

Nonradiative recombination centers in Ga(As,N) and their annealing behavior studied by Raman spectroscopy

M. Ramsteiner,^{a)} D. S. Jiang,^{b)} J. S. Harris,^{c)} and K. H. Ploog
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5–7, 10117 Berlin, Germany

(Received 1 December 2003; accepted 16 January 2004)

Nitrogen-related defects in diluted Ga(As,N) have been detected by Raman scattering in resonance with the localized E_+ transition. These defects are attributed to local vibrational modes of nitrogen dimers on Ga- and As-lattice sites. Rapid thermal annealing under appropriate conditions is found to be able to remove the nitrogen dimers. The required minimum annealing temperature coincides with the threshold-like onset of strong, near-band-gap photoluminescence. This finding suggests that the nitrogen dimers are connected with nonradiative recombination centers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1687465]

The diluted nitride-arsenide semiconductors Ga(As,N) and (In,Ga)(As,N) are promising materials for optoelectronic applications making them a subject of intense research efforts in recent years.^{1–4} There is also strong interest from a fundamental point of view which is partly based on the finding that the incorporation of N into Ga(As,N) leads to the formation of a localized impurity-like energy band resonant in the conduction band connected with a strong reduction of the fundamental band-gap energy with increasing N content.^{5,6} Despite the technological progress made in recent years, state-of-the-art material contains a considerable amount of electronic traps involved in the nonradiative recombination of electron–hole pairs.⁷ These recombination centers have to be removed by thermal annealing in order to achieve sufficient photoluminescence (PL) intensities. Two dominant nitrogen-related electron traps in Ga(As,N) have been previously associated with split interstitial defects.⁸ One of these defects contains a nitrogen and an arsenic atom on a single As lattice site (AsN_{As}) and the other consists of N dimers, i.e., two N atoms on a single As site (NN_{As}). The dimer defect NN_{As} has been found in as-grown material with concentrations in the range of 10^{18} cm^{-3} predominantly near the Ga(As,N) surface. This result is in accordance with the enhanced nitrogen concentration at Ga(As,N)/GaAs interfaces observed by a transmission electron microscopy investigation.⁹ The accumulation of N atoms at the interfaces as well as the large concentration of NN_{As} defects can be removed by annealing.^{8,9} The purpose of this work is to identify such N dimers by Raman scattering and to investigate the origin of N-induced defects in Ga(As,N) as well as their annealing behavior and connection to nonradiative recombination centers.

All investigated samples were grown by solid-source molecular beam epitaxy on GaAs(001) substrates using rf plasma sources for nitrogen supply. Details of the growth conditions are published elsewhere.^{7,10} Sample A was grown

at 525 °C consisting of a single Ga(As,N) layer of 200 nm thickness followed by a 5 nm GaAs cap layer. Sample B comprises a ten-period superlattice consisting of 10 nm Ga(As,N) and 20 nm GaAs layers as well as a 100-nm-thick GaAs cap layer grown at 450 °C. The nominal N concentrations are 1.5% and 0.6% in samples A and B, respectively. Our experimental findings were confirmed by investigating additional samples of type A with different N concentrations. Sample B was treated by rapid thermal annealing (RTA) in the temperature range of 650–950 °C by using a Jetfirst 100 furnace. In order to avoid arsenic desorption, the samples were proximity-capped with a GaAs wafer during the annealing.

The Raman measurements were carried out in the back-scattering configuration from the epilayer surface with the sample temperature controlled by a continuous-flow cryostat. The scattered light was analyzed by a LABRAM single spectrograph equipped with a cooled charge-coupled-device array. For optical excitation, we used He–Ne and Kr-ion laser lines with photon energies between 1.92 and 3.00 eV. Depolarized and polarized Raman spectra were recorded in the $z(x,y)\bar{z}$ and $z(y,y)\bar{z}$ scattering configurations, where x , y , z , and \bar{z} denote the [100], [010], [001], and [00 $\bar{1}$] crystallographic directions of the GaAs substrate. PL spectra of sample B have been excited by a He–Ne laser and detected by a Ge diode at a sample temperature of 10 K. The wavelength of the PL peak from recombination near the fundamental band gap was blueshifted from 915 nm before to 875 nm after annealing at temperatures up to 950 °C.

