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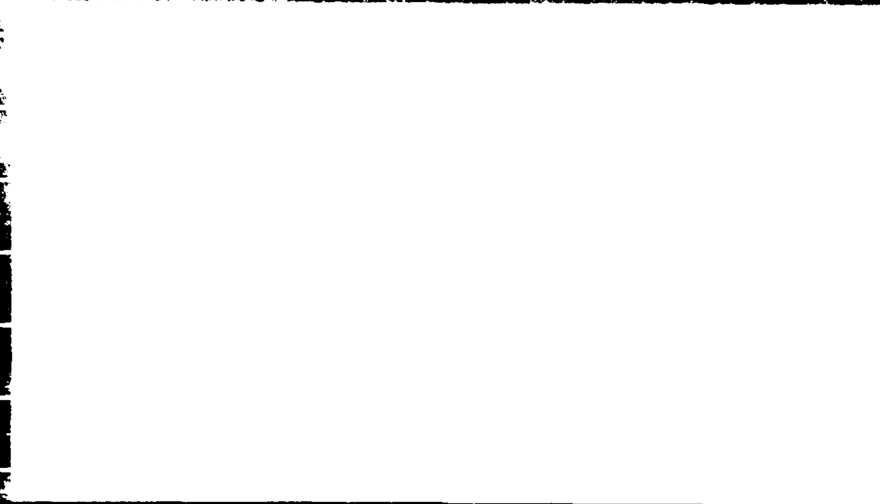

Final Technical Report

"Optoelectronic III-V Heterostructures on Si Substrates"

The results of a three-year program to investigate the epitaxial growth of the III-V semiconductors, particularly the InGaAsP/InP materials system, on Si substrates is presented. The heterostructures were grown by gas-source molecular beam epitaxy (GSMBE) and were designed for applications in optoelectronics. With regard to growth of InP and InGaAsP alloys on Si, the research program was successful in reducing misfit dislocations and stacking faults resulting from the 8% lattice mismatch between InP and Si. A strained layer superlattice of $In_xGa_{1-x}P/In_yGa_{1-y}P$ ($x \neq y$) was used as a buffer layer. Detailed characterization using double crystal x-ray diffraction, photoluminescence, and Hall measurements revealed high quality InP, $In_{0.53}Ga_{0.47}As$ and $In_{0.83}Ga_{0.17}As_{0.37}P_{.63}$ could be obtained with GSMBE growth on misoriented Si substrates and thermal annealing after growth.

The use of InGaP as buffer layers led to extensive development, in parallel with the InP-on-Si work, of InGaP layers by GSMBE. The Schottky barrier energies for both n-type and p-type materials were measured for the first time for the wide bandgap alloys InGaP and InGaAlP when lattice matched to GaAs. A gold metallization was used and the barrier energy was measured on chemically etched surfaces using conventional current-voltage and photoemission techniques. In the range of alloy composition investigated, the sum of the n-type and p-type barriers was found not to equal the value of the energy gap determined from optical measurements. For $In_xGa_{1-x-y}Al_yP$ lattice matched to GaAs, the n-type Schottky barrier energy was found to decrease, while the p-type barrier increased, with increasing Al content y.

Deep level transient spectroscopy was also used to characterize n-type $In_{0.48}Ga_{0.52}P$. Only one electron trap was detected in both unintentionally doped and Si-doped material, with the thermal emission energy barrier varying somewhat with measurement conditions. For a bias pulse duration of 10 ms, the emission barrier energy was 0.24±0.3 ev and the capture barrier energy was 0.06±0.02 eV. The trap concentration was less than $3x10^{14}$ cm^{-3} and was found to be independent of Si doping for concentrations up to $4x10^{18}$ cm^{-3} and to oxygen contamination in the range $(0.5-1.5)x10^{18}$ cm^{-3}. These results indicate that GSMBE InGaP has a lower or comparable trap density to any other method of epitaxial growth.

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"Optoelectronic III-V Heterostructures on Si Substrates"

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Summary

The results of a three-year program to investigate the epitaxial growth of the III-V semiconductors, particularly the InGaAsP/InP materials system, on Si substrates is presented. The heterostructures were grown by gas-source molecular beam epitaxy (GSMBE) and were designed for applications in optoelectronics. With regard to growth of InP and InGaAsP alloys on Si, the research program was successful in reducing misfit dislocations and stacking faults resulting from the 8% lattice mismatch between InP and Si. A strained layer superlattice of $In_xGa_{1-x}P/In_yGa_{1-y}P$ ($x \neq y$) was used as a buffer layer. Detailed characterization using double crystal x-ray diffraction, photoluminescence, and Hall measurements revealed high quality InP, $In_{0.53}Ga_{0.47}As$ and $In_{0.83}Ga_{0.17}As_{0.37}P_{.63}$ could be obtained with GSMBE growth on misoriented Si substrates and thermal annealing after growth.

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Deep level transient spectroscopy was also used to characterize n-type $In_{0.48}Ga_{0.52}P$. Only one electron trap was detected in both unintentionally doped and Si-doped material, with the thermal emission energy barrier varying somewhat with measurement conditions. For a bias pulse duration of 10 ms, the emission barrier energy was 0.24±0.3 ev and the capture barrier energy was 0.06±0.02 eV. The trap concentration was less than 3×10^{14} cm^{-3} and was found to be independent of Si doping for concentrations up to 4×10^{18} cm^{-3} and to oxygen contamination in the range $(0.5\text{-}1.5) \times 10^{18}$ cm^{-3}. These results indicate that GSMBE InGaP has a lower or comparable trap density to any other method of epitaxial growth.

I. Introduction

The objective of this AFOSR research program was to investigate the epitaxial growth of heterostructures of InP and InGaAsP on Si substrates. The technique of growth was gas-source molecular beam epitaxy (GSMBE), a technique ideally suited for quantum well heterostructures containing phosphide layers. Our laboratory at Colorado State was the first US university to make a GSMBE system operational, partially as a result of a DoD URIP grant administered by AFOSR. The research focused on exploring methods to reduce misfit dislocations and thus, achieve InGaAsP/InP heteroepitaxial material suitable for high quality optoelectronic devices on Si substrates. InP and lattice-matched InGaAsP alloys are the primary material for high speed optoelectronic telecommunication systems, and an InP-on-Si materials technology would enable VLSI photonics to become a reality. Furthermore, an InP-on-Si technology has applications in light weight, radiation hard InP solar cells for space-borne systems and for III-V optoelectronic devices operating at wavelengths (λ >1.2 μm) requiring a transparent substrate.

In addition to systematically studying the conditions for optimum GSMBE growth, extensive optical, electrical, and structural characterization of the epitaxial films was carried out in order to assess their suitability for device applications. Collaboration with other researchers included transmission electron microscopy analysis by M. Al-Jassim at the National Renewal Energy Laboratory and N. Otsuka at Purdue University and mobility profiling by J. P. Lorenzo at AF Hanscom Laboratories.

