaAs because required amounts of Ga and As must be weighed precisely. Materials used were semiconductor-grade In, InP, InAs, and GaAs. The experi-

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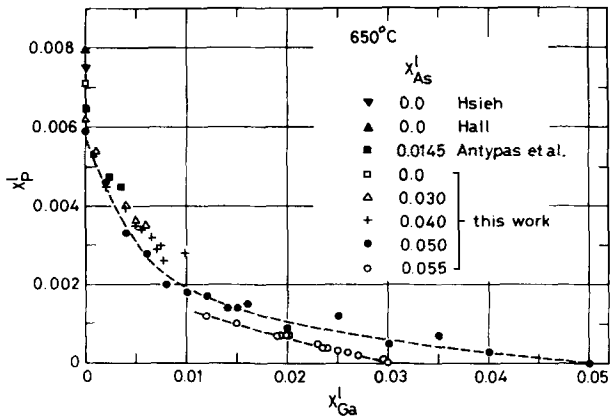

FIG. 1. 650 °C liquidus isotherms in the In-Ga-As-P quaternary system at several X^l_{As} determined by the seed-dissolution technique. Liquidus data includes values from this work (□,Δ,+,●,○), Ref. 44 (▲), Ref. 45 (▲), and Refs. 24 and 25 (■). Broken lines are the experimental liquidus isotherms at $X^l_{As}=0.050$ and 0.055.

mental apparatus consisted of a horizontal furnace system and a conventional sliding graphite boat. Pd-purified H_2 was flowed through the fused-silica tube set in the furnace.

In the strict sense, equilibrium cannot be established between an In+Ga+As+P solution and an InP seed because the solid in equilibrium with such a solution must be a quaternary $In_{1-x}Ga_xAs_{1-y}P_y$ alloy. However, it was found experimentally that a steady state was reached when sufficient InP had dissolved to saturate the liquid phase with P. Similar phenomena were observed in the Al-Ga-As and Al-Ga-P systems by Ilegems and Pearson[34] and Ilegems and Panish,[35] respectively. Their interpretation is that the phenomena occurred by the formation, on the surface of the seed in contact with the melt, of a very thin epitaxial layer of the equlibrium ternary alloy, which protected the seed from further dissolution. In the In-Ga-As-P system, once the liquidus composition is reached by dissolution of the InP seed, the quaternary equilibrium solid forms on it. This solid probably protects the seed from further attack.

In order to know the exact weight loss of the seed after removal of the melt, the quaternary solid film was removed from the seed with nitric acid. In most cases, the solid film could dissolve uniformly and completely over the surface of the seed in the acid. In some cases, however, the film did not grow uniformly and could not be entirely taken off. When this occurred, the experimental results were rejected. Some trials to use other kinds of seed were made. When an InAs seen was used, the seed always dissolved completely in a quaternary melt. Similar observations were reported in other systems.[36–38] In the case of a GaAs seed, the quaternary solid film grown on it could not be taken off by chemical processing without dissolving the seed.

Other techniques such as differential thermal analysis (DTA) and the liquid-observation method[39,40] can be used to determine liqud compositions. We previously used DTA for determination of liquidus isotherms of other quaternary systems.[41,42] However, both liquidus temperatures observed upon cooling and heating were much different from each other because of supercooling and overheating effects.[41,43] There are some reports[28,36] about the liquidus determination of quaternary systems by using the liquid-observation method. These results are generally believed to be accurate to within ±2 °C. The difference between the two results which were determined by the seed-dissolution technique and the liquid-observation method was found to be small in the Al-Ga-P-As system by Ilegems and Panish.[36] Therefore, we adopted the former technique in appreciation of its facility for LPE growth.