Raman spectra of sample A are shown in Fig. 1 for excitation at different incident photon energies. In these spectra, the expected GaN-like longitudinal optical (LO_2) phonon line of Ga(As,N) is observed at 474 cm^{-1} superimposed on a background of second-order phonon scattering.¹¹ The peak at 463 cm^{-1} is either due to scattering by GaN-like transverse optical (TO_2) phonons or two GaAs-like longitudinal acoustic phonons (2LA_1).^{12,13} The Raman features at frequencies larger than 490 cm^{-1} are due to second-order scattering by GaAs-like optical (TO_1 and LO_1) phonons.¹³ The two additional peaks at 409 cm^{-1} (line X) and 427 cm^{-1} (line Y), however, cannot be explained by Ga(As,N) lattice phonons. Since their integral intensity is

^{a)}Electronic mail: mer@pdi-berlin.de

^{b)}Permanent address: NLSM, Institute of Semiconductors, CAS, Beijing 100083, China.

^{c)}Permanent address: Solid State and Photonics Laboratory, Stanford University, Stanford, California 94305.

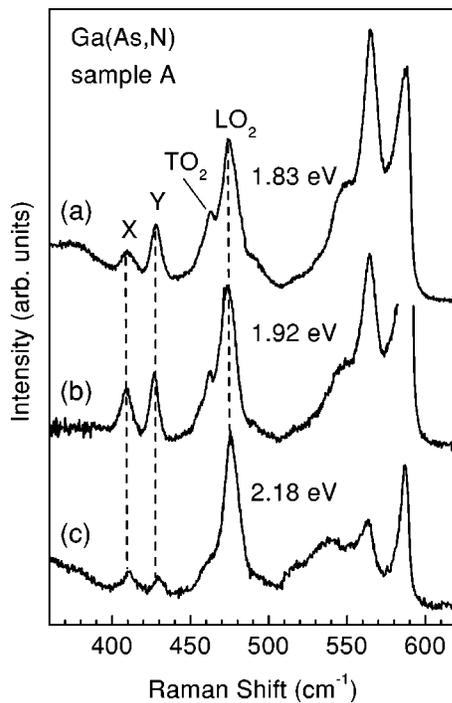


FIG. 1. Raman spectra of sample A excited at the different photon energies indicated.

related to the N concentration, lines X and Y are attributed to N-related defects. The origins of the two defect-related lines are different, since their relative intensities vary from sample to sample as can be seen, e.g., from the comparison of Figs. 1(b) and 3(a). Their frequencies are in the range of those found for local vibrational modes (LVMs) of ^{28}Si on Ga

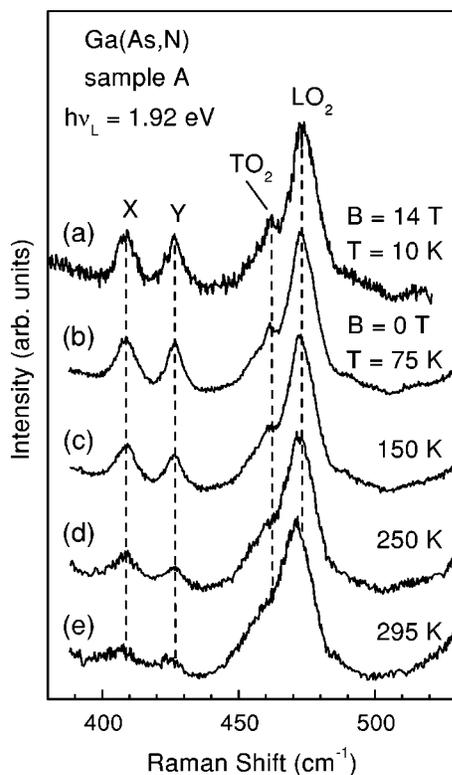


FIG. 2. Raman spectra of sample A (a) with and (b)–(e) without application of an external magnetic field $B=14$ T at the different sample temperatures indicated. Excitation was at 1.92 eV.