II. Major Accomplishments

The major accomplishments of the InP-on-Si program are as follows:

* First successful MBE growth of InP on Si,

* First report of the effects of dislocations on the carrier mobility in III-V films on Si,

* Using strained layer superlattices of InGaP/InP as buffer layers, the adverse effects of dislocations were substantially reduced, and

* Established methods for growth of high quality InP, InGaAs, InGaAsP films on Si.

The use of InGaP/InP buffer layers led to extensive development, in parallel with the InP-on-Si work, of high quality InGaP alloy layers by gas-source MBE. Using AFOSR support and support from other sources, the following additional major accomplishments were obtained:

* First direct measurement of the InGaP/GaAs heterojunction band offset energies,

* First report of picosecond carrier dynamics in InGaP,

* First measurement of Schottky barrier energies in n-type and p-type InGaP and InGaAlP,

* First systematic study of deep levels in InGaP grown by MBE, and

* Discovery of a spontaneous change in growth orientation triggered by heterointerfaces of InGaP/GaAs.

III. Publications Under AFOSR Sponsorship

(Total number during same period = 36)

Key: *+ Work preformed in collaboration with workers at Air Force Hanscom Laboratories.*
** Work preformed in collaboration with workers at Purdue University who are sponsored under a separate AFOSR contract.*

1. T.E. Crumbaker, H.Y. Lee, M.J. Hafich, G.Y. Robinson, M.M. Al- Jassim, and K.M. Jones, "Heteroepitaxy of InP on Si: Reduction of Defects by Substrate Misorientation and Thermal Annealing", J. Vac. Sc. Technol. **B 8** (2), 261 (Mar/April 1990).

2. M. A. Haase, M. J. Hafich, and G.Y. Robinson, "Internal Photoemission and Energy Band Offsets in GaAs-GaInP pIN Heterojunctions", Appl. Phys. Letters **58** (6), 616 (11 February 1991).

3. J. Chen, J.R. Sites, I.L. Spain, M.J. Hafich, and G.Y. Robinson, "The Band Offset of GaAs/InGaP Measured Under Hydrostatic Pressure", Appl. Phys. Letters **58**(7), 744 (18 February

1991).

4. M. J. Hafich, H. Y. Lee, P. Silvestre, and G. Y. Robinson, "GSMBE Growth of GaAs at Low AsH_3 Cracking Temperatures", J. Crystal Growth **111**, 507 (1991).

5. P.Thiagarajan, J.F. Schmerge, C.S. Menoni, M. Marconi, O.E. Martinez, J.J. Rocca, M. J. Hafich, H.Y. Lee, and G.Y. Robinson, "Picosecond Absorption Dynamics of Photoexcited InGaP Epitaxial Films", Appl. Phys. Letters **59** (1), 90 (1 July 1991).

+ 6. T.E. Crumbaker, M.J. Hafich, G.Y. Robinson, K.M. Jones, M.M. Al- Jassim, A. Davis, and J.P. Lorenzo, "The Influence of Dislocation Density on Electron Mobility in InP Films on Si", Appl. Phys. Letters **59** (9), 1090 (26 August 1991).

* 7. Y. Nakamura, K. Mahalingam, N. Otsuka, H.Y. Lee, M.J. Hafich, and G.Y. Robinson, "Spontaneous Change of Growth Orientation of InGaP/GaAs Superlattices in MBE", J. Vac. Sc. Technol. **B 9** (4), 2445 (July/Aug 1991).

8. M.J. Hafich, H.Y. Lee, T.E. Crumbaker, T.J. Vogt, P. Silvestre, and G.Y. Robinson, "Gas-Source MBE Growth of InGaAlP", J. Vac. Sc. Technol. **B 10** (2), 969 (Mar/Apr 1992).

9. G.A. Patrizi, H.Y. Lee, M.J. Hafich, P. Silvestre, and G.Y. Robinson, "Excitonic Absorption in InGaP/GaAs Multiple Quantum Wells", Electronics Letters **27**, 2363 (5 December 1991).

10. A. Nanda, M.J Hafich, T.J. Vogt, L.M. Woods, and G.Y. Robinson, "Measurement of Schottky Barrier Energy on InGaP and InGaAlP Films Lattice Matched to GaAs", Appl. Phys. Letters **61**, 81 (6 July 1992).

11. M.J. Hafich, L.M. Woods, H.S. Kim, G.A. Patrizi, and G.Y. Robinson, "On-Site Phosphine Purification for Gas-Source MBE of InGaAlP", to appear in J. Crystal Growth, 1993.

12. O. Buccafusca, J.A.L. Chilla, C.S. Menoni, J.J. Rocca, M.J. Hafich, L.M. Woods, and G.Y. Robinson, "Non-resonant Tunneling in InGaP/InAlP Asymmetric Double Quantum Wells", to appear in Appl. Phys. Letters, 1993.

13. H.S. Kim, M.J. Hafich, G.A. Patrizi, A. Nanda, T.J. Vogt, L.M. Woods, and G.Y. Robinson, "Electron Traps in InGaP Grown by Gas-Source Molecular Beam Epitaxy", submitted to Appl. Phys. Letters, December 1992.

IV. Conference Presentations Under AFOSR Sponsorship
(Total number in same period = 48)

1. M. J. Hafich and G. Y. Robinson, "Gas-source MBE Technology for Growth of III-V Heterostructures", 36th National Symposium of the National Vacuum Society, Boston, MA, October, 1989.

2. T. E. Crumbaker, H. Y. Lee, H. J. Hafich, G. Y. Robinson, M. M. Al-Jassim, and K. M. Jones, "Heteroepitaxy of InP on Si: Reduction of Defects by Substrate Misorientation and Thermal

Annealing", Tenth Molecular Beam Epitaxy Workshop, North Carolina State University, September 1989.

3. T. E. Crumbaker, M. J. Hafich, G. Y. Robinson, A. Davis, and J. P. Lorenzo, "Heteroepitaxy on Si: Variation of Electron Concentration and Mobility with Depth", Second International Conference on Indium Phosphide and Related Materials, Denver, April 1990.

4. G. A. Patrizi, D. G. Wu, M. J. Hafich, H. Y. Lee, P. Silvestre, and G. Y. Robinson, "Quantum-Confined Stark Effect in InGaP/GaAs Multiple Quantum Wells", Electronic Materials Conference, Santa Barbara, June 1990.

5. M. J. Hafich, H. Y. Lee, P. Silvestre, and G. Y. Robinson, "GSMBE Growth of GaAs at Low AsH_3 Cracking Temperatures", Sixth International Conference on Molecular Beam Epitaxy, San Diego, August 1990.

