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Power-Dependent Photoluminescence Spectral Shift in InGaAsP Semiconductors

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ABSTRACT

The peak position and shape of photoluminescence emission from InGaAsP depends significantly on the incident power density. For some 1.3- µ m-bandgap InGaAsP layers, the peak position at 9 K can vary by as much as 30 nm (24 meV) as the incident power is changed by a factor of twenty. The effect is particularly pronounced for layers without intentional doping grown by liquid phase epitaxy between layers of doped tnP. The shift is reduced for samples that are annealed at high temperatures, are heavily p-doped with zinc, or are grown by MOCVD. The peak shift and shape changes are shown to be due to tunneling-assisted radiative emission due to inhomogeneities within the bulk quaternary material. In addition to causing inhomogeneous broadening of the photoluminescence emission, the tunneling-assisted transitions are expected to be significant in the operation of optoelectronic devices made from the material.

INTRODUCTION

Direct-bandgap III-V-compound semiconductors are widely used to produce optoelectronic devices, such as laser diodes, light-emitting diodes, and photodiodes. The quaternary $In_{\mu x}Ga_yAs_yP_{\mu y}$ lattice-matched to InP is of particular interest for the production of light sources and

detectors for long-range optical-fiber communication systems. The quaternary compositions most commonly used for emitters are 1300 nm and 1550 nm, due to the low spectral shift or loss for silica-based optical fibers at these wavelengths.

High-quality epitaxial layers are grown by a number of techniques such as liquid phase epitaxy (LPE), metal organic chemical vapor deposition (MOCVD), and molecular beam epitaxy (MBE). Independent of growth method, the existence of a miscibility gap in the phase diagram of this quaternary alloy can lead to a systematic generation of ordered and modulated structures over a range of temperatures and composition.^{1,2}This modulation (also called spinodal decomposition) is expected to affect device performance or reliability but its influence has not been well established.

In this report, photoluminescence is used to characterize InP/InGaAsP/InP double-heterostructure wafers that are typical of those used to fabricate diode lasers. Photoluminescence is a powerful, nondestructive analysis method that is commonly used to probe the composition and quality of these crystals. The low-temperature photoluminescence technique reveals details of semiconductor properties that are unresolved at room temperature. The

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spectral intensity and shape variations are studied over a wide power range and a prominent photoluminescence spectral shift is observed for samples with certain characteristics.

EXPERIMENTAL DETAILS

The samples used for this study were double-heterostructure wafers consisting of an n-doped InP buffer layer [, 6μ m thick, $n \cdot 1 \ge 10^{18}$ cm⁻³], a quaternary (In₇₂Ga₂₈As₆P₃₉) active layer [0.15 **m** m, $\lambda \cdot 1300$ nm at room temperature, $\Delta a/a \cdot -3 \ge 10^{-4}$], and a *p*-doped InP clad layer [0.6 **m** m, $p \cdot 1 \ge 10^{18}$ cm⁻³]. An additional thin quaternary cap layer was grown to protect the surface from thermal decomposition. This layer was removed prior to the photoluminescence measurements described here.

The InP/InGaAsP/InP double-heterostructure wafers were prepared by two quite different growth methods: liquid phase epitaxy (LPE) and metal organic chemical vapor deposition (MOCVD). Single-crystal multilayer structures were deposited on InP substrates that have a (001) $(\pm 0.25^{\circ})$ surface orientation. The LPE layers were grown from iridium solutions using a single-phase step-cooling technique with temperatures in the range of 610-630° C. The MOCVD samples were grown using triethylgallium, trimethylindium, arsine, and phosphine at low pressure and a temperature of about 570°C. In both growth systems, the wafers were rapidly cooled once the growth sequence was completed.

The dopants used in the epitaxial layers were zinc for the p-type layers and tin (for LPE) or silicon (for MOCVD) for the n-type layers. A list of all the samples is shown in Table 1. It should be noted that, while the active layer was not intentionally doped in most of the wafers, some degree of zinc diffusion from the p-clad layer is anticipated. In addition, there is always expected to be low concentrations ($\# 10^{16} \text{ cm}^3$) of both acceptors and donors due to unintentional impurities.