Figure 1 shows the experimental 650 °C liquidus isotherms at $X^l_{As}=0.0$, 0.030, 0.040, 0.050, and 0.055, where X^l_i represents the atomic fraction of one element i in the liquid. The broken lines are drawn through experimental points at $X^l_{As}=0.050$ and 0.055. A part of the data at $X^l_{As}=0.030$ and 0.050 were reported in our previous work.[26] The liquidus data at $X^l_{As}=0.0145$ by Antypas and Moon[24] and Antypas and Edgecumbe[25] shown in Fig. 1 in consistent with this work. The solubility of P in an In-P binary melt at 650 °C by Hsieh[44] and Hall[45] is also shown in Fig. 1. The main effect of the addition of Ga to quaternary melts is to appreciably decrease the solubility of P in the melts. Figure 1 shows good reproducibility of these data.

2. Solidus determination

The 650 °C solidus isotherms were determined by electron-microprobe analysis performed on surfaces of $In_{1-x}Ga_xAs_{1-y}P_y$ epitaxial layers grown on Sn-doped InP (111)B substrates. The apparatus was the same as that used for the saturation experiments. Prior to growth, the undersaturated In+Ga+As melt was held on an InP source for 1 h at 650±0.5 °C to achieve saturation. Then it was moved over the substrate, while simultaneously the cooling cycle was started. A constant cooling rate of 0.5 °C/min was used starting from an initial temperature of 650±0.5°C. The melt was then cooled through 12–16 °C before the growth was terminated by pushing the melt away. No supersaturated melts were used in this growth. Just prior to loading, the substrate was etched in a 0.3 vol% bromine-methanol solution for several minutes.

An electron-probe microanalyzer (EPMA), employing wavelength dispersive x-ray detection, was used to measure layer compositions. These compositions were determined from the ratios of the x-ray intensities of the GaK_α, AsK_α, and P$K\alpha$ lines from the unknowns to those of the known stoichiometric standards GaP and InAs. The electron-beam energy was 25 keV. The measured intensities were converted to concentrations by performing the atomic number, absorption, and fluorescence corrections.

The composition of each quaternary layer is supposed to grade to lower Ga and P concentrations with distance away from the substrate as a result of the depletion of the melt in these elements near the growing interface. In order to measure the composition variation with distance from the substrate by EPMA, a layer with a thickness of 15 μm was grown from 600 °C over a 44 °C temperature interval. The Ga concentration scarcely graded, but the P concentration

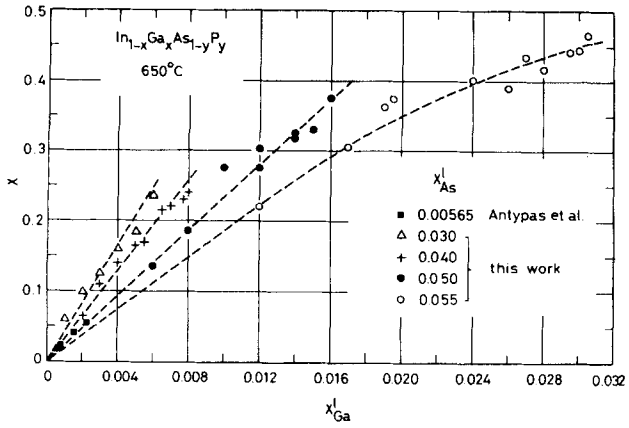

FIG. 2. 650 °C solid solubility isotherms for Ga into $In_{1-x}Ga_xAs_{1-y}P_y$ alloys at several X^l_{As}, including points from this work (Δ, +, ●, ○), and Refs. 24 and 25 (■).

varied from $y=0.62$ (close to the substrate-layer interface) to $y=0.45$ (near the surface of the layer). The composition variation of a layer grown from 650 °C was smaller than that from 600 °C. The layer used for the determination of the solidus isotherms was grown as thinly as possible to know the composition of the initial growth region of the quaternary alloy. Thicknesses of the layers were in a range from 2.5 to 4.0 μm. The depth of the layer under the influence of an electron beam of EPMA was estimated to be less than 2.0 μm.