6. P. Thiagarajan, J.F. Schmerge, C.S. Menoni, M. Marconi, O.E. Martinez, J.J. Rocca, M. J. Hafich, H.Y. Lee, and G.Y. Robinson, "Study of Picosecond Carrier Dynamics in Photoexcited InGaP Epitaxial Films", Quantum Electronics Laser Science Conference, Baltimore, May 1991.

* 7. K. Mahalingam, Y. Nakamura, N. Otsuka, H.Y. Lee, M.J. Hafich, and G.Y. Robinson, "Spontaneous Change of Growth Orientation during MBE of InGaP/GaAs Superlattices", Electronic Materials Conference, Boulder, June 1991.

8. M.J. Hafich, H.Y. Lee, T.E. Crumbaker, T.J. Vogt, P. Silvestre, and G.Y. Robinson, "Gas-Source MBE Growth of InGaAlP", Eleventh Molecular Beam Workshop, Austin, September 1991.

9. M.C. Marconi, C.S. Menoni, O. Buccafusca, M. Prasad, J.J. Rocca, M.J. Hafich, G.Y. Robinson, and S. Goodnick, "Photoexcited Carrier Relaxation in InGaP Bulk and InGaP/InAlP Multiple Quantum Wells", Conference on Lasers and Electro-Optics (CLEO), Anaheim, May 1992.

10. A. Nanda, M.J Hafich, T.J. Vogt, L.M. Woods, and G.Y. Robinson, "Schottky Barrier Energy for InGaP and InGaAlP Films Lattice Matched to GaAs", Electronic Materials Conference, Boston, June 1992.

11. H.S. Kim, A. Nanda, M.J. Hafich, T.J. Vogt, L.M. Woods, and G.Y. Robinson, "Electron and Hole Traps in InGaP Grown by Gas-Source MBE", Electronic Materials Conference, Boston, June 1992.

12. M.J. Hafich, L.M. Woods, H.S. Kim, and G.Y. Robinson, "On-Site Phosphine Purification for Gas-Source MBE of InGaAlP", Seventh International Conference on Molecular Beam Epitaxy, Germany, August 1992.

13. G.Y. Robinson, "Gas-Source Molecular Beam Epitaxy of III-V Semiconductors" (invited paper), Sixth Canadian Semiconductor Conference, Ottawa, August 1992.

14. M.J. Hafich, H.S. Kim, G.A. Patrizi, and G.Y. Robinson, "The Effect of Oxygen on the

Properties of InGaAlP Grown by Gas-Source MBE", North American Conference on Molecular Beam Epitaxy, Ottawa, Canada, October 1992.

15. O. Buccafusca, J.L.A. Chilla, C.S. Menoni, J.J. Rocca, M.J. Hafich, L.M. Woods, and G.Y. Robinson, "Picosecond Photoluminescence Study of Tunneling in InGaP/InAlP Asymmetric Double Quantum Wells," Conference on Quantum Electronics and Lasers, Baltimore, May 1993.

16. M. Prasad, C.S. Menoni, O.E. Martinez, D. Patel, J.L.A. Chilla, O. Buccafusca, J.J. Rocca, M.J. Hafich, and G.Y. Robinson, "Transient Grating and Time-Resolved Photoluminescence Measurements in InGaP/InAlP Quantum Wells", Conference on Quantum Electronics and Lasers, Baltimore, May 1993.

V. Personnel

A. Students Supported by AFOSR:

1. T. E. Crumbaker, Physics, PhD Oct 1991, US citizen. Now a Post-Doctoral Fellow, USAF Hanscom Labs, MA.

2. H. Y. Lee, Electrical Engineering, PhD Dec 1991, US citizen. Now a research scientist at WPAFB, Ohio.

3. A. Nanda, Electrical Engineering, MS June 1992, non-US citizen. Now an engineer at International Rectifier Corporation, California.

4. T. J. Vogt, Electrical Engineering, PhD, US citizen.

5. P. Thiagarajan, Electrical Engineering, PhD, non-US citizen (green card).

B. Post-Doctorates Supported by AFOSR:

1. M. J. Hafich, PhD in Electrical Engineering from University of Minnesota, US citizen.

VI. Research Results

Many of our results on growth of InP and InGaAsP layers on Si has been described in detail in previous AFOSR reports for this contract. Thus, we summarize here only the highlights of the results of GSMBE growth of InP-on-Si structures below. In the remaining sections, we present recent results on measurement of Schottky barrier energies on InGaP and InGaAlP and on determination of the electron traps in InGaP.

A. InP and InGaAsP on Si

A systematic study of the growth and properties of single-crystal InP and InGaAsP films on Si substrates has been carried out using GSMBE. To accommodate the 8% lattice mismatch between InP and Si, three types of epitaxial buffer layers were used, and for purposes of comparison, InP was also grown on commercial GaAs-on-Si wafers. InP films of nominally 4 μm in thickness were grown on both (100) orientated and (100) misoriented 4° toward the [011] Si wafers. Using a buffer layer of four $In_xGa_{1-x}P/In_yGa_{1-y}P$ ($x \neq y$) strained-layer superlattices (SLS), InP films on misoriented substrates were found to be mirror-like over the entire 3-inch wafer and exhibited a factor of two lower dislocation density than for films on oriented substrates, as determined by double crystal x-ray (DCXR) diffraction and transmission electron microscopy (TEM). Post-growth annealing resulted in a significant enhancement of the near band-edge photoluminescence (PL) emission and a decrease in the density of dislocations and stacking faults. Growths on GaAs-on-Si substrates produced InP films with very good morpholgy but otherwise, the DCXR and PL linewidths were similar to InP grown using the InGaP SLS buffer layers. The best results for InP films were obtained for annealed films on misoriented substrates using InGaP SLS, with an x-ray line of 400 arc sec, a TEM dislocation density of approximately 1×10^8 cm^{-2}, a stacking fault density of 1×10^7 cm^{-2}, and a PL linewidth of 6 meV at 13 K.

In addition, the average electron mobility and dislocation density were measured as functions of the film thickness. In a region extending from about 2 μm form the Si interface, the density of dislocations were found to be very high, the dislocations become entangled, and formed clusters. The clusters scatter the electrons in the InP and greatly reduce the mobility. Beyond 2 μm, clustering was not observed, the density of dislocations decreased, and the average mobility increased with increasing film thickness. Thus, the threading dislocations created by the large InP-Si lattice mismatch can significantly degrade the carrier mobility in the InP near the Si substrate. However, for film thicknesses of the order of 4 μm or more, the mobility of InP-on-Si approached that of bulk InP.