(Si_{Ga}) and As (Si_{As}) sites in GaAs.¹⁴ Actually, the frequencies of lines X and Y are both larger by the same factor of 1.07 than the ones of the LVMs induced by Si_{Ga} (384 cm^{-1}) and Si_{As} (398 cm^{-1}). Since N_2 molecules have the same atomic weight as ^{28}Si , it is reasonable to attribute lines X and Y to N dimers on Ga site (NN_{Ga}) and As site (NN_{As}), respectively. Thereby, we assume that the whole molecule is vibrating as one unit like the ^{28}Si impurity, but with force constants increased by about 3.5% ($=\sqrt{1.07}-1$). If there is a triple bond between the nitrogen-dimer atoms, like in free nitrogen molecules, there are four valence electrons, which are still available for the bonding with the Ga or As host atoms. This is a further analogy to Si on Ga or As site. Our assignment is also based on the fact that N dimers are very likely to exist because of the exceptionally strong N–N bond and the small size of the N atom.¹⁵

The defect-induced Raman scattering efficiency is strong only for excitation at photon energies in the range between 1.8 and 2.0 eV [cf. Figs. 1(a) and 1(b)]. For larger photon energies, the intensities of the Raman lines X and Y decrease [cf. Fig. 1(c)] and could not be detected above 2.3 eV (not shown here). A similar resonance behavior of the LO_2 phonon signal in the energy range around 1.9–2.0 eV has previously been attributed to the enhancement of the Raman efficiency for photon energies approaching the localized E_+ transition in Ga(As,N).¹¹ From the comparison with the LO_2 intensities in Fig. 2, it is obvious that the resonance profile for the lines X and Y is even more narrow. In contrast to the latter ones, the LO_2 peak is observed even for excitation at 3.0 eV (not shown here). Assuming an inhomogeneous concentration along the growth direction, the relative intensity of defect-induced Raman scattering might also depend on the variation in the optical probing depth when changing the incident photon energy. However, the different resonance behavior observed for the two defect-induced lines [cf. Figs. 1(a) and 1(b)] provides more evidence for the assertion that they are not of the same origin. This finding is consistent with our above assignment to N dimers on different lattice sites (NN_{Ga} and NN_{As}).

External magnetic fields up to 14 T do not lead to any splitting or shift of the Raman lines X and Y, as illustrated in Fig. 2(a) for sample A. This observation is consistent with their assignment to vibrational modes. At elevated temperatures above 150 K, the intensities of the defect-induced lines start to decrease, making them difficult to detect at room temperature [cf. Figs. 2(b)–2(e)]. This intensity decrease might be partly due to the degrading resonance condition, when the electronic states shift with temperature, but the photon energy for excitation is fixed at 1.92 eV. Concerning the assignment of the defect-induced Raman lines, two remarks should be added. First, a Raman peak at a frequency close to line Y has recently been attributed to Ga–N vibrations in N-rich hard boundary clusters based on a percolation model suggested by Pages *et al.*¹⁶ However, the Raman peak observed in their work is much broader than line Y and explained by atypical TO multimodes, representative of *intrinsic* nonrandom N substitution. Second, we did not succeed in detecting Raman lines due to stretching vibrations of N dimers, which might occur at frequencies around 2300 cm^{-1} , but possibly with a too low scattering efficiency. AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

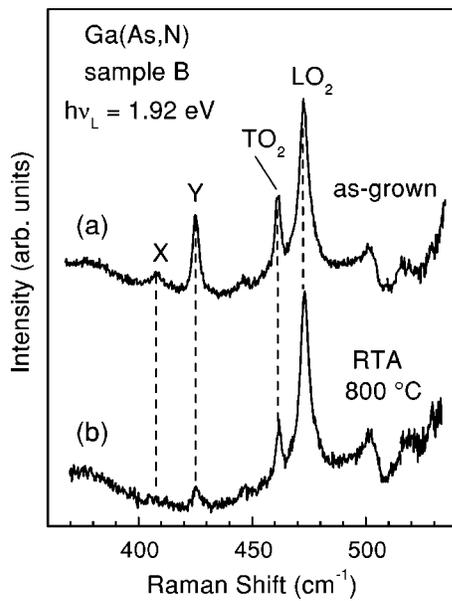


FIG. 3. Raman spectra of sample B (a) before and (b) after rapid thermal annealing (RTA) at 800 °C for excitation at 1.92 eV.

