Band edge optical transitions in dilute-nitride GaNSb

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Dilute-nitride GaNSb bulk materials with up to 1.4% nitrogen were grown by molecular beam epitaxy on GaSb substrates. Hall measurements indicate residual hole concentrations of nearly 10^{19} cm^{-3} at room temperature, but a decrease to below 10^{16} cm^{-3} and a hole mobility of 1300 cm^2/V s at 4.5 K for a sample with 0.6% nitrogen. Photoluminescence (PL) and optical absorption measurements demonstrate a bandgap reduction by up to 300 meV with increasing nitrogen incorporation. The experimental absorption spectra are well fit by a functional dependence corresponding to direct allowed optical transitions, and the PL spectra are also consistent with that interpretation. Room temperature carrier relaxation times in the picosecond range are measured using an ultrafast PL upconversion technique. © *2009 American Institute of Physics.*
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A strong reduction in the fundamental bandgap with increased nitrogen content has been predicted for GaNSb alloys.[1] A theoretical tight-binding analysis of how nitrogen incorporation affects the material bandgap revealed a strong sensitivity to N complexes,[2] implying a restricted applicability of the widely used band anticrossing model.[3] While a redshift of the absorption edge with increased nitrogen content was observed for GaNSb grown on lattice mismatched GaAs substrates (corresponding to a tensile strain above 7%),[4,5] it was not apparent which optical transitions (i.e., direct or indirect; allowed or forbidden) accounted for the observed spectra. No reports on the corresponding photoluminescence (PL) from GaNSb bulk materials have been published so far. The observed PL from dilute-nitride-antimonide quantum-well samples[6,7] is more complicated to interpret with regard to the fundamental material bandgap.

This work will present the results of a comprehensive absorption and PL study of GaNSb bulk materials grown on nearly lattice-matched GaSb substrates. The data reveal the effect of nitrogen incorporation on the fundamental bandgap, and on the character of band edge optical transitions in dilute-nitride GaNSb bulk materials.

The dilute-nitride alloys were grown by solid-source molecular beam epitaxy (MBE) on nominally undoped GaSb substrates (residual p-type doping level $\approx 10^{17}$ cm^{-3} at room temperature). Nitrogen was introduced into the growth chamber using a rf plasma gas source. The nitrogen compositions were determined from high-resolution x-ray rocking curves to vary from 0.3% to 1.4%. Since the lattice mismatch between the substrate and the GaNSb epitaxial layers corresponds to a tensile strain below 0.4%, little (if any) strain relaxation is expected. Further details of the growth conditions and x-ray properties will be published elsewhere.

Two groups of samples were grown and characterized. One group (A) was designed for absorption studies. These samples comprised a 2-μm-thick GaN$_x$Sb$_{1-x}$ layer grown directly onto a GaSb buffer. The other group (B) was designed for PL and Hall analysis. These samples comprised a 1-μm-thick GaN$_x$Sb$_{1-x}$ layer sandwiched between Al-containing wide bandgap materials to assure confinement of the carriers and electrical isolation from the substrate. A thin GaSb cap was grown on top to prevent rapid oxidation of the AlAsSb in atmosphere.

Figure 1 shows temperature-dependent Hall charge carrier densities and mobilities acquired at a magnetic field of 1 T for two samples from group B with nitrogen concentrations of 0.6% (solid circles) and 1.2% (open squares). The AlAsSb barriers in these samples electrically isolate the GaNSb epilayers from the conducting GaSb substrates. Both samples are found to be p-type, with concentrations ranging from $(7-9) \times 10^{18}$ cm^{-3} at 300 K to as little as 7
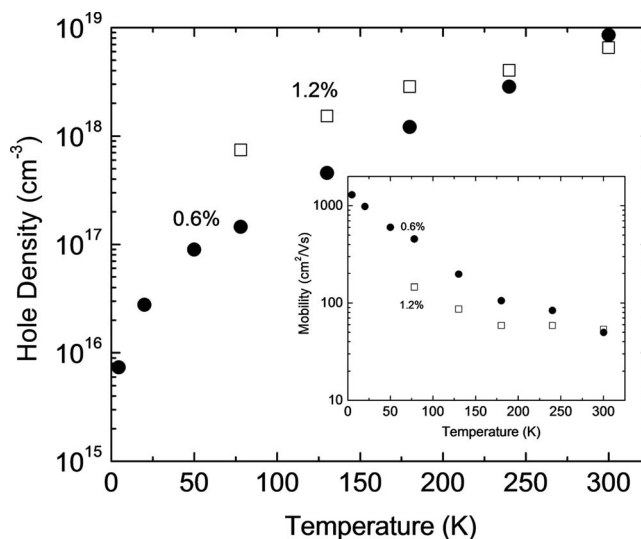