In addition to InP, we have examined the growth of InGaAsP alloy films on 4-μm thick layers of InP on Si. Two lattice-matched alloy compositions were chosen: $In_{0.53}Ga_{0.47}As$ and $In_{0.83}Ga_{0.17}As_{0.37}P_{0.63}$ (composition corresponding to a bandgap emission at λ = 1.15 μm). Using

DCXR diffraction, the annealed InGaAs and InGaAsP films were found to be the same crystal quality as the best of our InP-on-Si films. For the InGaAs/InP/Si samples, the lowest DCXR linewidth obtained was 530 arc sec and the PL linewidth at 300K was 89 meV. For the InGaAsP/InP/Si samples, the lowest DCXR linewidth was 370 arcsec and the PL linewidth at 300K was 71 meV. These results compare very favorably with state-of-the-art InP-on-Si obtained with other epitaxial growth methods.

In summary, high quality InP, InGaAs, and InGaAsP were grown on Si substrates by gas-source MBE. The layers were single crystal over the entire 3-inch diameter Si wafer, with excellent morphology and with adequate electron mobilities for films over 4 μm in thickness. Strong PL emission at room temperature from lightly doped InGaAs/InP/Si and InGaAsP/InP/Si indicate the feasibility of using these materials for optoelectronic applications.

B. Schottky Barriers on InGaP and InGaAlP

Heterostructures of the semiconducting alloys InGaP and InGaAlP, when lattice-matched to GaAs substrates, are finding an increasing number of applications in laser diodes [1-5], light-emitting diodes [6,7] and bipolar transistors [8,9]. However, little is known about the surface properties of these alloys. In particular the position of the Fermi level E_f relative to the band edges will control the nature of the surface space charge region (i.e., depletion or accumulation) and thus could significantly affect device performance.

Traditionally, measurements of the surface barrier energy in Schottky diodes, when formed with a non-reactive metal such as Au, are used to determine E_f on chemically etched surfaces. Kuech and McGaldin [10] have measured the dependence of the Schottky barrier energy ϕ_{Bn} on the In mole fraction x in n-type Au/$In_xGa_{1-x}P$ diodes. Using the dependence of the bandgap energy E_g on x and the relation

$$\phi_{Bn} + \phi_{Bp} = E_g, \qquad (1)$$

they calculated the Schottky barrier energy ϕ_{Bp} for p-type $In_xGa_{1-x}P$. They found ϕ_{Bp} to be independent of composition and thus concluded that InGaP alloys obey the "common anion" rule,

where it is assumed that the position of E_f at the surface relative to the valence band is fixed and determined by the anion of the semiconductor. We report here the first direct measurements of both ϕ_{Bn} and ϕ_{Bp} for Au/$In_{0.48}Ga_{0.52}P$ barriers and do not find agreement with Eq. (1). Furthermore, we report values of Schottky barrier energies for the quaternary alloy $In_xGa_{1-x-y}Al_yP$ for a range of the Al mole fraction y from 0 to 0.27 when lattice matched to GaAs (x = 0.48).

Schottky diodes were formed on InGaP and InGaAlP films grown by gas-source molecular beam epitaxy (MBE) using techniques previously reported [11,12]. The films were nominally lattice matched to (100) GaAs substrates and the dopants were Be for the p-type films and Si for the n-type films [13]. The InGaP epitaxial structures consisted of a GaAs buffer layer (0.15 μm thickness) and a InGaP active layer (0.9 μm). The InGaAlP test structures consisted of a GaAs buffer layer (0.15 μm thickness), a unintentionally-doped InGaAlP buffer layer (0.5 μm), a InGaAlP active layer (1.0 μm), and a heavily doped (~10^{18} cm^{-3}) GaAs contact layer. The top GaAs contact layer was found to be necessary in the InGaAlP samples in order to obtain low resistance ohmic contacts to the InGaAlP active layer. Room temperature photoluminescence (PL) and double crystal x-ray diffraction (DCXR) were used to determine bandgap energy and alloy composition. The InGaP and InGaAlP heterostructures were of high crystal quality as evidenced by narrow DCXR peaks (i.e., 25 arc sec) and lattice mismatch relative to the GaAs substrate of less than 800 ppm [13]. The conductivity type and carrier concentration of the active layers were determined, after removal of the GaAs contact layer in the InGaAlP samples, by either Hall measurements or capacitance-voltage measurements using a Hg probe.

The Schottky diodes were fabricated by first making ohmic contacts to the top layer using In-Sn (n-type) or In-Zn (p-type) eutectic preforms, alloyed at 300°C for 3 minutes. The InGaP samples were then cleaned in $HF:HCl:H_2O:H_2O_2$ (12:12:48:1) solution just prior to metal deposition. For the InGaAlP samples, the GaAs contact layer was selectively removed in a solution of $NH_4OH:H_2O_2:H_2O$ (2:1:10). The samples were immediately placed in a oil-diffusion pumped evaporator and semi-transparent Au dots (approximately 25 nm thick) having a diameter of 350 μm were deposited using a shadow mask. Another deposition with a second shadow mask aligned with first, was used to provide small area Au/Ni bonding pads at the perimeter of the Au dots. Each deposition was carried out at a pressure less than 10^{-6} Torr.

Two standard methods were used to measure ϕ_B: (1) the forward-biased current-voltage (I-V) method, and (2) the internal photoemission method. For the I-V method, the current was assumed to flow by thermionic emission and curve fitting the data yielded ϕ_B and the diode ideality factor n using the electron effective mass 0.11 m_o and the hole effective mass 0.6 m_o for both $In_{0.48}Ga_{0.52}P$ [14] and $In_{0.48}Ga_{0.52-y}Al_yP$ [15]. The photoresponse measurements utilized a conventional monochromator and lock-in amplifier, the diodes were illuminated on the front surface, and the photocurrent was measured at zero bias.

All diodes exhibited rectifying I-V characteristics with reverse breakdown voltages of 3 to 7 V and typical dark currents of 0.3 μA at a reverse bias of 2 V. The results of the measurement of ϕ_{Bn} and ϕ_{Bp} are summarized in Table 1, along with the values of E_g determined from the photoresponse measurements. All of the values of ϕ_B in Table 1 have been corrected for the

Table 1. Schottky barrier energies for $In_xGa_{1-x-y}Al_yP$ with x=0.48.

y	Type & Carrier Concentration (cm^{-3}) and type	I-V Barrier Energy (eV) ϕ_B	n	Photoresponse Energy (eV) ϕ_B	$\phi_{Bn}+\phi_{Bp}$	E_g
0	$n=2x10^{17}$ $p=2x10^{17}$	0.95 0.68	1.05 1.28	1.009 0.706	1.715	1.866 1.863
0.04	$n=2x10^{17}$	0.86	1.43	1.003	...	2.067
0.10	$n=2x10^{17}$ $p=5x10^{16}$	0.83 0.70	1.36 1.40	0.951 0.746	1.697	2.050 2.033
0.27	$n=2x10^{17}$	.079	2.08	...	...	2.150

image-force barrier lowering energy $\Delta\phi_B$ [16] using the measured carrier concentrations.