The 650 °C solidus isotherms in equilibrium with quaternary liquids containing $X^l_{Ga}<0.031$ and $X^l_{As}=0.030$, 0.040, 0.050, and 0.055 were determined. These As compositions and temperature were selected to permit the LPE growth of $In_{1-x}Ga_xAs_{1-y}P_y$ ($0\leqslant x\leqslant 0.47$, $0\leqslant y\leqslant 1.0$) lattice-matched layers on InP under reasonable conditions. Figure 2 shows the solid solubility isotherms for Ga into quaternary alloys at 650 °C. These solidus isotherms indicate that the distribution coefficient for Ga increases with decreasing X^l_{As}, and the solubility of Ga in quaternary alloys is almost linearly dependent on X^l_{Ga} in the InP-rich end ($X^l_{Ga}\leqslant 0.016$) at constant X^l_{As}. Figure 3 shows the solid solubility isotherms for P into quaternary alloys at 650 °C. These isotherms indicate that the distribution coefficient for P increases with decreasing X^l_{As}, and the atomic ratio of P to As in the alloy is nearly independent of X^l_{Ga} in the InP-rich end ($X^l_{Ga}<0.010$) at constant X^l_{As}. When X^l_{Ga} becomes larger than 0.010, the P concentration in alloys decreases remarkably with increasing X^l_{Ga} at constant X^l_{As}. The 650 °C solidus data at $X^l_{As}=0.00565$ by Antypas and Moon[24] and by Antypas and Edgecumbe[25] are also included in Figs. 2 and 3. Present results of the solid solubility for Ga are a little higher than those reported by them, as shown in Fig. 2.

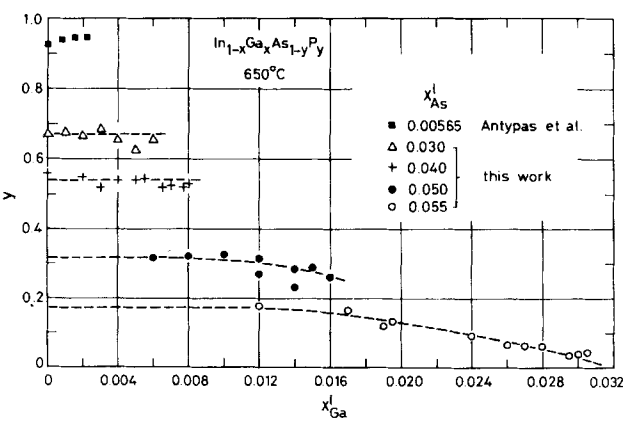

FIG. 3. 650 °C solid solubility isotherms for P into $In_{1-x}Ga_xAs_{1-y}P_y$ alloys at several X^l_{As}, including points from this work (Δ, +, ●, ○), and Refs. 24 and 25 (■).

B. LPE growth conditions for lattice matching

The LPE growth conditions of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ ($0\leqslant x\leqslant 0.47$, $0\leqslant y\leqslant 1.0$) layers on InP were found from the results of the phase-diagram and lattice-constant measurements. Lattice constants were measured by an x-ray-diffraction technique. The precise diffraction angle of the layer was determined from the (444) CuK_β reflection by using the substrate reflection as an internal standard. The double-crystal x-ray-diffraction technique was used for nearly lattice-matched samples. Samples used were 1.5–3.0-μm-thick epitaxial layers grown on InP (111)B substrates by the ramp cooling described in Sec. II A 2.

