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Band gap bowing in \( \text{GaP}_{1-x}\text{N}_x \) alloys

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The interband optical absorption edge of \( \text{GaP}_{1-x}\text{N}_x \) alloys grown by molecular beam epitaxy has been investigated by photoluminescence and photoluminescence excitation (PLE) spectroscopy. The results demonstrate the transition from nitrogen-bound exciton luminescence indicative of isoelectronic traps in lightly doped films of \( \text{GaP}:\text{N} \) to the formation of indirect band gap alloys in the heavily N-doped GaP films. A large red shift or reduction in band gap energy with increasing N concentration which is observed in PLE spectroscopy identifies the \( \text{GaP}_{1-x}\text{N}_x \) alloy system as one of the limited number of alloy systems whose intermediate compositions can have band gaps smaller than those of either of the constituent binary compounds.

A recent study\(^1\) of the growth of epitaxial nitrogen-doped GaP by molecular beam epitaxy (MBE) has demonstrated that it is possible to incorporate concentrations of N as high as \( 1.9 \times 10^{21} \text{ cm}^{-3} \) (7.6\%) by this technique. These results exceed by an order of magnitude the concentrations of N which can be incorporated in GaP by conventional techniques.\(^2,3\) Photoluminescence (PL) studies\(^1\) of these N-doped epitaxial GaP films carried out at 77 K exhibited a continuous red shift from 2.18 to 1.96 eV for N concentrations ranging from \( (5-7) \times 10^{19} \) to \( 6 \times 10^{20} \text{ cm}^{-3} \). These results were interpreted in terms of the formation of \( \text{GaP}_{1-x}\text{N}_x \) alloys whose band gap energies varied as a function of N concentration in accordance with the predictions of the dielectric theory of electronegativity.\(^4\)

In the present work, PL and photoluminescence excitation (PLE) measurements have been carried out at 5 K on the same samples to investigate the concentration dependence of the interband absorption edge in these epitaxial films. The results clearly demonstrate the transition from the N-bound exciton PL bands\(^5,6\) indicative of isoelectronic traps in lightly doped films of \( \text{GaP}:\text{N} \), to the formation of indirect band gap alloys in the heavily N-doped GaP films. The concentration dependence of the alloy band gaps, as measured by the low energy onsets of the PLE spectra, exhibits a large red shift or reduction in band gap energy with increasing N concentration which is indicative of a significant “bowing” in the \( \text{GaP}_{1-x}\text{N}_x \) alloy system. This result, which is qualitatively consistent with the Van Vechten theory,\(^4\) identifies the \( \text{GaP}_{1-x}\text{N}_x \) alloy system as one of the limited number of alloy systems\(^7,8\) whose immediate compositions can have band gaps smaller than those of either of the constituent binary compounds.

The samples were grown by MBE\(^1\) using \( \text{NH}_3 \) and \( \text{PH}_3 \) as the source materials for column V elements. The epilayers, typically 1–2 \( \mu \text{m} \) thick, were deposited on S-doped (n-type) [001] GaP substrates. PL experiments were performed at liquid helium temperature with excitation provided by the 514.5 nm line of an Ar\(^+\) laser or tunable monochromatic light (for PLE) created by the combination of a 150 W xenon arc lamp and a 0.22 m double grating monochromator. The PLE intensity was normalized to the output power of the lamp-monochromator source. In PL and PLE, the luminescence was analyzed by a 1.0 m grating monochromator and a GaAs photocathode photomultiplier tube (PMT).

The 5 K PL spectra from the \( \text{GaP}:\text{N} \) films with various nitrogen concentrations and a GaP substrate are displayed in Fig. 1. As shown in Fig. 1(a), the PL spectrum from the S-doped GaP substrate consists of two distinct emission bands. The higher energy band, including multiple lines with energies centered around 2200 meV, is attributable to distant donor-acceptor pair (DAP) recombinations and their LO-phonon replicas\(^7,10\) which involve S donor and C acceptor impurities in the substrate. The broad lower energy band, which peaks at about 1700 meV, is probably related to complexes\(^11\) arising from group VI donors, such as S, and gallium vacancies.

![FIG. 1. The 5 K PL spectra excited by 1 mW of 514.5 nm light from the heavily N-doped GaP samples and a GaP substrate.](image-url)
The PL spectra for samples with low N concentrations [Fig. 1(b)] exhibit emission bands similar to those observed in the substrate, and additional strong, sharp lines in the vicinity of the substrate DAP band. These sharp lines, which agree in detail with earlier PL studies,5,6 are attributable to excitons bound at the isoelectronic traps formed by N pairs. With increasing N doping, the bound exciton PL bands evolve into a broad emission that dominates the spectra as shown in Figs. 1(c)–1(e). The energy of this broad emission band exhibits a dramatic red shift when the N concentration is increased. These strong emission bands are attributable to the N impurities in the epilayers, and are referred to as the “N band” in the following discussion.

