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Physical properties and efficiency of GaNP light emitting diodes

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GaNP/GaP is promising for yellow-amber-red light emitting diodes (LEDs). In this study, pressure and temperature dependent electroluminescence and photocurrent measurements on bulk GaP/$GaN_{0.006}P_{0.994}$/GaP LED structures are presented. Below ~110 K, emission is observed from several localized nitrogen states. At room temperature, the band-edge energy increases weakly with pressure at a rate of +1.6 meV/kbar, substantially lower than the Γ band gap of GaP (+9.5 meV/kbar). Thus, despite the multiplicity of nitrogen levels, the band anticrossing model reasonably describes this system based on an average of the nitrogen states. Furthermore, carrier leakage into the *X* minima of GaP reduces the efficiency in GaNP-LEDs with increasing pressure. *© 2008 American Institute of Physics*. [DOI: 10.1063/1.2830696]

For a number of years, nitrogen has been added to the indirect semiconductor GaP to act as a radiative defect center to produce light emitting diodes (LEDs).[1] Recently, there has been renewed interest in III-V-N semiconductors due to the large band-gap bowing that is observed in such materials when only a few percent of nitrogen is added. The interaction between the localized N states and the conduction band (CB) minimum has been effectively modeled with both the band anticrossing (BAC) model[2] and the empirical pseudopotential method.[3] This has recently led to activity in dilute nitrides based on GaP where the fraction of nitrogen can be carefully controlled via molecular beam epitaxy (MBE) growth. Additionally, yellow-amber-red GaNP LEDs may offer better device characteristics than current AlInGaP devices due to a weaker dependence of the band gap[4] and lower thermal resistivity.[5] In this letter, we investigate the validity of a simple BAC model in GaNP-based materials and consider the factors limiting the electro-optic efficiency of LEDs based on GaNP.

The devices studied here were grown by MBE and utilize simplified chip processing by one-step growth on transparent 350 μm thick *n*-type GaP (100) substrates. The epitaxial layers consist of a 0.3 μm thick *n*-GaP layer (Si doped), 0.15/0.1/0.15 μm thick undoped GaP/$GaN_{0.006}P_{0.994}$/GaP active region, and 0.8 μm thick *p*-GaP (Be doped) contact layer. LED chips were fabricated using Ge/Au/Ni/Au and AuZn metallization for *n*- and *p*-type contacts, respectively.

We employ temperature dependent measurements performed with a standard closed cycle cryostat setup over the temperature range of 70–300 K. This gives temperature and current dependencies of the electroluminescence (EL) spectra. The application of high hydrostatic pressure causes an increase in the direct band gap, and a reduction in the indirect *X* minima, thereby allowing investigations of the band structure and leakage effects into the indirect minima of GaP. Pressure dependent measurements were performed over the range of 0–10 kbar using gaseous helium as the pressure medium. In the dilute nitrides, high pressure can also be used to tune the interaction between the nitrogen level(s) and the conduction band of the host material, forming a useful means of investigating the validity of the BAC model.[2,6–9]

Shown in Fig. 1 is the pressure dependence of the EL peak energy position (squares), taken from EL spectra of GaNP LEDs, which blueshifts with increasing pressure at a rate of +1.6 meV/kbar, consistent with previous spectroscopic[2] and theoretical[3] studies. Also shown are the pressure dependencies of the Γ and *X* minima of GaP. It can be clearly seen that the change of the peak energy does not correlate with either minima, suggesting that the emission peak is strongly influenced by the addition of nitrogen. It is, therefore, interesting to see if the BAC model can describe this pressure dependence. This simple model[9] describes the effects of nitrogen in dilute nitrides and allows the prediction of temperature and pressure dependencies of CB states. The

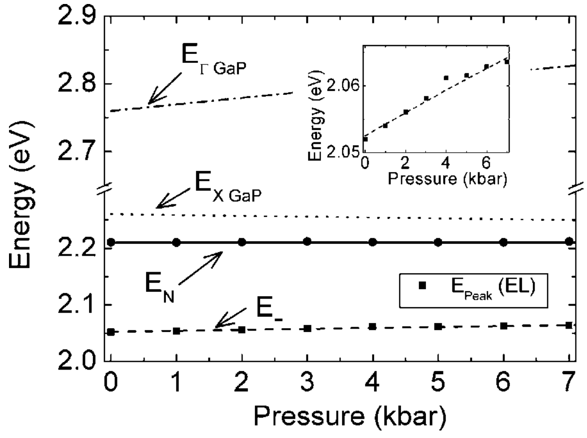

FIG. 1. The measured pressure dependence of peak EL (squares) for GaNP LEDs. Also shown is the pressure dependence of Γ (GaP) (dot-dashed line), *X* (GaP) (dotted line). The nitrogen level position was determined by PC measurements (solid line) and show negligible movement with pressure. The change in peak EL with pressure can be predicted using the BAC model (dashed). The inset shows the fit in greater detail.