Figure 4 shows compositions of quaternary melts, X^l_{As}, X^l_P, and X^l_{Ga}, required for the LPE growth of lattice-matched layers at 600 and 650 °C. The results at 600 °C were derived from our previous work.[23] The dotted and chained lines are our experimental results of X^l_{As} and X^l_P at 600 °C, respectively. The broken and solid lines are also our results of X^l_{As} and X^l_P at 650 °C, respectively. These data are listed in Table I. The data reported by numerous authors are also shown in Fig. 4. All of them except Sankaran *et al.*,[30] howev-

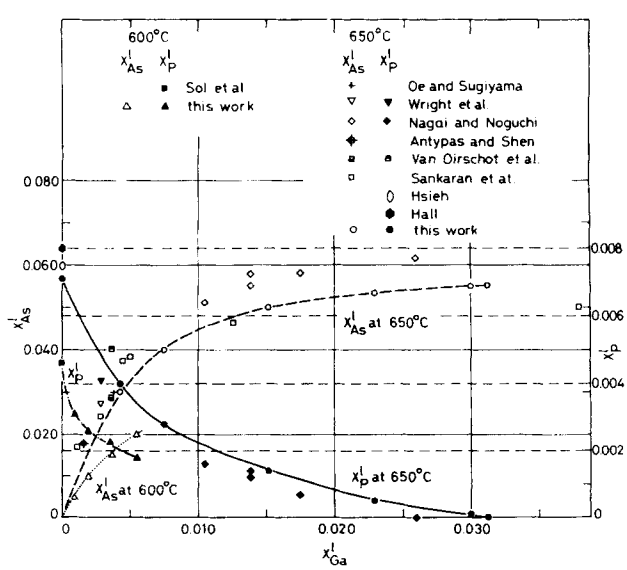

FIG. 4. Liquid compositions (X^l_{Ga}, X^l_{As}, and X^l_P) for the growth of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ layers on InP at 600 and 650 °C. These data include values from this work (Δ, ▲, ○, ●), Ref. 8 (+), Ref. 13 (▽, ▲), Ref. 18 (◇, ◆), Ref. 27 (⊕), Ref. 29 (⬓, ⬒), Ref. 30 (□), Ref. 44 (○), Ref. 45 ●), and Ref. 46 (■).

TABLE I. Liquid and solid compositions at 600 and 650 °C, under the LPE growth conditions to prepare the lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ solid solutions on InP, and the band gaps of these quaternary solids measured at 300 and 77 K.

Growth temp.	Liquid composition (atomic fraction)				Solid composition		Band gap (eV)	
(°C)	X^l_{Ga}	X^l_{In}	X^l_{As}	X^l_P	x	y	300 K	77 K
600	0.0008	0.9911	0.0050	0.0031	0.065	0.855	1.254	1.340
600	0.0018	0.9856	0.0100	0.0026	0.124	0.736	1.189	1.248
650	0.0043	0.9617	0.0300	0.0040	0.152	0.638	1.102	1.168
650	0.0075	0.9497	0.0400	0.0028	0.245	0.456	1.014	1.080
650	0.0152	0.9334	0.0500	0.0014	0.330	0.290	0.914	0.976
650	0.0230	0.9230	0.0535	0.0005	0.390	0.163	0.838	0.898
650	0.0300	0.9149	0.0550	0.0001	0.445	0.045	0.766	0.828
650	0.0310	0.9137	0.0553	0.0	0.470	0.0	0.749	0.806

er, determined the growth conditions by using supersaturated melts by up to 10 °C. Only a few data[13,18,19] about P concentrations in quaternary melts have been reported. We now present the more systematic data at 600 and 650 °C. Our results at 650 °C are in good agreement with those of several investigators.[8,13,29,30] Figure 5 shows the solidus isoconcentration curves of Ga and P at 650 °C. These curves were obtained by interpolation of the results of solidus isotherms shown in Figs. 2 and 3. The relation between the liquid and solid compositions at 650 °C can be shown in Fig. 5. The broken line represents melt compositions (X^l_{As} versus X^l_{Ga}) shown in Fig. 4. By using the information shown in Figs. 4 and 5, lattice-matched layers with various band gaps (from 1.34 to 0.74 eV at RT) can be grown throughout the whole alloy compositional range.

In the growth of $Ga_xAs_{1-x}P$ on GaAs, Stringfellow[47] observed that over a certain range of melt compositions all the LPE layers had the composition that was lattice matched to GaAs, rather than varying in composition in a manner consistent with the bulk equilibrium phase diagram. Our detailed studies and those of Hsieh *et al.*[28] of the composition of $In_{1-x}Ga_xAs_{1-y}P_y$ grown on InP indicate that no appreciable distortion of the crystal composition can be detected.