Figure 3 displays Raman spectra of sample B before and after annealing at a temperature of 800 °C. From these spectra it becomes evident that the defects responsible for the Raman lines X and Y can be removed by annealing. The same finding has previously been reported for NN_{As} defects,⁸ which supports our above assignment. The relative intensity of the two defect-induced Raman lines (normalized to the intensity of GaAs-like LO phonon peak) is shown in Fig. 4 as a function of annealing temperature. Annealing at $T_A = 700$ °C and higher temperatures leads to very small intensities of lines X and Y. At the same annealing temperature of 700 °C, the PL intensity starts to increase, as shown in Fig. 4. This coincidence implies that the defects responsible for the Raman lines X and Y are connected with nonradiative recombination centers. The decrease in the PL intensity for annealing temperatures above 850 °C is caused by RTA-induced defects that become relevant after the optimum RTA-temperature is exceeded.¹⁰

In conclusion, defect-induced Raman scattering in Ga(As,N) has been discovered for excitation in resonance with the localized E_+ transition. The two observed Raman lines are attributed to local vibrational modes of N dimers on As and Ga sites. These N dimers are found to be connected with nonradiative recombination centers and can be removed by annealing under appropriate conditions.

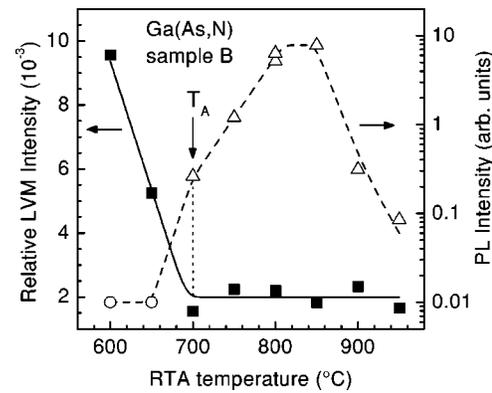


FIG. 4. Integrated Raman intensity of the defect lines X and Y as well as the intensity of near-band-gap photoluminescence (PL) as a function of annealing temperature. The intensity of the LVM Raman lines has been normalized to the intensity of LO phonon scattering. Data points for the as-grown sample are shown at 600 °C. No PL signal could be detected for annealing below $T_A = 650$ °C. The solid and dashed lines are drawn as guides to the eye.

The authors would like to acknowledge the sample preparation by M. Wassermeier and S.G. Spruytte as well as helpful discussions with P. Krispin and W. Ulrici.

- ¹M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, *Jpn. J. Appl. Phys., Part 1* **35**, 1273 (1996).
- ²S. R. Kurtz, A. A. Allermann, D. E. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, *Appl. Phys. Lett.* **74**, 729 (1999).
- ³J. B. Heroux, X. Wang, and W. I. Wang, *Appl. Phys. Lett.* **75**, 2716 (1999).
- ⁴H. Riechert, A. Ramakrishnan, and G. Steinle, *Semicond. Sci. Technol.* **17**, 892 (2002).
- ⁵W. G. Bi and C. W. Tu, *Appl. Phys. Lett.* **70**, 1608 (1997).
- ⁶L. Bellaiche, S.-H. Wei, and A. Zunger, *Appl. Phys. Lett.* **70**, 3558 (1997).
- ⁷S. G. Spruytte, C. W. Coldren, J. S. Harris, W. Wampler, P. Krispin, K. H. Ploog, and M. C. Larson, *J. Appl. Phys.* **89**, 4401 (2001).
- ⁸P. Krispin, V. Gambin, J. S. Harris, and K. H. Ploog, *J. Appl. Phys.* **93**, 6095 (2003).
- ⁹J. M. Chauveau, A. Trampert, K. H. Ploog, and E. Tournie, *Appl. Phys. Lett.* (submitted).
- ¹⁰G. Mussler, L. Däweritz, K. H. Ploog, J. W. Tomm, and V. Talalaev, *Appl. Phys. Lett.* **83**, 1343 (2003).
- ¹¹J. Wagner, K. Köhler, P. Ganser, and N. Herres, *Appl. Phys. Lett.* **77**, 3592 (2000).
- ¹²A. M. Mintairov, P. A. Blagnov, V. G. Melehin, N. N. Faleev, J. L. Merz, Y. Qiu, S. A. Nikishin, and H. Temkin, *Phys. Rev. B* **56**, 15 836 (1997).
- ¹³J. Wagner, T. Geppert, K. Köhler, P. Ganser, and N. Herres, *J. Appl. Phys.* **90**, 5027 (2001).
- ¹⁴W. M. Theis and W. G. Spitzer, *J. Appl. Phys.* **56**, 890 (1984).
- ¹⁵S. B. Zhang and S. H. Wei, *Phys. Rev. Lett.* **86**, 1789 (2001).
- ¹⁶O. Pages, T. Tite, D. Bormann, E. Tournie, O. Maksimov, and M. C. Tamargo, *Appl. Phys. Lett.* **82**, 2808 (2003).