FIG. 1. Hole concentrations and mobilities (inset) vs temperature for group B samples with 0.6% and 1.2% nitrogen, from Hall measurements at 1 T. Data for the 1.2% sample became unreliable at the lowest temperatures.

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$\times 10^{15}$ cm^{-3} for the 0.6% sample at 4.5 K. The nature of the gradual freeze-out of the hole population is not understood. The inset in Fig. 1 plots corresponding dependences of the hole mobilities on temperature. From ≈ 50 cm^2/V s at 300 K, the hole mobility in the 0.6% sample increases to 450 and 1300 cm^2/V s at $T=77$ and 4.5 K, respectively. Hall mobilities obtained for reference samples with GaSb epilayer in place of GaSbN ones are ~ 900 and 9000 cm^2/V s at 300 and 77 K, respectively. The residual hole concentration in the reference sample was mid-10^{16}-cm^{-3} at 300 K and mid-10^{15}-cm^{-3} at 77 K.

Optical absorption spectra were determined from transmission measurements made using a Fourier transform infrared spectrometer equipped with liquid nitrogen cooled InSb and mercury cadmium telluride detectors. The transmission spectra were analyzed assuming multiple reflections in the sample and the absence of fringes.[8] Transmission measurements were performed for both the grown samples and their substrates. With residual hole concentrations of the order 10^{17} cm^{-3}, the GaSb substrates exhibited free carrier absorption coefficients of ≈ 40 cm^{-1} at 0.3 eV, which are similar to previous reports.[8] The substrate absorption spectra were subtracted from those of the samples to isolate the epilayer band-to-band absorption from the free carrier absorption.[8] The resulting absorption spectra $\alpha(h\nu)$ obtained for samples with nitrogen compositions of 0.3%, 0.7%, and 1.4% are presented in Fig. 2(a).

At photon energies approaching the room temperature GaSb bandgap of ≈ 0.72 eV, the extracted experimental transmission spectra become distorted by strong absorption in the thick substrates. Note also that the spectrum for the sample with 0.3% nitrogen shows some Fabry–Pérot fringing. This sample belongs to group B, for which the AlAsSb carrier confinement layers surrounding the GaNSb provide a large refractive-index contrast. On the other hand, the two samples from group A (0.7% and 1.4% of nitrogen) display no significant fringing. The GaNSb absorption edge is seen to experience a significant redshift with increasing nitrogen content, in agreement with previously published data.[4,5] Figure 2(b) shows the same GaNSb spectra plotted in coordinates of $(\alpha \cdot h\nu)^2$ versus $h\nu$, for which direct allowed optical transitions between parabolic bands should appear as straight lines (see, for instance, Ref. 9). Near the band edge, experimental absorption edges typically fit the expression $\alpha \propto \sqrt{h\nu - E_g}/h\nu$. The increased absorption in the GaN$_{0.014}$Sb$_{0.986}$ sample at energies above 0.55 eV can be attributed to the strong conduction band nonparabolicity expected in dilute nitrides. The fit of the sample with 0.3% of nitrogen is less satisfactory, presumably due to the observed spectral fringing and its close proximity to the GaSb edge.

