Effects of nitrogen on the band structure of GaN_xP_{1-x} alloys

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We report that the incorporation of N in GaN_xP_{1-x} alloys ($x \geqslant 0.43\%$) leads to a direct band-gap behavior of GaNP. For N concentration lower than 0.43%, a series of sharp emission lines from the various N pair centers are observed for GaNP bulk layers. With increasing N concentration higher than 0.43%, a strong photoluminescence (PL) emission from GaNP bulk layers is observed at room temperature. While the PL peak redshifts with increasing N concentration to 3.1%, the PL intensity remains as intense. Absorption measurements show a direct band-gap behavior of GaNP alloys. © *2000 American Institute of Physics.* [S0003-6951(00)03510-5]

Although much effort has been made in an attempt to grow GaAs or InP on Si, a large number of dislocations in the epilayer limits the material quality and prevents their practical use, due to the large lattice mismatch between them and Si.[1–3] With the emergence of nitrides, there is an increasing interest in the growth of III–N–V compounds because of the possibility of lattice matching to Si,[4–8] such as $GaN_{0.02}P_{0.98}$. Furthermore, theoretical calculations show a direct band gap of GaNP alloys with very low nitrogen concentrations.[9] It is also possible that the number of dislocations may be drastically reduced, leading to an improvement of the material quality and the possibility of integrating GaNP-based optoelectronics with Si electronics technology.

It is well known that at very low concentrations ($\sim 10^{16}\,cm^{-3}$), an isolated N introduces a highly localized state in GaP, where the energy level is located slightly below the conduction band minimum.[10,11] Such a spatial localization leads to a quasi-direct transition in GaP:N, which makes GaP:N a widely used material for green light-emitting diodes even though GaP has an indirect band gap.[10–12] With slightly increasing N concentrations, N forms NN_i pairs, which shift light emission wavelength from green to yellow.[13,14] With increasing N concentration, Baillargen *et al.* pointed out that GaN_xP_{1-x} alloy ($x \geqslant 0.45\%$) was an indirect band-gap semiconductor because of the reduction of the photoluminescence (PL) intensity.[6] Bellaiche *et al.*, however, using 512-atom supercell pseudopotential band structure calculations, predicted a transition from indirect to direct band gap at a N concentration of 3% for GaNP alloys.[9]

In this letter, we show that the incorporation of N in GaN_xP_{1-x} alloys ($x \geqslant 0.43\%$) leads to a direct band-gap behavior of GaNP due to the strong interaction among N-related bound states which exhibit a quasi-direct nature in the optical transition, and thus produces a very strong PL emission at room temperature (RT).

The GaNP bulk samples were grown on (100) GaP substrates by gas-source molecular-beam epitaxy in a modified Varian Gen-II system. 7N elemental Ga and thermally cracked PH_3 at 980 °C were used. High-purity N_2 was injected through a N radical beam source (Oxford Applied Research Model MPD21) operated at a radio frequency (rf) of 13.56 MHz to generate active N species. For the GaP buffer layers, the growth temperature was 640 °C. For GaNP bulk layers, the growth temperature was decreased to 520 °C to incorporate N.

The N composition was determined by high-resolution x-ray rocking curve (XRC) measurements and theoretical dynamical simulations. XRC measurements were performed using a Phillip x-ray diffractometer. Low-temperature PL measurements were carried out by mounting the samples in a liquid He cryostat and using the 514.5 nm line of an Ar^+ laser as the excitation source. A GaAs cathode photomultiplier tube was used to detect the signal at the exit of a 50 cm monochromator through an amplifier. Optical absorption measurements were performed using a broadband halogen lamp. The signal was detected at the exit of a 600 lines/mm monochromator by a Si photodiode.

(400) XRCs of GaN_xP_{1-x} bulk layers are shown in Fig. 1, where the dashed lines show the dynamical theoretical simulations. Curves (a) and (b) correspond to 2500 Å thick GaN_xP_{1-x} layers with N concentration of 0.43% and 0.81%, respectively. The Pendelloesung fringes are well resolved, indicating high crystalline quality. Curve (c) corresponds to a 7500 Å thick GaN_xP_{1-x} layer with N concentration of 2.3%. Due to the much larger thickness than the critical layer thickness calculated from the Matthews and Blakeslee's model ($\sim$500 Å),[15] the $GaN_{0.023}P_{0.977}$ sample was partially relaxed and the x-ray peak is broader than that of the simulation result.