Although there are emissions from the N-doped samples in the spectral ranges where the substrate luminescence dominates, we cannot exclude the possibility that the N-doped films also emit at these energies. For this reason the high energy emission band (~2200 meV) from the N-doped samples is simply labeled as the “green band,” although it is recognized that it may consist primarily of the substrate DAP band. Correspondingly, the broad low energy emission band centered near 1700 meV is labeled as the “red band” [see Fig. 1(d)].

The interpretation of PLE spectra can be complicated when PL bands originating from film and substrate overlap or coincide in energy. When the PLE measurement is performed on an emission band originating exclusively from the substrate, the spectrum is shaped by a combination of the transmission spectrum of the film and the absorption spectrum of the substrate. For an emission band originating only from the epilayer, the PLE spectrum is primarily a manifestation of epilayer absorption. If the emission band is a mixture of PL from both the epilayer and the substrate, the PLE spectrum depends on the detailed nature and the relative intensities of the PL contributions from the substrate and the epilayer, as well as their transmission and absorption characteristics.

To illustrate, Fig. 2 shows the PLE spectra of the red, green, and N PL bands obtained at 5 K from sample 603, with detected energies indicated by the arrows on the typical PL spectrum. The PLE spectrum of the green band (the substrate DAP band, 2206 meV) behaves just like the PLE spectrum from a bare GaP substrate,13 until the excitation energy exceeds the direct band gap of the film; at this energy the PLE intensity experiences a sharp drop and then continues to diminish at higher energies. In contrast, the PLE spectrum of the red band (1675 meV) increases in intensity above the direct gap. In addition, the absorption edge of this heavily N-doped film extends to much lower energy than the GaP indirect gap.

The N band, on the other hand, arises predominantly from the epilayer. Its PLE spectrum, which is representative of the absorption spectrum of the film, contrasts dramatically with those of the green and red PL bands. The red-shifted position of the low energy onset of the PLE spectrum clearly demonstrates that the indirect absorption edge of the N-doped film is extended to much lower energy. Other N-doped samples display qualitatively similar behavior.

The PLE spectra of the N bands have been used to investigate the absorption edge as a function of the N concentration. In Fig. 3, the low energy portions of the N band PLE spectra from the heavily N-doped samples are plotted on a square-root intensity scale, along with a PLE spectrum from the substrate detected at the red band. (The PLE spectra have been normalized to the intensities at energies much higher than the direct gap of the epilayers.) The phonon-assisted absorption steps which are characteristic of indirect band gap semiconductors are clearly seen in the substrate PLE. With increasing N concentration, these steps in the PLE spectra broaden and eventually disappear because of the alloy fluctuations introduced by the concentrations of N impurities. In addition, the absorption edges of the heavily N-doped epilayers, as manifested by the onset energies of the PLE spectra, exhibit a dramatic red shift with increasing N concentration. This PLE behavior is consistent with the interpretation of the red-shifted emission band in terms of a reduction in the indirect band gap of the films induced by the formation of dilute GaP$_{1-x}$N$_x$ alloys.
Extrapolation to minimum intensity of the steeply rising linear portions in the square-root plot of the red-shifted PLE spectra provides an estimate of the indirect band gap of these alloys as a function of nitrogen content. The results of this procedure for the PLE spectra shown in Fig. 3 are plotted in Fig. 4. For the sake of comparison, the peak positions of the dominant 5 K N-band emissions shown in Fig. 1 have also been plotted in Fig. 4.

According to the theory developed by Van Vechten, the very large difference in electronegativity between N atoms and P atoms will result in a large reduction in the energy gap as N is alloyed with GaP. A numerical calculation based on this theory and known parameters for GaP and GaN has been carried out for low temperature and the result is reproduced in Fig. 4. The representations of the nitrogen induced red shift of the indirect band gap in the films shown in Fig. 4 are qualitatively consistent with one another. However, because the N-band originates from the recombination in disorder-induced, below-gap and tail states, the onset of the red-shifted PLE is regarded as the most realistic measure of the indirect band gap and absorption edge in the films. As shown in Fig. 4, the energy difference between the N band PL and PLE onset decreases as the N content is increased, and approaches zero at the highest N concentration presented here. This indicates that the band tail states merge almost completely with the absorption band edge of the film.

In conclusion, PL and PLE spectroscopy at 5 K have shown that the indirect interband absorption edge is dramatically red shifted with increasing nitrogen concentration in GaP$_{1-x}$N$_x$ alloys grown by MBE. For the N concentrations up to 2.4% studied in this work, the experimentally observed band edge bowing is consistent with the predictions of the Van Vechten dielectric theory of electronegativity for this alloy system.

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