C. Composition dependence of band gaps

Band gaps were determined by photoluminescence (PL) measurements at 300 and 77 K. Lattice-matched quaternary layers grown on Sn-doped InP (111)*B* substrates were used as PL samples. All the samples were undoped. A cw 50-mW Ar ion laser at 4880 Å was used as the optical-pumping source. The laser light was chopped at a frequency of 200 Hz and focused on the sample to a spot about 0.5 mm in diameter. The PL light emitted from the sample was focused into a JASCO CT-50 monochromator with a PbS detector cooled at 77 K. The output signal was amplified and separated from the noise by a PAR HR-8 lock-in amplifier. Samples were etched in a solution of $H_3PO_4 : H_2O_2 : H_2O = 40 : 1 : 40$ for 30 sec prior to measurements. Hall measurements of lattice-matched layers grown on Cr-doped InP (111)*B* substrates were made in a magnetic field of 2 kG. They were *n* type with carrier concentrations in the range 5×10^{15} to 3×10^{17} cm^{-3}.

Layer thicknesses of PL samples were kept thinner than 1.0 μm because the band gap of the initial growth region of the quaternary layer must be measured. The layer has two areas with different thicknesses. The growth of it was begun by transporting the melt to the substrate, and then the melt was pushed by one-half a length of the substrate in the midst of the growth. The thin ($<1.0\,\mu$m) and thick (2.5–4.0 μm) parts of the layer were used for PL and EPMA measurements, respectively. Layers with lattice mismatch less than 0.05% were used as the lattice-matched PL samples.

The typical PL spectra for various values of alloy-composition parameters at 300 and 77 K are shown in Figs. 6(a) and 6(b), respectively. The spectra were normalized to the same maximum value. The RT band gap of undoped GaAs ($n=1\times10^{16}$ cm^{-3}) was 1.425 eV under the same experimental condition. It is only 10 MeV lower than that reported by Sturge[48]; therefore, the band gap can be determined with an accuracy of 1%. Figure 7 shows the band gap of lattice-matched layers as a function of X^l_{As} as 600 and 650 °C. The band gap varies abruptly with increasing X^l_{As} in the range of the narrower band gap than 0.9 eV. From the information involved in Figs. 4, 5, and 7, the growth conditions for lattice-matched layers with desired band gaps can be easily

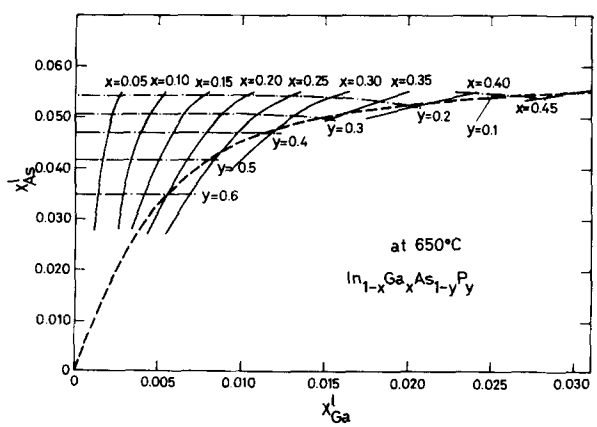

FIG. 5. Solidus isoconcentration curves of Ga and P at 650 °C. Broken line represents liquid compositions (X^l_{Ga} and X^l_{As}) for the growth of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ layers on InP at 650 °C.