With regard to the ϕ_B values obtained from the I-V measurements, for thermionic emission to be the only current flow mechanism the ideality factor n should be less than 1.1 [16], which is

not the case for most of our diodes. Thus, it is most likely that tunneling through the barrier is also occurring in forward bias and the ϕ_B(I-V) values in Table 1 underestimate the actual value of the barrier energy. This conclusion appears to be supported by the photoresponse data. Hence, we believe the photoresponse method to be the more accurate of the two methods used to obtain ϕ_B.

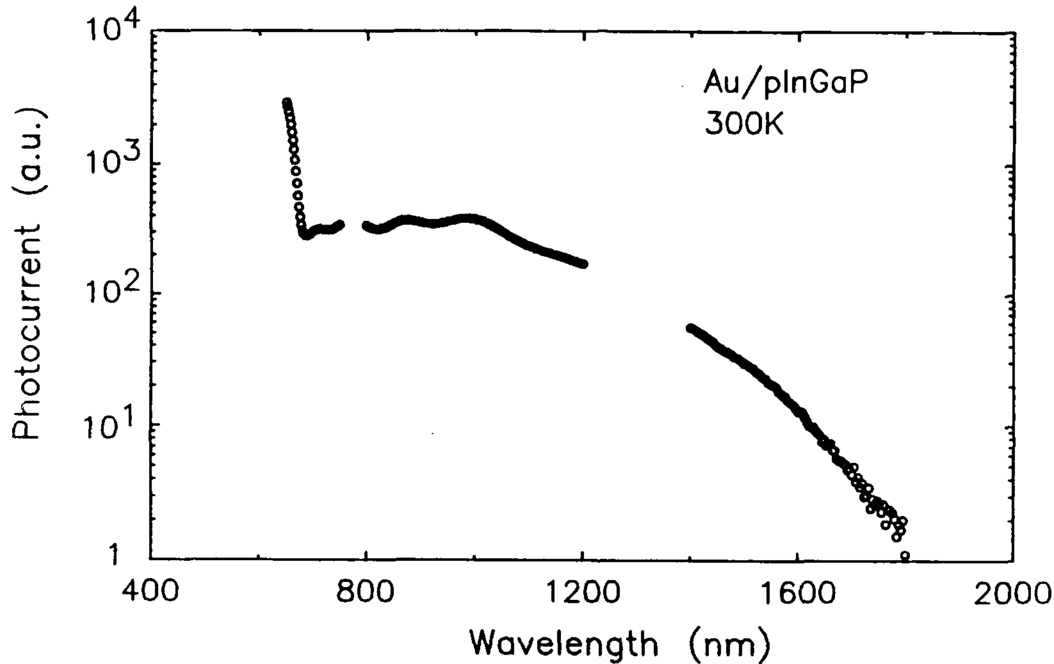

Figure 1. Internal photoemission data for a Au/pInGaP Schottky diode at 300K at zero bias.

Typical photoresponse data are shown in Figure 1, where the measured photocurrent as a function of wavelength for a p-type InGaP diode is given. The abrupt shoulder at about 660 nm is due to band-to-band excitation within the semiconductor and was used to determine E_g. The slow decrease in photocurrent with increasing wavelength in the range 1200 to 1800 nm is due to photoemission of carriers from the metal into the InGaP. The same photoemission data is also shown in Figure 2 along with data from three other samples. Here the data is plotted as the (photocarriers per absorbed photon)$^{1/2}$ versus photon energy, and the intercept on the energy axis of a straight line fit is taken to be ϕ_B-$\Delta\phi_B$ [16]. Note that as Al is added to InGaP, the n-type barrier decreases and the p-type barrier increases. For n-type $In_{0.48}Ga_{0.52}P$, we obtain a value of

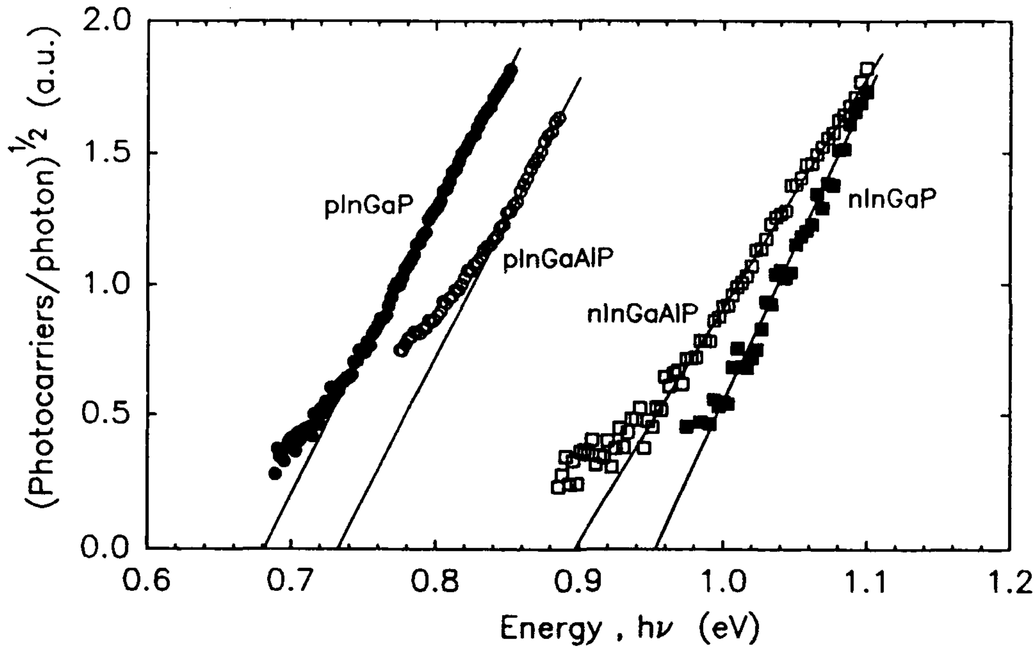

Figure 2. Photoresponse as a function of incident photon energy for Au/InGaP and Au/InGaAlP.

ϕ_{Bn} - $\Delta\phi_{Bn}$ of 0.953±0.042 eV by averaging over all measurements, which is in excellent agreement with 0.96 eV obtained by Kuech and McGaldin [10] and 0.95 eV by Su et al. [17] for Au Schottky barriers on InGaP of similar composition grown by liquid phase epitaxy.

The observed compositional variation in ϕ_{Bn}, ϕ_{Bp}, and E_g with y for the quaternary alloy $In_xGa_{1-x-y}Al_yP$, with x fixed at 0.48, is shown in Figure 3. E_g was measured by both PL and photoresponse and the results were found to be in close agreement. Furthermore, the increase in E_g with y was found to agree with a linear extrapolation between the direct bandgaps of $In_{0.48}Ga_{0.52}P$ and $In_{0.49}Al_{0.51}P$.