Figure 2 shows PL spectra of 2500 Å thick GaN_xP_{1-x} with $x \leqslant 0.81\%$ at 10 K. For the very low N concentration sample ($x = 0.05\%$, corresponding to $10^{19}\,cm^{-3}$), there are a series of sharp emission lines from different NN_i ($i \leqslant 5$) pairs, similar to previous reports.[10,11,14] With increasing N concentration up to 0.43%, the sharp emissions from NN_i pairs disappear and a broad PL peak with strong intensity from the GaNP alloy appears. The PL peak redshifts and the intensity also increases with increasing N concentration.

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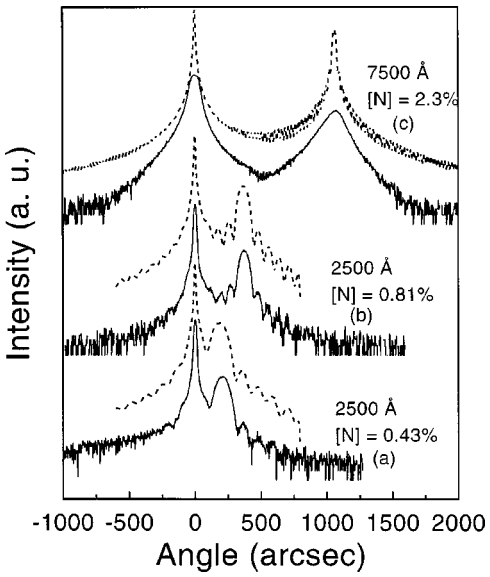

FIG. 1. (400) XRCs of GaN_xP_{1-x} bulk layers. The dashed lines show the dynamical theoretical simulations.

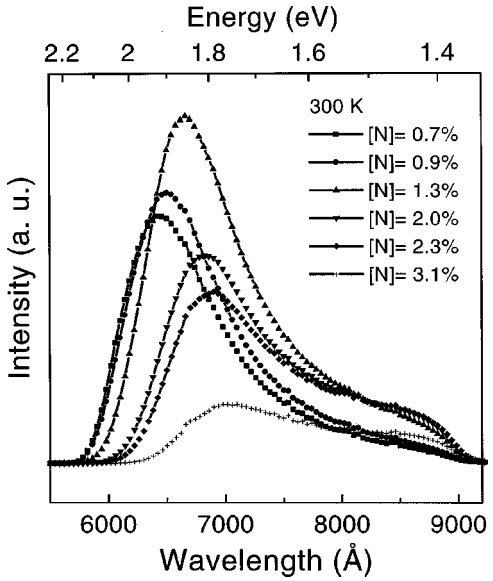

FIG. 3. Room-temperature PL spectra for 7500 Å thick GaN_xP_{1-x} ($x \geqslant 0.7\%$) bulk layers.

Figure 3 shows PL spectra for 7500 Å thick GaN_xP_{1-x} ($x \geqslant 0.7\%$) bulk layers at RT. The PL intensity is very strong. A red spot can be seen even with a naked eye. The PL intensity of GaNP bulk layers increases with increasing N concentration, up to 1.3%, contrary to Baillargen *et al.*'s report, where PL intensity decreased.[6] The PL intensity increases with higher N concentration mainly due to the increased matrix element for the transition from the conduction band to the valence band.[9] With a N concentration more than 1.3%, PL intensity decreases due to decreased sample quality partly as a result of increased strain.