The fundamental bandgap (E_g) can be estimated from the intercept, as shown in Fig. 2(b). A bandgap reduction of about 300 meV compared to GaSb is observed in the 1.4% nitrogen sample. This number is in rough agreement with tight-binding and pseudopotential supercell calculations[1,2] predicting GaSbN bandgap in the range of 0.4–0.45 meV for 1.5% of nitrogen. The large absorption coefficient approaching 10^4 cm^{-1} and the absorption edge's functional dependence on energy imply that this GaNSb material indeed has a
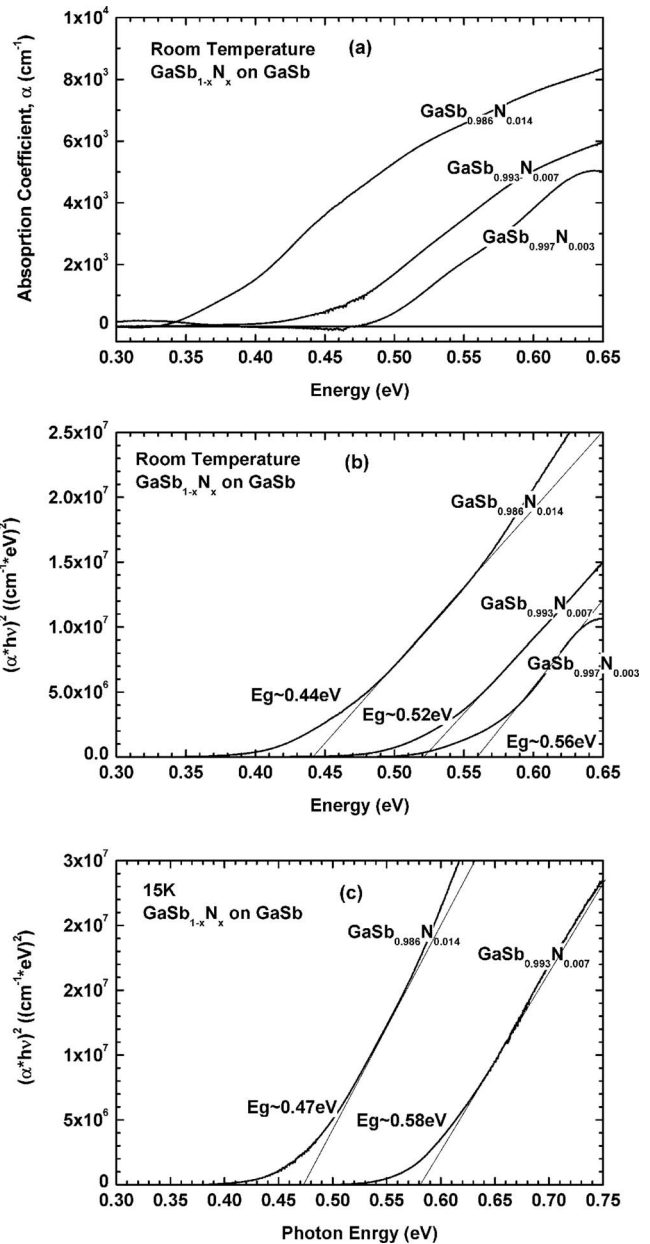

FIG. 2. (a) Absorption spectra at room temperature for three GaNSb layers; (b) room temperature absorption spectra plotted in coordinates corresponding to direct allowed optical transitions; (c) absorption spectra at 15 K.

direct bandgap as predicted by theoretical calculations.[1,2] The absorption spectra of the samples with 0.7% and 1.4% nitrogen were also measured at 15 K [Fig. 2(c)]. As expected, the GaNSb bandgap increases with decreasing temperature, although the observed effect becomes less pronounced at higher nitrogen content (~ 85 meV for GaSb,[10] ~ 60 meV for GaN$_{0.007}$Sb$_{0.993}$, and only ~ 30 meV for GaN$_{0.014}$Sb$_{0.986}$), the direction predicted by theory.[11] For a hole density of 10^{19} cm^{-3}, the Moss–Burstein shift at room temperature is estimated to be ≈ 35 meV, assuming the valence band of GaNSb is similar to that of GaSb. This implies that the actual energy gap is smaller than the value indicated in Fig. 2 by that amount. At low temperatures, the carrier freeze-out leads to a negligible shift of the absorption edge.