Sample #	Growth Method	InP Clad Zn Doping (cm ⁻³)	Active Zinc (cm ⁻³)	300 K λ 20 mW (nm)	9 K		
					λ 20 mW (nm)	λ 1 mW (nm)	$\lambda_1 - \lambda_2$ (nm)
41035	LPE	u	u	1287	1217	1217	0
41046	LPE	1×10^{18}	d	1286	1257	1286	29
41112	LPE	1×10^{18}	7×10^{17}	1293	1248	1271	23
41116	LPE	1×10^{18}	3×10^{17}	1289	1243	1273	30
41123	LPE	1×10^{18}	12×10^{17}	1296	1241	1251	10
70187	MOCVD	1×10^{18}	d	1306	1257	1264	7
70196	MOCVD	u	u	1303	1223	1223	0

u = No intentional doping.

d = Some zinc diffusion from p-clad expected

Table 1. Summary of samples.

The layer thicknesses were confirmed by scanning electron microscope measurements. The carrier concentrations of

the layers were measured with a Polaron electrochemical C-V profiler, and the lattice mismatch was checked with a double-crystal X-ray diffractometer.

Photoluminescence measurements were made at 300 K and 9 K. The samples were mounted in a strain-free manner in a closed-cycle helium cryostat. Excitation of the active layer was attained by 1064-nm illumination of a CW Nd:YAG laser through the thin p-clad layer at an incident angle of about 45°. The luminescence was collected normal to the surface from an area smaller than the illuminated area and was detected with conventional lock-in techniques using a cooled germanium photodiode. By means of neutral-density filters, the incident power was varied from 1 mW to 20 mW with a spot size of 5.6 x 10^{-5} cm², leading to an estimated density of injected carriers from about 10^{16} to 10^{17} cm⁻³. No corrections were applied to the photoluminescence spectra to account for the wavelength response of the detection system, but a blackbody calibration confirms that no structure and little variation in detection efficiency exists over the spectral range reported here.

RESULTS

For wafers with zinc doping in the *p*-clad or active layers, the spectra in Figure 1 demonstrate the spectral shift that is the object of this study. This particular sample is from an LPE wafer with a doped *p* -clad layer. At 1-mW incident power, the emission peak is near 1286 nm. As the excitation power is increased, the emission increases in intensity and shifts to about 1257 nm. The direction of this 29-nm shift is opposite to that expected from increasing temperature, so the spectral shift is truly a reflection of the available density of states in the active material rather than an artifact of sample heating.



Figure 1. Photoluminescence spectra at 9 K for Zn-doped clad sample 41046 at (a) 1 mW, (b) 13 mW, and (c) 20 mW incident power.

The spectral shift also occurs when the wafer is grown by MOCVD, though the shift is smaller. The 9 K spectra for a MOCVD wafer with a p-clad doped to the same level as the first wafer show a 7-nm shift over the same incident power range. Other than the smaller shift, the direction of the movement as well as the changes in peak shape and breadth are very similar to the first sample.

In contrast, wafers without zinc doping exhibit narrow peaks that do not shift over the power levels examined here. Figure 2 shows the spectra from a reference LPE sample that was grown with no zinc doping in either the active or p-clad layers. The peak position, shape, and width are unchanged over the entire incident power range to within the resolution of the measurement. The peak position is different than for the zinc-doped wafers, but this is merely due to the low density of unintentional acceptors in undoped InGaAsP, leading to a donor-band transition. The spectral peak width is controlled by statistical fluctuations in the x and y coefficients in the $In_{1x}Ga_xAs_yP_{1-y}$ material. These composition fluctuations are known to cause broadening of band-to-band radiative recombination in this systems However, the peak widths seen here are much less than the ordered domain broadening seen in $Ga_{0.5}In_{0.5}P$.⁴⁷



Figure 2. Photoluminescence spectra at 9 K for undoped clad sample 41035 at (a) 1 mW, (b) 13 mW, and (c) 20 mW incident power.

A comparison of the 9 K emission peaks as a function of incident power is summarized in Figure 3 and in Table 1. The spectral shift for wafers with zinc-doped p-clad layers can be seen in the lower two curves. The asymptotic value at high incident power is about 30 meV below the band-edge emission from the undoped samples. This shift is just about the value for a transition involving a zinc acceptor. However, at low excitation levels, the energy is much lower than expected from a simple acceptor transition. In these wafers, as the incident power is lowered, the quasi-Fermi

level for holes is "tuned" through a substantial range of energies which extends well into the bandgap.

