Doping and carrier transport in $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ alloys

Wei Li* and Markus Pessa

Optoelectronics Research Center, Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland

Juha Toivonen and Harri Lipsanen

Optoelectronics Laboratory, Helsinki University of Technology, PL 3000, 02015 TKK, Finland

(Received 20 March 2001; published 29 August 2001)

Si- and Be-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}(0 \le x \le 3\%)$ layers are grown on GaAs substrates by gas-source molecular beam epitaxy with a nitrogen radical beam source. The carrier concentration and mobility are observed to decrease substantially with increasing nitrogen content in both *p*- and *n*-type GaInNAs films. After rapid thermal annealing at 750 °C, the Be dopants are almost fully activated in *p*-type material; yet only a small fraction of the Si dopants are activated in *n*-type GaInNAs films. At low temperature a broad photoluminescence band centered at 1.041 eV (about 120 meV below the band gap) is observed in *n*-type GaInNAs, which suggests the possible compensating centers present in Si-doped GaInNAs.

DOI: 10.1103/PhysRevB.64.113308

GaInNAs alloy containing a few percent of nitrogen has received much interest both because of a practical and a fundamental point of view.¹⁻³ Incorporation of nitrogen into GaInAs reduces the strain of InGaAs layers grown on GaAs. In addition, the band gap decreases as N is added due to a large band gap bowing.⁴ Recent advances in the GaInNAs/ GaAs material system has led to much progress on the application of this material system for a variety of devices, such as 1.3 μ m vertical-cavity surface emitting lasers on GaAs substrates,¹ and high efficiency multijunction solar cell as well as heterojunction bipolar transistors (HBT).^{5,6} Although the optical properties of GaInNAs/GaAs heterostructures have been extensively studied, comparatively little is known concerning the transport properties of GaInNAs on GaAs.^{7,8} In this Brief Report, we report the transport properties of Si- and Be-doped $Ga_{1-3r}In_{3r}N_rAs_{1-r}$ layers ($0 \le x$ ≤ 0.03) lattice matched on semi-insulating GaAs substrates. The carrier concentration and Hall mobility are observed to decrease significantly with increasing the nitrogen content in both p- and n-type GaInNAs films. After rapid thermal annealing (RTA) at 750 °C, the Be dopants are almost fully activated in *p*-type GaInNAs layers; yet only a small fraction of the Si dopants are activated in *n*-type GaInNAs films. A broad photoluminescence band centered at 1.041 eV is observed in annealed Si-doped material, which suggests the possible compensating deep levels present in n-type GaInNAs.

0.5 μ m thick Si- and Be-doped Ga_{1-3x}In_{3x}N_xAs_{1-x} layers lattice matched ($-400 \le \Delta a/a \le 400$ ppm) on semiinsulating (100) GaAs substrates were grown by gas-source molecular beam epitaxy (GSMBE). Group III fluxes are produced by thermal effusion cells, group V flux is provided by a thermally cracking AsH₃, and reactive nitrogen is provided by a radio frequency (rf) plasma cell. The GaInNAs films were grown at 440 °C to incorporate N into the GaInAs layers. The free carrier concentration of unintentionally doped GaInNAs bulk layer was around 5×10^{15} cm⁻³ of *n*-type conduction. The detailed growth conditions were reported in Ref. 9. Silicon and beryllium were used as *n*- and *p*-type dopant for GaInNAs, respectively. The N content was deterPACS number(s): 73.61.Ey, 81.15.Hi, 78.55.Cr

mined using high-resolution x-ray diffraction on a GaAsN epitaxial layer grown under the same conditions (plasma cell operation, substrate temperature) and assuming that the N content is the same in the GaAsN and GaInNA layers. RTA was performed on these samples at 750 °C in a flowing N₂ ambient in order to improve the crystalline quality of N-containing material.⁹ The free carrier concentration and mobility were determined from Hall effect measurements in the Van der Pauw geometry. The photoluminescence measurements were performed using the 514.5 nm line of an Ar⁺ laser as the excitation source. A liquid-nitrogen-cooled Ge detector was used to detect the signal at the exit of a 50 cm monochromator associated with a standard lock-in technique.

Figure 1 shows the hole concentrations and Hall mobility for as-grown and annealed GaInNAs samples as a function



FIG. 1. Concentrations (a) and Hall mobility (b) of holes as a function of RTA time for as-grown and annealed GaInNAs samples doped with $Be(3 \times 10^{18} \text{ cm}^{-3})$.



FIG. 2. Concentrations (a) and Hall mobility (b) of electrons as a function of RTA time for as-grown and annealed GaInNAs samples doped with $Si(2 \times 10^{18} \text{ cm}^{-3})$.

of RTA time. The p-type GaInNAs samples are doped with Be at the same level of 3×10^{18} cm⁻³. With 0.2% of nitrogen, the hole concentration and Hall mobility of GaNAs film are found to be nearly the same as that of GaAs layer. While, with further increasing of N concentrations up to 3%, the hole concentration of the as-grown GaInNAs samples decreases by about two orders of magnitude. The corresponding room temperature hole mobilities, as determined by the Hall measurements, are also reduced significantly as shown in Fig. 1(b). It is found that H atom is incorporated alongside N in as-grown GaInNAs samples and dissociate from the layer by annealing from secondary ion mass spectrometry (SIMS) measurements. Therefore, the free hole concentration decreases with N incorporation mainly due to the formation of H-N-Be complexes, which would passivate the acceptors in GaInNAs. Similar results are also reported in metalorganic chemical vapor deposition and GSMBE-grown GaInNAs samples.7,8

In order to depassivate the acceptors and improve the crystalline quality of GaInNAs layer,⁹ RTA at 750 °C was performed on the Be-doped samples. As shown in Fig. 1, the depassivation of the Be acceptors has converted the as-grown high-resistivity GaInNAs:Be into *p*-conducting materials, and the acceptors are almost fully activated independent of the N content of the material. The hole concentration and mobility increase rapidly in the initial stage of RTA. As the annealing continues, both the hole concentration and mobility reach constant values. The reduction of the Hall mobility with N incorporation is mainly caused by the strong alloy disorder scattering in GaInNAs alloys.