In Figure 3, ϕ_{Bn} is seen to decrease markedly and ϕ_{Bp} to increase slightly with increasing y. The changes with composition are small but systematic and for the photoemission data,

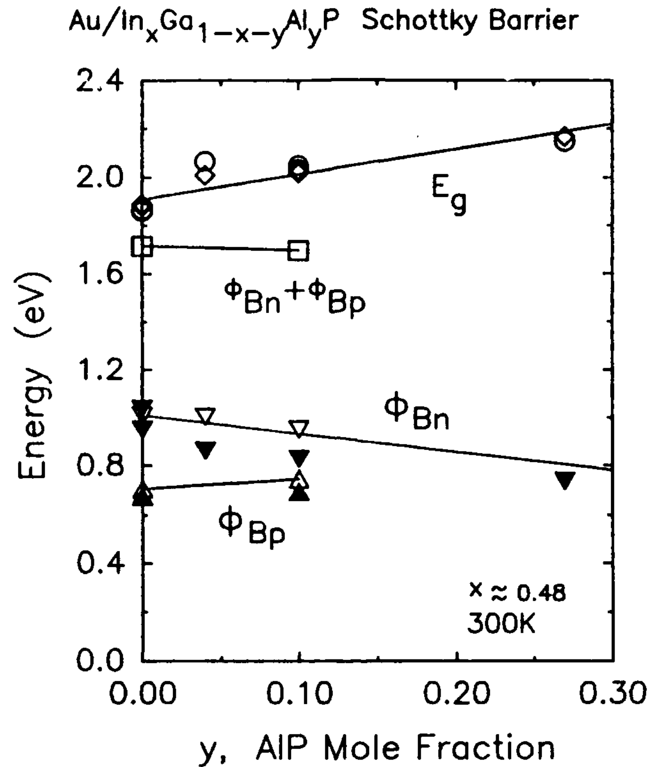

Figure 3. Compositional dependence of Schottky barrier energies in InGaAlP alloys.

significantly larger than the experimental error. Using the separately measured ϕ_{Bn} and ϕ_{Bp} from the photoemission data, we show the sum $\phi_{Bn}+\phi_{Bp}$ in Table 1 and Figure 3. The measurements indicate that the sum of $\phi_{Bn}+\phi_{Bp}$ is less than E_g by 0.148±0.015 eV for InGaP (y=0) and 0.345±0.015 eV for InGaAlP (y=0.10). Thus Equation (1) does not appear to apply to the alloys InGaP and InGaAlP. This is a surprising result, since Eq. (1) is generally accepted to be valid for chemically etched surfaces and has been experimentally verified for many semiconductors, including GaAs, InP, and Si [18]. The reason for this discrepancy is not as yet evident. Eq. (1) assumes that interfacial states are present at the semiconductor surface large enough in concentration to pin the Fermi level and that a thin interfacial layer exists between the deposited metal and the semiconductor [19]. Furthermore, for Eq. (1) to be valid, the physical character of the surface states and interfacial layer must be the same in both the p-and n-type Schottky barriers. This would require the energy distribution of any surface states present, and the

thickness and permittivity of the interfacial layer formed during deposition of the Au layer, to be identical on both materials. The Schottky barrier data in Table 1 and Figure 3 imply that there may be, however unlikely, a measurable difference in the character of the interface states on p-and n-type InGaP, and on InGaAlP as well.

The energy gap of InGaP is known to be influenced by alloy ordering on the group-III sublattice [20], with ordered InGaP exhibiting a lower E_g than disordered InGaP. If the measurement of ϕ_B is sensitive to ordered regions and the measurement of E_g to disordered regions, some of the disagreement between the data and Eq. (1) could be explained. The method of epitaxial growth as well as the growth conditions determines the degree of ordering; MOCVD has produced ordered InGaP [20-22] and InGaAlP [23,24], while LPE and solid-source MBE [25] have yielded disordered InGaP. Experimental evidence indicates that if ordered regions are present in our gas-source MBE material, the regions are very limited in extent. InGaP and InGaAlP films grown under the same conditions as those used in this study were examined by transmission electron diffraction and preliminary results show weak elongated super structure reflections along [011] directions, indicating the existence of some ordered microdomains. However, our InGaP when measured by PL at room temperature exhibits an E_g = 1.88 - 1.89 eV, which is closer to that previously reported for highly disordered material (1.89 eV for solid-source MBE [25] and 1.90-1.91 eV for MOCVD) than to ordered material (1.82-1.85 eV for MOCVD [21,21]). Thus our gas-source MBE InGaP appears to be mostly disordered and is not clear that ordering is an important factor in accounting for the energy difference between $\phi_{Bn}+\phi_{Bp}$ and E_g.

In conclusion, we have measured the Schottky barrier energies on both n-type and p-type $In_{0.48}Ga_{0.52}P$ using a Au metallization and found that the sum of the barrier energies is significantly smaller than the measured energy gap. In addition, we report for the first time the Schottky barrier energies for the quaternary alloy $In_xGa_{1-x-y}Al_yP$ lattice matched to GaAs, and we find that ϕ_{Bn} decreases and ϕ_{Bp} increases with increasing y. Since ϕ_{Bp} is not independent of composition, the "common anion" rule does not appear to hold for the InGaAlP system. This is in agreement with the results of Best for another Al-containing alloy, AlGaAs [26].

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C. Electron Traps in InGaP

The III-V alloy InGaP is widely used in the active region of double-heterojunction lasers

and light emitting diodes operating in the visible spectrum and, more recently for replacement of AlGaAs cladding layers in high power lasers operating at wavelengths near 1 μm [1,2]. InGaP is also used as a wide bandgap emitter in heterojunction bipolar transistors [3,4]. In all of these applications deep levels can appreciably degrade device performance by introducing non-radiative recombination centers and reducing carrier lifetime. Previously, deep level transient spectroscopy (DLTS) has been used to characterize InGaP films grown by a variety of epitaxial techniques and electron trap concentrations of 10^{14} to $5x10^{16}$ cm^{-3} have been reported [5-10], depending on the dopant used and the method of film growth. We report here DLTS measurements of electron traps in InGaP grown by gas-source molecular beam epitaxy (MBE). We find only one trapping center, and we have characterized the trap with respect to Si doping concentration and oxygen content of the InGaP.