The zinc in the samples discussed so far comes into the active layer by diffusion from the p-clad layer. To allow better control over the zinc concentration, a series of three LPE wafers were grown with zinc deliberately introduced into the active layer. The range of active doping was from 3 to 12×10^{17} cm⁻³ as measured by electrochemical profiling. Spectra from wafers at both ends of this range are shown in Figure 4. Even at 20-mW incident power, the spectrum



Figure 3. Dependence of 9 K emission energy on incident power for ■ 41035 LPE undoped clad sample, + 41046 LPE doped clad sample, ▲70196 MOCVD undoped clad sample, and □ 70187 MOCVD doped clad sample.



Figure 4. Photoluminescence spectra at 9 K and 20 mW for samples with Zn-doped active layer with carrier concentration of (a) 3×10^{17} (sample 41116) and (b) 12×10^{17} (sample 41123).



Figure 5. Dependence of 9 K emission energy on incident power for doped active layer samples: $+ 3x10^{17}$ (41116), **7** x10¹⁷ (41112), and **1** 2x10¹⁷ (41123).

from the wafer with low active doping is very broad with a long tail toward lower energies. As the incident power is reduced, the emission peak moves sharply down in energy. As shown in Figure 5, the range of spectral shift is largest for the wafer with lowest doping and smallest for the wafer with highest doping. From this result, it is clear that the anomalous emission from these wafers is not due to zinc precipitates that can occur at high doping levels.

DISCUSSION

The spectral shift demonstrated in these results is clearly an interaction between the density of carriers created by the incident light and the zinc acceptors located in the active material. For an undoped sample, the quasi-Fermi levels for electrons and holes are virtually locked at the edge of the conduction and valance bands at all the power levels explored here. This is because the photo-created carriers overwhelm the small number of unintentional dopants which pushes the quasi-Fermi levels up to the very high densities of states that exist at the band-edges. For the samples with zinc doping, the acceptor concentration in the active layer is higher than the density of photo-excited carriers, so the quasi-Fermi level for holes lies in the range of acceptor energies. As the incident light intensity is varied, the hole quasi-Fermi level is tuned through the available acceptor energy levels. The surprising results of this study are that the acceptor transitions occur over such a large energy range and that these levels exist down into the bandgap, well below normal acceptor ionization energies. Furthermore, the greatest spectral shifts are seen for wafers with the lowest (non-zero) acceptor concentrations.

The explanation for this anomalous behavior is expected to be tunneling-assisted radiative recombination. An intensity-dependent photoluminescence, very similar to what is shown here, has been reported in closely compensated

GaAs.⁸⁹ Due to Coulomb effects, statistical fluctuations in the dopant concentrations perturb the local band structure of the active material. In a region with a concentration of acceptors, the valence and conduction bands are pulled up in energy slightly; in a region with many donors, the bands move down. The lowest energy transitions are between donors in regions where the conduction band is relatively low and acceptors in regions where the valance band is relatively high. However, at low doping levels, such transitions require spatial tunneling between the dopant sites. ¹⁰ Analogous effects are also seen in electroluminescence of nipi structures. Tunneling-assisted radiative recombination is generally observable only when donor and acceptor concentrations are both relatively low, since normal recombination will dominate if either dopant is present in high concentrations.

The tunneling model must be distinguished from simple donor-acceptor pair recombination. In semiconductors with very low concentrations of donors and acceptors, the photon energies resulting from radiative recombination often depend on the separation distance of the pairs. Due to electrostatic attraction within the nearly insulating matrix, transitions involving donor-acceptor pairs that are close together release photons with larger energies than pairs that are far apart. This can result in a series of finely spaced emission lines with the lowest levels belonging to recombination due to far-removed pairs and the highest levels due to near-neighbor pairs. The simple donor-acceptor pair model does not explain the low energy transitions seen in this study, which extend down into the bandgap.