The transport properties of *n*-type GaInNAs (doped with Si at a level of 2×10^{18} cm⁻³) are also investigated as shown in Fig. 2. In contrast to *p*-type GaInNAs, the electron mobility, as determined by the Hall measurements, is reduced sig-



FIG. 3. Low-temperature photoluminescence spectra of Si- and Be-doped GaInNAs($N \sim 1.6\%$) annealed at 750 °C for 10 sec.

nificantly when only 0.2% of nitrogen incorporated. The electron concentrations are also reduced with increasing the N content in the *n*-type GaInNAs layer. After annealing at 750 °C only a small fraction of the Si dopants are activated in *n*-type films with higher N content. The higher the N concentration is, the less the free electron concentration obtained in the annealed *n*-type GaInNAs layers. In addition, the Hall mobility of annealed samples decreases with N incorporation, which can be attributed to the strong alloy disorder scattering as well as to the enhanced electron effective mass in these GaInNAs alloys.

The results presented above suggest the possible formation of N-related defects compensating the donors in annealed *n*-type GaInNAs. Further information on the low doping efficiency of Si donor in GaInNAs was obtained from low temperature PL measurements. In Fig. 3, a comparison is shown between the PL of Si-doped and Be-doped GaInNAs samples after annealing at 750 °C. The curves were intentionally offset along y axis with respect to each other for better clarity. For p-type GaInNAs, the PL emission has a asymmetric line shape with a sharp high energy cutoff and an exponential low-energy tail, which is attributed to the transitions between either acceptors or holes and photogenerated electrons trapped by localized states (induced by alloy potential fluctuations) below the band edge. In contrast to p-type samples, however, it is found that the PL spectra line shape of Si-doped samples consists of a high-energy luminescence peak and a broad low-energy band centered at 1.041 eV about 120 meV below the band gap. The broad low-energy band exhibits a strong dependence on measurement temperature and excitation power. In particular, a temperature in



FIG. 4. Proposed model of the luminescence in *n*-type GaInNAs layer.

crease causes quenching of the PL intensity, accompanied by a strong redshift of the PL maximum position. Therefore, the appearance of this broad low-energy band in PL spectra of an Si-doped sample suggests the possible existence of acceptorlike states below the bottom of the conduction band.

In order to explain the results mentioned above, we propose a model as shown schematically in Fig. 4. The acceptorlike centers in *n*-type GaInNAs samples, we believe, are probably related to N-induced localized states due to alloy composition inhomogeneity. These localized states in the band gap act as acceptors to compensate the Si donors in *n*-type material, while for *p*-type and semi-insulating GaInNAs they are in neutral charge states (as expected for an isoelectronic impurity). Moreover, the formation of these acceptorlike centers can be enhanced due to the energy gained

- ¹M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, Jpn. J. Appl. Phys., Part 1 **35**, 1273 (1996).
- ²S. Sato, Y. Osawa, T. Saitoh, and I. Fujimura, Electron. Lett. 33, 1386 (1997).
- ³M. C. Larson, M. Kondow, T. Kitatani, K. Nakahara, K. Tamura, H. Inoue, and K. Uomi, IEEE Photonics Technol. Lett. **10**, 188 (1998).
- ⁴K. Uesugi, N. Marooka, and I. Suemune, Appl. Phys. Lett. 74, 1254 (1999).

by partly compensating the donors or by forming energetically stable N-related complexes with Si donors.

In summary, Si- and Be-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}(0 \le x \le 3\%)$ layers are grown on GaAs substrates by gassource molecular beam epitaxy with a nitrogen radical beam source. The carrier concentration and mobility are observed to decrease substantially with increasing nitrogen content in both *p*- and *n*-type GaInNAs films. After rapid thermal annealing at 750 °C, the Be dopants are almost fully activated in *p*-type material; yet only a small fraction of the Si dopants are activated in *n*-type films. At low temperature a broad photoluminescence band around 1.041 eV (about 120 meV below the band gap) is observed in *n*-type samples, probably related to N-induced localized states acting as acceptors to compensate Si donors.

- ⁵S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, Appl. Phys. Lett. **74**, 729 (1999).
- ⁶N. Y. Li, P. C. Chang, A. G. Baca, X. M. Xie, P. R. Sharps, and H. Q. Hou, Electron. Lett. **36**, 81 (2000).
- ⁷H. P. Xin, C. W. Tu, and M. Geva, Appl. Phys. Lett. **75**, 1416 (1999).
- ⁸J. F. Geisz, D. J. Friedman, J. M. Olson, S. R. Kurtz, and B. M. Keyes, J. Cryst. Growth **195**, 401 (1999).
- ⁹W. Li, J. Turpeinen, P. Melanen, P. Savolainen, P. Uusimaa, and M. Pessa, Appl. Phys. Lett. **78**, 91 (2001).

^{*}Electronic mail: wei.li@orc.tut.fi