The InGaP samples were grown nominally lattice-matched to n^+ (100) GaAs substrates and consisted of a n^+ GaAs buffer layer (0.15 μm thickness) followed by an n-type $In_{0.48}Ga_{0.52}P$ active layer (0.9 μm). Th InGaP layer was either unintentionally doped (refered to as "undoped") with

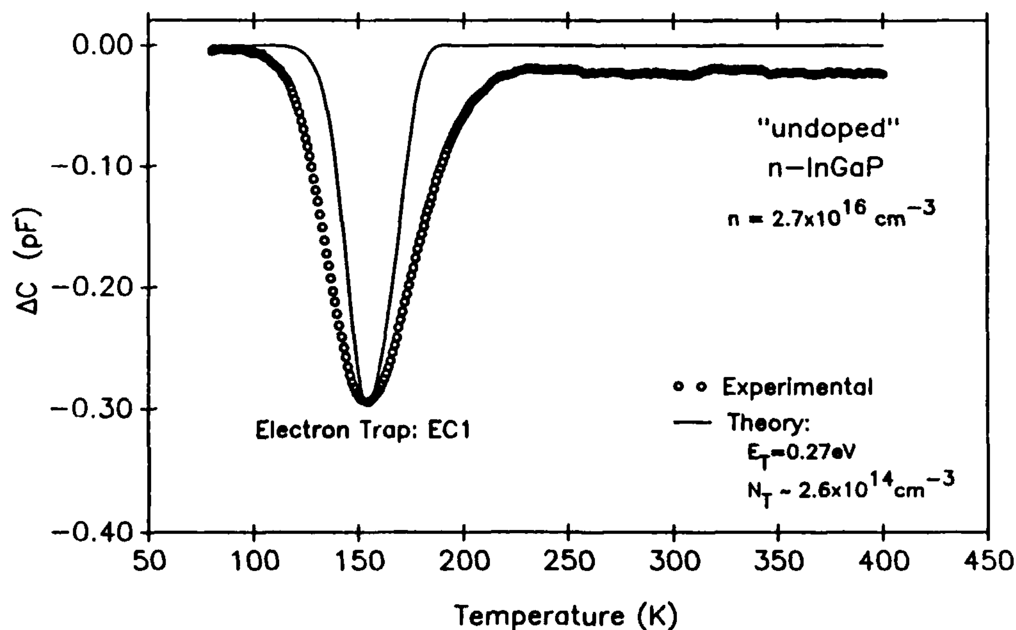

Figure 4. DLTS spectrum of "undoped" InGaP sample. Emission rate = 14 1/s, bias = -2 to -1 V, and pulse width = 10 ms.

an electron concentration of about 10^{16} cm^{-3} or doped with Si in the range $2x10^{17}$ to $4x10^{18}$ cm^{-3}. In and Ga molecular beams were derived from conventional effusion cells and P_2 and As_2 beams were produced by thermal decomposition of PH_3 and AsH_3, respectively. InGaP growth was carried out at 530 C, 1.0 μm/hr, and 8 sccm of PH_3. On-site purification of PH_3 was accomplished by passing 100% PH_3 gas through a molecular sieve filter to remove H_2O [11]. The InGaP layers were of high quality as evidenced by a narrow x-ray diffraction peaks (i.e., 25 arcsec) and intense room temperature photoluminescence. For DLTS measurements, Au/InGaP Schottky diodes were fabricated. The diodes exhibited rectifying current-voltage characteristics with a barrier energy of about 0.96 eV and an ideality factor of less than 1.08 [12]. A computer-controlled DLTS system was used to apply a bias pulse and to record the resulting diode capacitance transient as a function of temperature. The carrier concentration was determined by capacitance-voltage measurements at 300K.

A typical DLTS spectrum of an "undoped" InGaP sample is shown in Figure 4. With an estimated measurement sensitivity of about $3x10^{12}$ traps/cm^3 for this sample with an electron concentration of $2.7x10^{16}$ cm^{-3}, only one trap is detected. Using conventional band-to-impurity recombination theory for a well-defined single-level trap, a fit of the data in Fig. 4 yields an emission barrier energy E_T of 0.27 eV and a trap concentration N_T of $2.6x10^{14}$ cm^{-3}. As discussed below, the value of E_T varies somewhat with the measurement conditions. The width of the experimental peak is much broader than the theoretical peak, which is similar to that found for solution-grown InGaP, where the broadening was attributed to a distribution in E_T as a result of the random nature of alloy bonding [9]. Using Schottky diodes on 12 different wafers, all with InGaP films nominally lattice matched to GaAs, we have observed only this one electron trap. Furthermore, we also examined an InGaP p^+n junction diode and detected only the same electron trap. For reference, we have labeled the trap EC1.

The temperature dependence of the emission rate time constant τ for EC1 in an "undoped" InGaP sample is shown in Figure 5. The energy E_T was found to depend on bias pulse width, with E_T varying from 0.23 to 0.41 eV for "undoped" material and from 0.19 to 0.22 eV for Si-doped ($1.6x10^{17}$ cm^{-3}) material, for pulse widths of 0.1 to 10 ms. The electron capture cross section σ_∞, found from the vertical axis intercept of the E_T curve of Figure 5, was about $1x10^{-12}$ cm^2 for "undoped" InGaP and from $7x10^{-15}$ to $8x10^{-13}$ cm^2 in Si-doped material. The dependence of

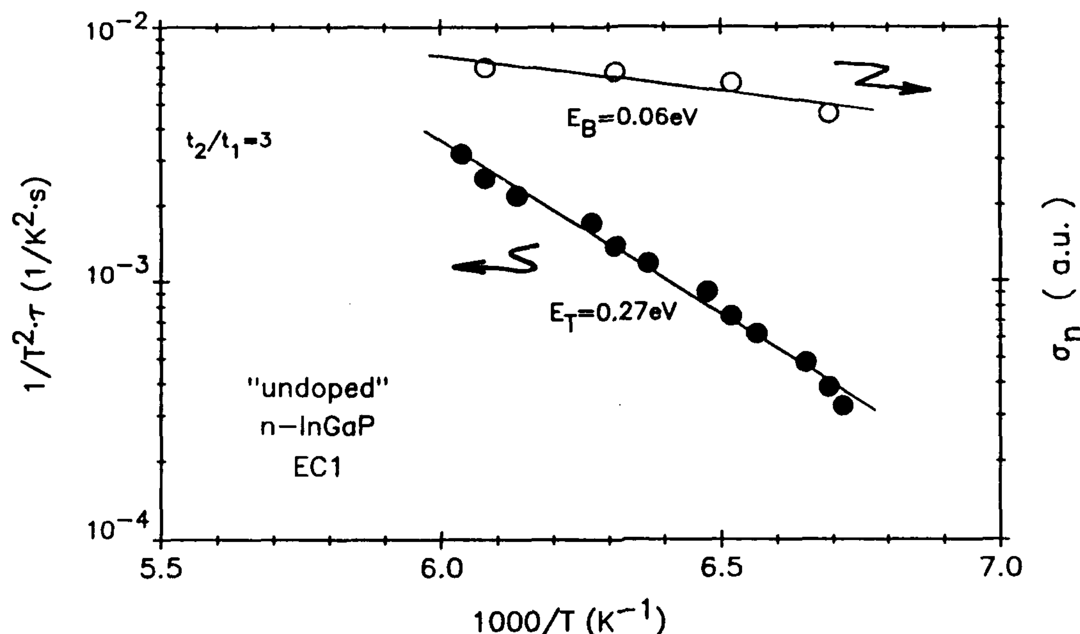

Figure 5. Activation energy plots for electron trap EC! in InGaP. Filled circles from emission data and open circiles from capture data.

emission barrier energy and capture cross section on measurement conditions and type of dopant is a widely observed characteristic of electron traps in InGaP [8-10]. For purposes of comparison, the value of E_T measured with a 10 ms pulse was taken as the characteristic emission energy.