The presence of spinodal fluctuations in active composition may enhance tunneling-assisted radiation recombination and may in fact explain why the spectral shift seen here is found up to net carrier concentrations of 1×10^{18} cm⁻³, much higher than in the case of compensated GaAs. Spinodal "decomposition" is always expected for In Ga As Py grown in this temperature and composition range.^{11,12} The microstructure that results from spinodal decomposition in $In_{1x}Ga_xAs_yP_{1-y}$ has been found to exist down to scales of a few nanometers. The periodic internal strain fields at this scale have been extensively studied by means of transmission electron microscopy and X-ray diffraction. These variations in composition and stress are expected to strongly influence the distribution and diffusion of dopant atoms. For example, the periodic strain fluctuations in a spinodal system are expected to result in a periodic pattern of stress-enhanced diffusion for zinc. The resulting pattern of high and low acceptor concentrations is ideal for the tunneling-assisted emission process.

A possible example of zinc diffusion in the presence of spinodal fluctuations is shown in Figure 6. In this case, an LPE wafer with a zinc-doped *p*-clad layer was chemically lapped at a very shallow angle. In this manner, the photoluminescence spectrum for the lower half of the active layer could be obtained. As shown in Figure 6(a), the maximum intensity was found at the position corresponding to



Figure 6. Photoluminescence spectra at 9 K and 20 mW of angle-lapped sample 40731 taken from (a) the lower half of the active layer, and (b) the normal location through the clad layer. The lesser intensity of peak (b) is due to smaller active volume and free surface recombination. The inset represents the two locations, though not to scale. The actual bevel was at a very shallow 10,000:1.

undoped quaternary material, but, in addition, a residual shoulder still remained in the longer wavelength region. As the power level was lowered, this broad shoulder grew to dominate the spectrum. From this result, it is clear that the lower half of the active layer has received low levels of acceptors from the p-clad. For comparison, the photoluminescence signal from the full active layer in Figure 6(b) shows a peak dominated by the more heavily doped quaternary material nearer the p-clad layer.

The results of this paper have a number of implications for other material, optical, and electronic properties. For instance, diffusion of high concentrations of zinc is known to cause homogenization of the spinodal fluctuations in composition.¹³⁻¹⁵ This is thought to be caused by iridium/ gallium intermixing due to an interchange or kick-out mechanism between the zinc atoms and the group III matrix elements. This equilibrium interchange mechanism could cause smoothing in the local composition variations of the quaternary material in this study.

The optoelectronic implications of these results depend on the current and photon densities in the device under nor-., mal operating conditions. At low densities, such as those achieved by photoluminescence in this study, the electronic states seen here could have a strong effect on device performance. For instance, the spatial separation of carriers implied by the tunneling-assisted emission model is expected to slow down the recombination time at low densities. In a light-emitting diode, this would affect frequency response because the trailing edge of a pulse will have a long, low intensity tail.

At higher density levels, the device implications are more subtle. When the electron and hole densities are high, the band tail states are completely filled. However, these electronic levels can still participate in Auger and optical transitions to higher electronic states. In a diode laser made from this material, Auger recombination, optical selfabsorption, and internal heating due to these effects strongly affect lasing threshold and efficiency. The acceptor transitions revealed in this study are key for the detailed understanding of such optoelectronic component performance.

CONCLUSIONS

The existence of photoluminescence spectral shift at low temperatures reveals microscopic details of the quaternary active layer that may well be important for the performance and reliability of devices fabricated from the material. The photoluminescence technique has advantages over other techniques that may also give aspects of this structure (such as TEM or Auger microprobe) in that the measurement is nondestructive, is relatively rapid, and requires no elaborate sample preparation. It is particularly suitable for the characterization of III-V material that is to be used for optoelectronic devices. The observed difference in spectral shift between the doped MOCVD and LPE wafers is an example of the type of detail that maybe relevant to device performance.

This paper has presented an extended study of power-dependent photoluminescence spectral shift in the InGaAsP semiconductors. Substantial spectral shift was observed from the active layers of heterostructures when low-tomoderate levels of zinc acceptors were present. The spectral shift was seen in wafers grown by LPE or by MOCVD. It was also seen independently of whether the zinc was deliberately introduced during active growth or unintentionally diffused in from the p-clad layer. A model involving tunneling-assisted emission, probably aided by spinodal decomposition, is shown to be the likely explanation for this effect.

ACKNOWLEDGEMENT

The authors would like to thank Bob Miller and Mark Mashas for providing the LPE and MOCVD samples, respectively, and would also like to acknowledge Randy Wilson for useful discussions.

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