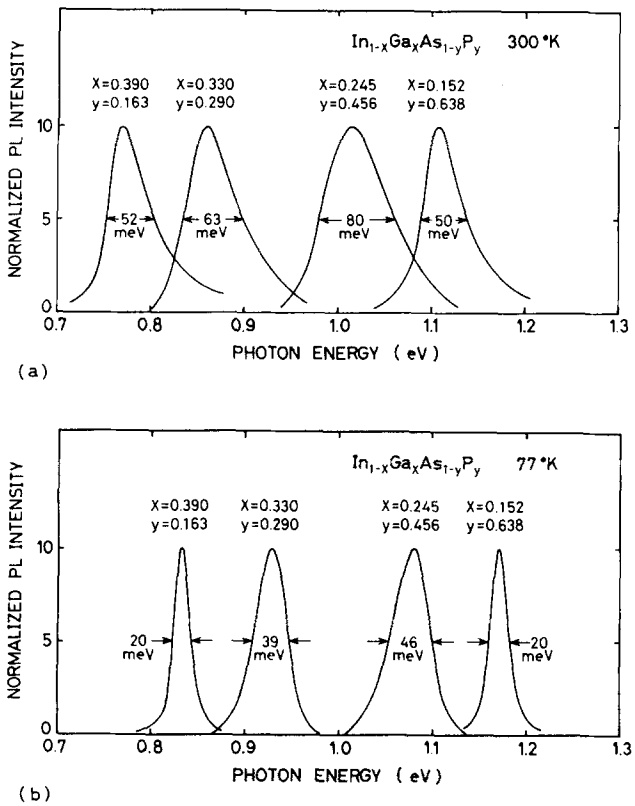

FIG. 6. Typical PL spectra of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ layers for various values of alloy-composition parameters x and y; (a) at 300 K and (b) at 77 K.

found. Figure 8 shows the composition dependence of the band gap of the lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ ($0 \leqslant x \leqslant 0.47$, $0 \leqslant y \leqslant 1.0$) alloy at 300 and 77 K. These values are also listed in Table I. The solid line shows alloy compositions of lattice-matched layers calculated on the basis of Vegard's law. The experimental points are in good agreement with the calculated results. The band gap at each temperature is linearly dependent on alloy composition and is expressed as a function of composition by $E_g = 1.35 - 1.30x$

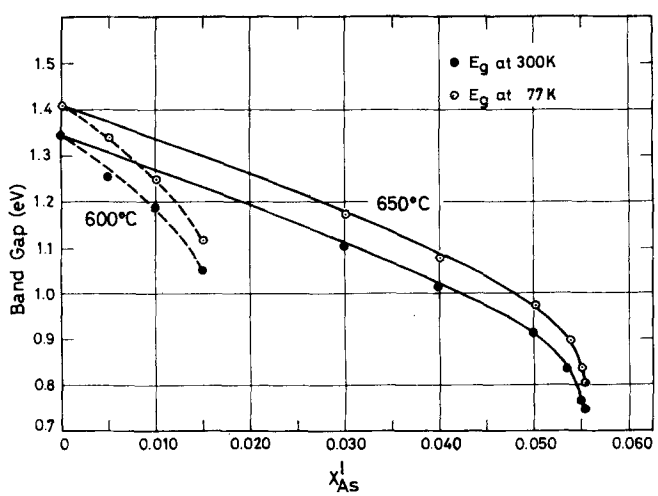

FIG. 7. Measured band gaps of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ alloys as a function of liquid composition (X^l_{As}) at 600 and 650 °C.

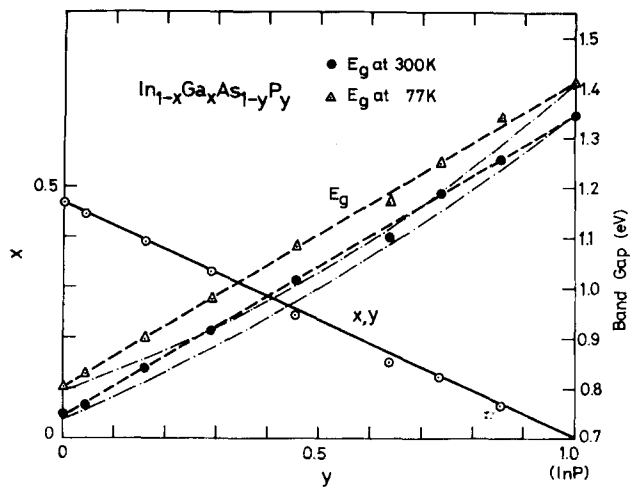

FIG. 8. Measured band gaps of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ alloys as a function of alloy-composition parameters x and y. Broken and chained lines show the experimental and calculated results of the band gap, respectively. Solid line is the calculated alloy composition on the basis of Vegard's law (see text).