We applied the ultrafast upconversion technique to study PL in GaNSb bulk materials.[12] In this experiment the light
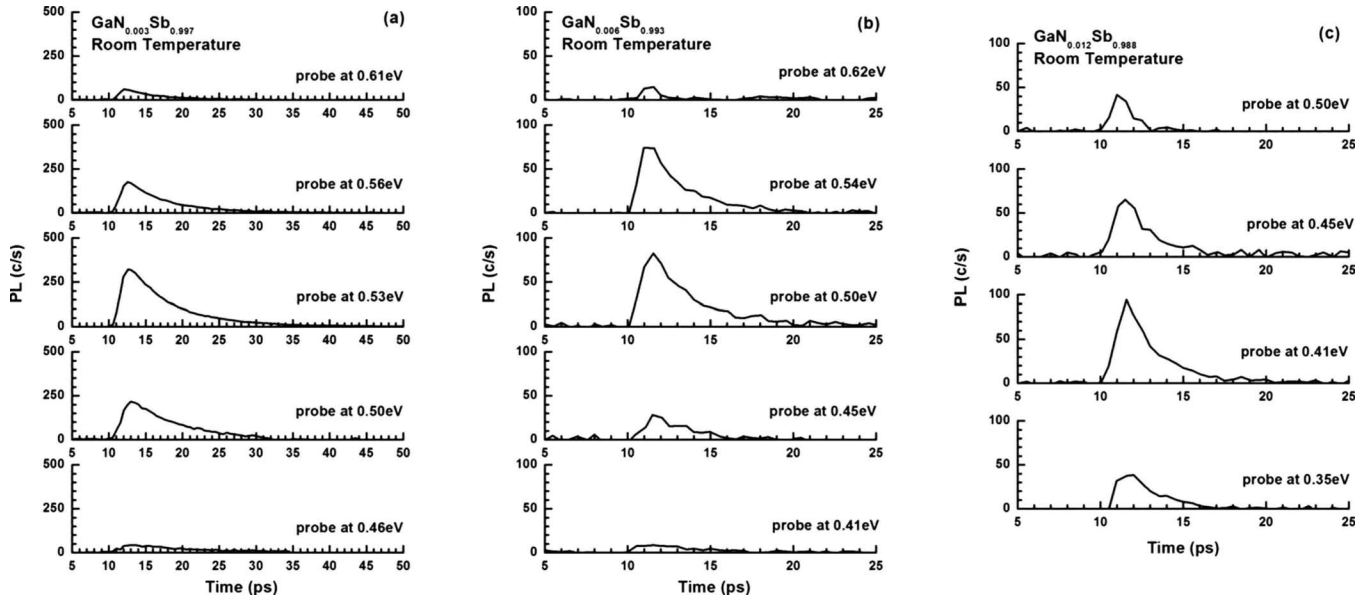
FIG. 3. PL relaxation curves measured at room temperature for (a) $GaN_{0.003}Sb_{0.997}$, (b)$GaN_{0.006}Sb_{0.993}$, and (c) $GaN_{0.012}Sb_{0.988}$. The energies of the photons being upconverted are shown in each graph.

from a Nd:glass mode-locked 200 fs/80 MHz laser was divided into two beams, with one beam for excitation and the other for upconversion. Mid-IR PL excited by the excitation pulse (20 mW average power focused down to 10^{-6} cm^2 on the sample) was mixed with the delayed upconversion pulse in a nonlinear crystal (periodically poled lithium niobate). The sum frequency radiation was then dispersed by a spectrometer and registered by a GaAs-cathode photomultiplier tube. The setup is capable of detecting PL from materials with very short carrier lifetimes (the system temporal resolution is about 0.5 ps as estimated from autocorrelation measurements). Periodically poled lithium niobate crystals with different poling periods allowed for the effective upconversion of mid-IR PL to cover the spectral range from below 2 μm to above 4 μm. The upconversion photon energies were selected by choosing the crystal period and spectrometer grating position. The photoexcitated carrier concentration necessary to observe the PL signal at room temperature was rather high, in the range of $(1-5) \times 10^{18}$ cm^{-3}.