Our results qualitatively agree with the theoretical calculation of Bellaiche *et al.*, where they found a transition point from indirect to direct band gap at a N concentration of 3% for GaNP.[9] In dilute $GaAs_{1-x}N_x$ and $GaInAs_{1-x}N_x$ alloys, the large band-gap reduction has previously been explained as a result of repulsion between the GaAs or GaInAs conduction band edge and a resonant state of the isolated nitrogen center.[16,17] However, recently, we have attributed the large band-gap reduction as well as the heavy conduction band effective mass and its unusual composition dependence to the formation of nitrogen related impurity band evolved from nitrogen pair bound states in heavily doped GaAs:N.[18] We believe that a very similar situation occurs in the $GaP_{1-x}N_x$ alloys studied here. In fact, in an earlier study of $GaP_{1-x}N_x$ alloys,[19] it has been pointed out that the heavy nitrogen doping in GaP causes a band formation from the bound states of the isolated nitrogen center and thus a band-gap reduction. Because of the fact that the absorption peak in Ref. 19 was observable at the energy of NN_1 for concentrations up to $x=2\%$, it appears that the new conduction band in $GaP_{1-x}N_x$ alloys is a convolution of all the nitrogen related bound states, which are inhomogeneously broadened with increasing N concentration. This is clearly established by the PL in Fig. 2 and by the PLE in Fig. 3 of Ref. 19. The intercenter interactions or the formation of large nitrogen clusters lead to band edge states extending to the energy region below that of the lowest bound state NN_1, and thus a further reduction of the band gap of the alloy, inducing the formation of a direct band gap. Therefore, a very strong PL emission is expected in GaNP bulk layers. No RT PL emission was reported previously in GaNP alloys with similar N compositions, likely due to poor sample quality, not the indirect nature of the band structure.[6,8]

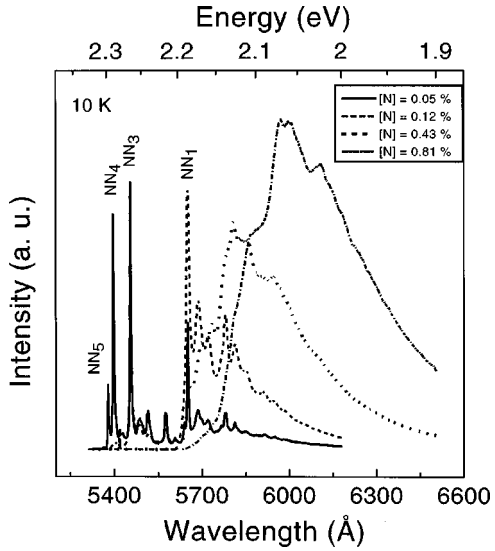

FIG. 2. 10 K PL spectra of 2500 Å thick GaN_xP_{1-x} with $x \leqslant 0.81\%$.

Figure 4 shows the square of the absorption coefficient of GaN_xP_{1-x} films as a function of photon energy. Quite obviously, the absorption coefficient obeys a square law, indicating a direct band-gap behavior of GaNP. Furthermore, as the N concentration is increased, the band edge of GaNP shifts to lower energy, indicating a reduction of band-gap energy.

In summary, we have shown that incorporation of N in GaN_xP_{1-x} alloys ($x \geqslant 0.43\%$) leads to a direct band-gap behavior of GaNP. With a N concentration lower than 0.43%, N forms pairs and produces a series of sharp emission lines. With increasing N concentration higher than 0.43%, the N pair bound states develop into a N-related impurity band. Therefore, the GaNP alloy becomes a direct band-gap mate-

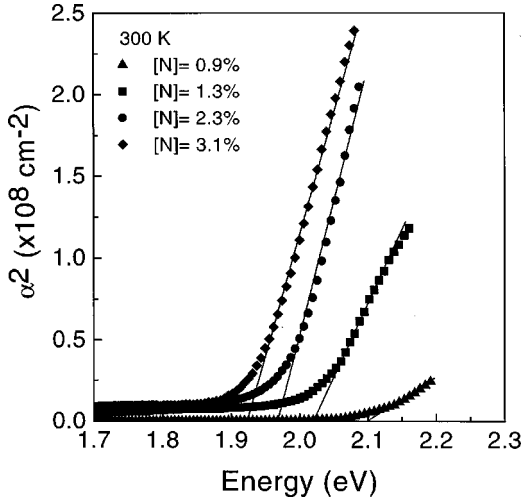

FIG. 4. Square of the absorption coefficient of GaN_xP_{1-x} films as a function of photon energy.

rial, and yields a high efficiency RT PL from the epilayer. The superior properties of direct band gap and lattice matching to Si make $GaN_{0.02}P_{0.98}$ a very promising light-emitting material for potential integration with Si electronics technology.

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