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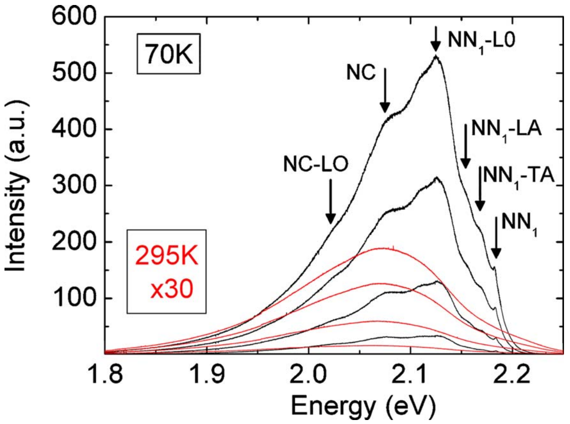

FIG. 2. (Color online) Measured EL spectra at 70 and 295 K for currents 20, 50, 100, and 150 mA, showing the multiple peaks at low temperature. The peak at 2.18 eV is the NN_1 level, and the peak at 2.07 eV is the nitrogen cluster level.

interaction between a localized N state and extended CB states splits the CB into two subbands, E_+ and E_-. Their energies are described by

$$E_{g\pm}(P) = \frac{1}{2}[(E_\Gamma(P) + E_N) \pm \sqrt{(E_\Gamma(P) - E_N)^2 + 4xC_{NM}^2}]. \tag{1}$$

Here, $E_\Gamma(P)$ is the host material pressure dependent Γ conduction band edge, E_N is the energy level of the localized N state, x is the N fraction, and C_{NM} is the coupling parameter determined by the strength of coupling between localized and extended states. All of these energies are defined with respect to the zone center valence band maximum. E_- is taken as the "band-gap" energy and compared with the peak value in pressure dependent EL measurements. E_N was found from photocurrent (PC) measurements (as in Peternai *et al.*[10]) and determined to be 2.21 eV, consistent with other findings[2,11] and shows negligible change with pressure, as previously observed[12] for isolated nitrogen impurities in GaP and calculated theoretically.[3] It is clearly seen in Fig. 1 that the BAC model gives good agreement with the experimental data for which $C_{NM}=4.38$ eV. We note that this is large compared with previous reported values for the GaInNAs/GaAs system for which C_{NM} is typically between 1.26 (Ref. 6) and 2.7 eV.[13] Figure 2 shows EL spectra taken at room temperature and 70 K. Below 110 K, additional sharp emission peaks become visible which can be associated with N–N pair states and N cluster levels.[14] Owing to the multiplicity of these levels, the two-level BAC model cannot completely describe the GaNP system, confirming the reports of Gungerich *et al.*[15] We note here that Kent and Zunger's supercell and multiband empirical pseudopotential calculations agree with our observed positive pressure coefficient,[3] suggesting that the conduction band edge of GaNP is more "direct-like." However, they conclude that intervalley coupling and band anticrossing between all nitrogen perturbed host states (Γ-X-L) and a consideration of cluster states is required to give a complete description of the effect of nitrogen incorporation in GaP. Nevertheless, a simple two-level BAC model based on an "average" of the nitrogen levels provides a useful predictive tool for the pressure dependence of the peak emission at room temperature and, hence, may be useful for tuning the properties of devices based upon this material.

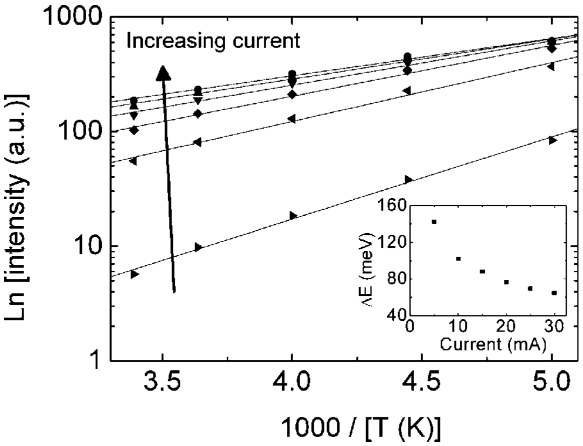

FIG. 3. Arrhenius plot of the integrated electroluminescence for GaNP LEDs at 5–30 mA in 5 mA steps. The slope of the curve relates to the energy splitting ΔE between the conduction band quasi-Fermi level and the X minima of the GaP barrier, which can be seen in the inset to decrease with increasing current, as expected.