at 300 K, and $E_g = 1.41 - 1.30x$ at 77 K. The broken lines show the composition dependence of the band gap at 300 and 77 K, and both lines have the same slope. Pearsall *et al.*[16] presented the equation $E_g = 1.35 - 1.14\times$ at 300 K, but it is not consistent with present data. The energy shift ΔE_g between the band gaps at 300 and 77 K was found to be constant over the whole composition. The value of ΔE_g was equal to 0.06 eV.

Numerous experimental results of the relation between emission wavelength and solid composition have been reported.[3-18,27-29] Figure 9 shows these results, but reports in which a degree of lattice matching was not clearly described were excepted. The broken lines are present experimental results shown in Fig. 8. These wavelengths were measured

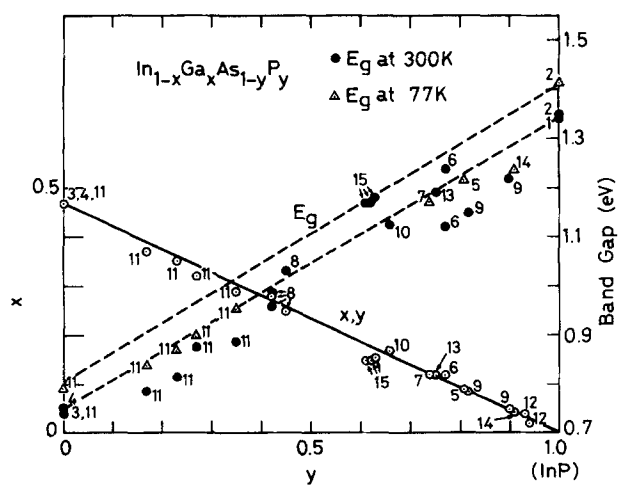

FIG. 9. Reported relation between band-gap and alloy composition for lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ alloys (see text). These data consist of values from Ref. 1 (1), Ref. 2 (1), Ref. 49 (2), Ref. 3 (3), Ref. 4 (4), Ref. 5 (5), Refs. 6 and 7 (6), Ref. 12 (7), Ref. 13 (7), Refs. 14 and 17 (8), Ref. 15 (9), Ref. 16 (10), Ref. 18 (11), Ref. 25 (12), Ref. 23 (13), Ref. 27 (14), and Ref. 29 (15). Broken and solid lines represent present experimental results shown in Fig. 8.

TABLE II. Published equations for band gap versus composition for the four ternary boundaries in the $In_{1-x}Ga_xAs_{1-y}P_y$ system.

System	Equation	Temp. (K)	Ref.
$InAs_{1-y}P_y$	$E_g=0.35+y-0.101y(1-y)$	300	53
$GaAs_{1-y}P_y$	$E_g=1.42+1.33y-0.210y(1-y)$	300	54
$In_{1-x}Ga_xP$	$E_g=1.35+1.40x-0.758x(1-x)$	300	55
$In_{1-x}Ga_xAs$	$E_g=0.35+1.07x-0.46x(1-x)$	300	56
$InAs_{1-y}P_y$	$E_g=0.412+0.995y-0.281y(1-y)$	77	53
$GaAs_{1-y}P_y$	$E_g=1.514+1.363y-0.210y(1-y)$	77	57
$In_{1-x}Ga_xP$	$E_g=1.414+1.452x-0.758x(1-x)$	77	58
$In_{1-x}Ga_xAs$	$E_g=0.41+1.10x-0.53x(1-x)$	77	56