The electron capture process was also examined for the sample of Figure 4 by measuring the change in the EC1 peak intensity with bias pulse width for pulse widths from 0.1 to 10 ms. The capture transient was found to consist of two exponentials, with an initial fast time constant followed by a slower time constant for pulse widths of 0.5 ms or longer. Using the slower time constant, the temperature dependence of the capture cross section σ_n was calculated and is plotted in Figure 5. The capture barrier energy E_B was found to be 0.06±0.02 eV. Similar capture transient behavior and the same value of E_B was found by Matsumoto et al. [9] for the electron trap SGE1 in Te doped solution-grown $In_{0.55}Ga_{0.45}P$.

A series of InGaP samples were grown in order to examine the dependence of the

properties of EC1 on oxygen content and Si doping density. The oxygen content was varied by using either raw or purified PH_3. E_T and N_T were measured and the results are shown in Figure 6. Prior investigations indicated that InGaP grown in our MBE system with purified PH_3 contained about $5x10^{17}$ cm^{-3} of oxygen and that the oxygen content increased by a factor of three with raw PH_3 [11]. InGaP grown with purified PH_3 exhibited somewhat lower trap densities and less scatter in E_T values, but otherwise the purification appeared to have little effect. The Si concentration was varied from about $2x10^{17}$ to $4x10^{18}$ cm^{-3} with no apparent effect on E_T and only a slight

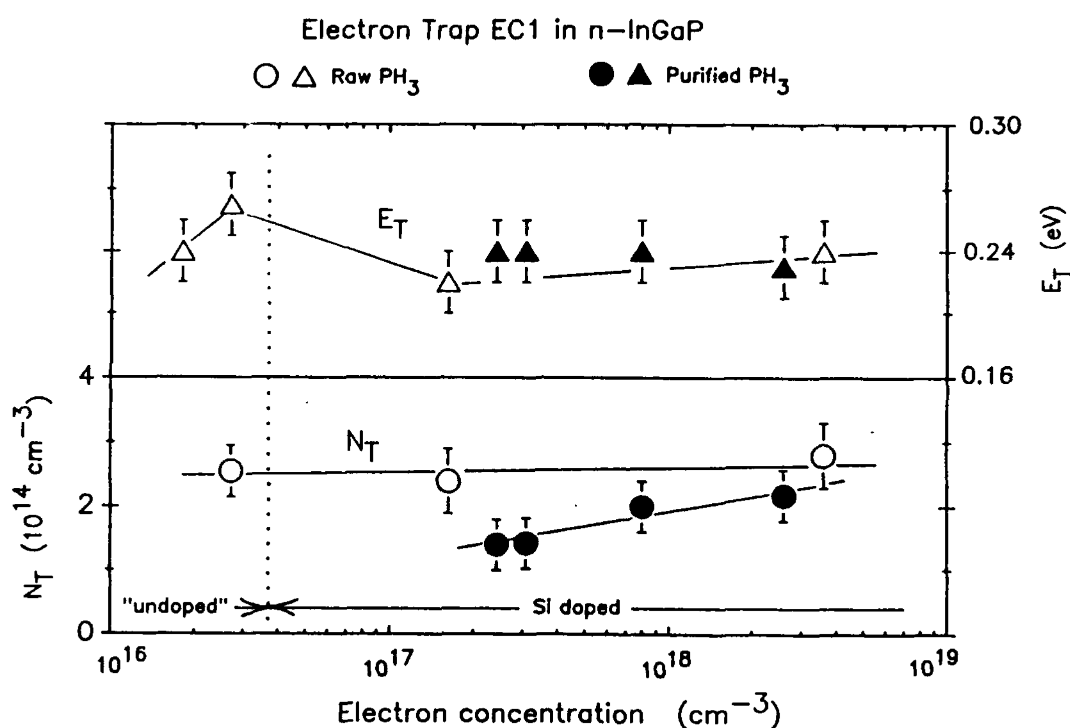

Figure 6. Variation of emission barrier energy E_T and trap density N_T for trap EC1.

increase in N_T with increasing Si concentration. Thus, EC1 does not depend significantly on Si or oxygen concentration in the impurity ranges explored, nor do the properties of EC1 depend on the chemical nature of the donor, assuming the residual dopant in our "undoped" InGaP is an impurity other than Si. Furthermore, the trap density is well below the donor and oxygen concentrations. Based on the measurements of all samples, the electron trap EC1 was found to be characterized by an emission barrier energy E_T = 0.24±0.03 eV, a capture barrier energy E_B = 0.06±0.02 eV, and a density N_T =(1-3)x10^{14} cm^{-3}.

In comparison to previous DLTS studies of $In_xGa_{1-x}P$ with x~0.5, from one to three electron traps have been observed in the same InGaP film with the properties of the traps varying considerably, depending on the crystal growth technique and dopant employed. The most commonly observed electron trap exhibits an E_T in the range 0.3-0.4 eV and has been reported in LPE undoped InGaP [5], S and Se doped VPE InGaP [6], solid-source MBE InGaP doped with Sn and Pb [7] and Si [8], and metalorganic MBE (MOMBE) InGaP doped with Si [10]. Trap EC1 exhibits a lower E_T than that of these earlier reports, yet is similar with respect to the dependence of E_T and capture cross section on measurement conditions. Solid-source MBE InGaP showed a single electron trap with a broad peak at E_T = 0.37 eV and N_T = $8x10^{14}$ cm^{-3} with a Si doping of $5x10^{16}$ cm^{-3} [8]. The dependence of N_T on Si concentration was not given. On the other hand, undoped MOMBE InGaP exhibited a trap at 0.82 eV; Si doping supressed the trap but also produced two new electron traps at about 0.32 eV and 0.37 eV[10]. Furthermore, the trap concentrations were found to increase with Si concentration. Thus, trap EC1 in gas-source MBE InGaP appears exhibit properties closer to that of solid-source MBE InGaP than MOMBE InGaP.

In conclusion, we report for the first time electron traps in InGaP grown by gas-source MBE. For both "undoped" and Si-doped InGaP lattice matched to GaAs, only one trap, EC1, was detected by DLTS. EC1 was characterized by an emission barrier energy of 0.24±0.03 eV, a capture barrier energy of 0.06±0.02 eV, and a density below $3x10^{14}$ cm^{-2}. Furthermore, the properties of EC1 were found to be largely independent of the Si doping density and oxygen content.

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