When considering the thermal behavior of the LEDs we find that, for a fixed current, the intensity reduces strongly with increasing temperature. This is consistent with a temperature dependent carrier leakage path. We note that in these structures, ignoring Coulombic effects, the valence band offset is zero and, hence, hole leakage is likely to occur. However, while it will decrease the efficiency of the devices, it is unlikely to be particularly temperature or pressure sensitive. The energy separation between the Fermi-level and the X minima of the GaP has been calculated to be $\sim$200 meV, while this is relatively large when compared with the AlInGaP material system, carrier leakage into the X minima may nevertheless occur and contribute to the temperature dependence due to the large density of states of the X minima. In Figure 3, we show an Arrhenius plot of the measured temperature dependence of the integrated EL. From the slope of this plot, we may determine ΔE, the energy separation between the conduction band quasi-Fermi level and the leakage level (here, the GaP X minima). The inset of Fig. 3 shows the current dependence of the extracted values of ΔE, which can be seen to decrease with increasing current. This is consistent with the Fermi level increasing in energy and moving toward the GaP X minima, as more carriers are injected. At low current, ΔE is less than 200 meV, and shows the Fermi level has already passed the E_- level. At high current, ΔE tends to level off with increasing current, consistent with the large density of states in the X minima of GaP.

Further investigations of the importance of the GaP X minima can be determined with the use of high pressure. We may assume that carriers can flow via two paths; radiatively producing a photon, or thermally leaking into the indirect barrier regions and recombining nonradiatively. Since pressure reduces the Γ-X intervalley separation, it may be used to probe the importance of this leakage path. In the presence of a leakage process, the radiative component of the injected current J_{rad} associated with the light emission may be written as

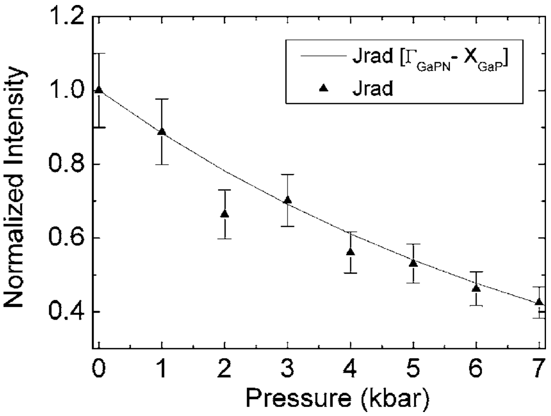

FIG. 4. Normalized intensity vs pressure at a fixed current for GaNP LEDs. The solid line shows the calculated change in normalized intensity due to electron leakage into X_{GaP}.

$$J_{\mathrm{rad}} = J_0 \exp\left(\frac{d\Delta E}{dP}\frac{P}{kT}\right), \tag{2}$$

where J_0 is a constant, $d\Delta E/dP$ is rate of change of the conduction band quasi-Fermi-level-leakage level splitting with pressure, k is the Boltzmann constant, T is the absolute temperature, and P is the pressure. The pressure dependence of the quasi-Fermi level is known (via the emission spectrum peak shift) and the pressure coefficient of the X minima in GaP is well known ($dE_{X(\mathrm{GaP})}/dP = -1.5$ meV/kbar).[16] Figure 4 shows the measured pressure dependence of the integrated EL spectra (normalized at atmospheric pressure) for a GaNP device at a fixed current. The decrease in EL intensity with pressure is strong evidence that carrier leakage into the X minima is significant. From earlier, the pressure coefficient of the emission peak energy and the X minima in GaP is known. Thus, $d\Delta E/dP = -3.1$ meV/kbar. Substituting this value of $d\Delta E/dP$ into Eq. (1) yields the solid line shown in Fig. 4. This provides an excellent agreement with the experimental data confirming that leakage into the X minima of GaP is the important nonradiative recombination process in these devices.

In summary, we have presented temperature and high pressure investigations into the material properties and device characteristics of GaNP-based LEDs. The evidence of several N levels in low temperature electroluminescence show that while the BAC model cannot fully describe this system, it can be used as a predictive tool based upon an average N position. Furthermore, high pressure measurements have shown that carrier leakage into the X minima of the GaP limits the efficiency of these devices.

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