by using various methods such as PL,[23,29] LED-emission,[15-18] and laser-emission[5-7,12-14] measurements. Impurity densities, dopants, thicknesses, and growth conditions of their samples varied from one report to another. In the strict sense, these data cannot be compared with each other and ours. The results reported by Hsieh *et al.*,[7] Pearsall *et al.*,[16] Oe *et al.*,[14,17] and Wieder *et al.*[26] for $In_{1-x}Ga_xAs_{1-y}P_y$, and by Sankaran *et al.*,[3] Takeda *et al.*,[4] and Nagai and Noguchi[18] for $In_{0.53}Ga_{0.47}As$ are consistent with present results. The band gaps of InP at 300 and 77 K were 1.345 and 1.41 eV, respectively. They are also in good agreement with the values determined by electroreflectance measurements (1.34 eV at 300 K),[1] by photoemission spectroscopy (1.34 eV at 300 K),[2] and by optical-absorption and PL measurements (1.351 eV at 300 K; 1.414 eV at 77 K).[49] The results for stimulated emission from InP diode lasers (1.37 eV at 77 K)[51] and for spontaneous emission from InP LED's (1.30 eV at 300 K; 1.378 eV at 77 K)[52] are lower than the present results.

III. DISCUSSION

The composition dependence of the band gap of the lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ alloy was calculated by using an interpolation formula proposed by Moon *et al.*[33] The published equations for band gap versus composition at 300 and 77 K for the four ternary boundaries in the quaternary system were used for this calculation and they are listed in Table II. The equations for the quaternary system are given by

$$E_g=0.35+1.07x+y+0.33xy$$
$$-(0.460+0.298y)x(1-x)-(0.101+0.109x)y(1-y)$$

at 300 K, and

$$E_g=0.41+1.10x+1.004y+0.352xy$$
$$-(0.530+0.228y)x(1-x)-(0.281-0.071x)y(1-y)$$

at 77 K. The chained lines shown in Fig. 8 are calculated results by using these equations. The calculated variation of the band gap with alloy composition is nonlinear and differs from the present experimental results.

In general, the experimentally determined lowest direct band gap in many III-V ternary alloys has an approximately quadratic composition dependence. Thompson and Woolley[59] attributed the deviation from linearity to the effect of microscopic inhomogeneity in the crystal potential. Van Vechten and Bergstresser[60] showed that even in the virtual-crystal approximation[61] this deviation could not be neglected, and proposed that the total bowing parameter, which was a measure of the nonlinearity, should be the sum of the intrinsic bowing found in the virtual-crystal approximation and the extrinsic bowing due to effects of aperiodicity of the crystal potential. Therefore, it is generally more reasonable that the band gap of the quaternary alloy has a nonlinear composition dependence like the calculated results shown in Fig. 8. In this work, the experimental band shows a linear composition dependence to first approximation. However, the exact argument concerning the bowing cannot be made because of the inherent measurement errors and the limited data available. In order to discuss the bowing, further studies are desired.

In the quaternary system, very thin and exactly lattice-matched epitaxial layers can be grown. In ternary systems, however, it is usually difficult to obtain epitaxial layers with no misfit strains or crystals with good uniformity of composition. Therefore, it must be noted that in the present experiments such quaternary layers with good uniformity of composition and no misfit strains were used as samples for PL measurements of band gaps.

IV. CONCLUSIONS

The In-Ga-As-P quaternary phase diagram was experimentally determined at 650 °C. The LPE growth conditions of exactly lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y$ ($0\leqslant x\leqslant 0.47$, $0\leqslant y\leqslant 1.0$) layers on InP (111)*B* substrates were obtained from the results of the phase-diagram and lattice-constant measurements. The band gaps of the lattice-matched layers were found to be linearly dependent on alloy composition x and y by PL measurements at 300 and 77 K.

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