Figure 3(a) shows the PL decay measured at different photon energies for the sample with 0.3% nitrogen. Immediately after the excitation pulse, the maximum PL signal occurs near 0.53 eV (whereas no PL signal could be registered in this spectral region for the reference sample that contained a GaSb layer in place of the GaNSb). This PL peak energy agrees with the bandgap energy estimated from the absorption studies (0.56 eV). Figures 3(b) and 3(c) show the PL decays obtained for the two samples from group B with 0.6% and 1.2% nitrogen. Again, the peak energies of the initial PL signals are consistent with the fundamental bandgaps estimated for the group A samples with similar nitrogen contents, i.e., near 0.5 and 0.41 eV. The presence of band-to-band PL again confirms the direct allowed nature of the optical transitions in dilute-nitride GaNSb bulk materials containing up to at least 1.4% nitrogen.

Figure 4 shows the PL temporal relaxation curves measured for the 0.3%, 0.6%, and 1.2% nitrogen samples at pho-

ton energies corresponding to the initial PL maximum. Assuming linear recombination, the estimated carrier lifetimes are $\approx$6–7 ps for $GaN_{0.003}Sb_{0.997}$ and 2–3 ps for $GaN_{0.006}Sb_{0.993}$ and $GaN_{0.012}Sb_{0.988}$. The latter two samples exhibited less intensive initial PL signals since their carrier relaxations competed with the PL rise times (note that in Fig. 4, the PL signal for the 0.3% sample is still growing at a point where it is already starting to decay for the other two). The relaxation curves seem to be well fit by a single time constant despite the high excitation intensity ($>10^{18}$ cm^{-3}), which may be associated with the large residual doping levels. The rapid carrier relaxation dynamics are probably associated with recombination through defect states in the forbidden gap.

Summarizing, GaSbN bulk materials were grown by MBE with nitrogen contents of up to 1.4%. Hall measure-
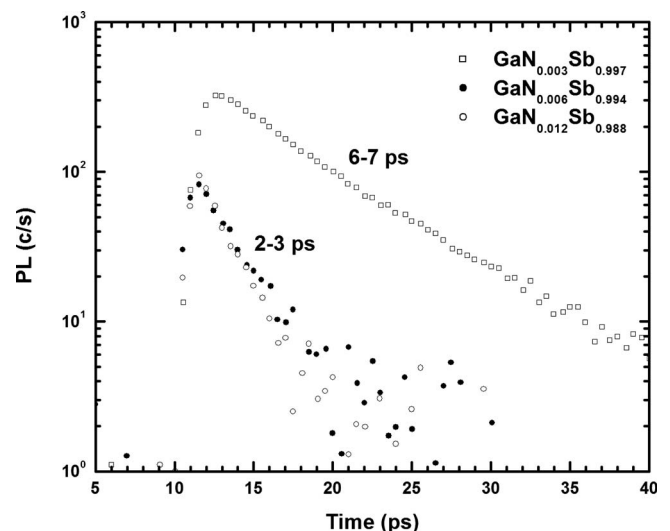

FIG. 4. PL relaxation curves measured at room temperature for photon energies corresponding to maximum initial PL signal for GaNSb bulk materials with 0.3% (0.53 eV), 0.6% (0.5 eV), and 1.2% (0.41 eV) of nitrogen.

ments indicate residual hole concentrations of nearly 10^{19} cm^{-3} at room temperature, but gradual freeze-out to below 10^{16} cm^{-3} (with hole mobility 1300 cm^2/V s) in the 0.6% nitrogen sample at 4.5 K. Transmission experiments show that the absorption edge energy decreases by nearly 300 meV compared to GaSb for the sample with 1.4% nitrogen. The energies of the radiative transitions correlate well with the bandgap energies estimated assuming direct allowed band-to-band optical transitions. The carrier lifetimes determined from a nonlinear upconversion technique, and assuming linear recombination, decrease from 6–7 to 2–3 ps when the nitrogen content is increased from 0.3% to 1.4%. Further studies are required to identify the physical mechanism responsible for the fast carrier relaxation dynamics in dilute-nitride GaNSb bulk materials.

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