J Mater Sci: Mater Electron (2009) 20:S425–S429
DOI 10.1007/s10854-008-9661-x

LO phonon–plasmon coupled modes and carrier mobilities in heavily Se-doped Ga(As, N) thin films

J. Ibáñez · E. Alarcón-Lladó · R. Cuscó · L. Artús · D. Fowler · A. Patanè · K. Uesugi · I. Suemune

Received: 19 July 2007 / Accepted: 15 February 2008 / Published online: 5 March 2008

Abstract We use Raman scattering to study the LO–plasmon coupled modes (LOPCMs) of *n*-type $GaAs_{1-x}N_x$ epilayers grown by molecular beam epitaxy ($0.1\% \leq x \leq 0.36\%$). We find that the LOPCMs are heavily damped in *n*-$GaAs_{1-x}N_x$ even for *x* as low as 0.1%. From a lineshape analysis based on the hydrodynamical model, we evaluate the lifetime of the LOPCMs in our samples. We compare the values thus obtained with the corresponding Hall mobilities. We find that both quantities decrease strongly with increasing *x*, which can be attributed to N-related alloy scattering of conduction band electrons in the $GaAs_{1-x}N_x$ alloy.

1 Introduction

Dilute nitride semiconductor alloys such as $GaAs_{1-x}N_x$ and $Ga_{1-y}In_yAs_{1-x}N_x (x \lesssim 5\%)$ have recently been the subject of intense research effort due to their remarkable optical and electronic properties, which could be exploited to develop GaAs-based long-wavelength photodetectors, diode lasers and high-performance solar cells [1].

Owing to the large difference in size and electronegativity between N and As atoms, N_{As} introduce quasi-localized electron states in Ga(In)As. These N-related states strongly interact with the extended band states of the matrix material, leading to a strong redshift of the band gap and to the splitting of the conduction band into two highly non-parabolic subbdands, E_- and E_+ [1].

Although the modified electronic band structure of Ga(In)AsN could be particularly advantageous to fabricate specific types of devices such as low-noise avalanche photodiodes [2] or terahertz emitters, [3] in general the use of dilute nitrides in device applications is currently limited by the drastic reduction of the *n*-type mobility of these compounds. Such low mobilities can be explained by the strong interaction between extended and localized electronic states, giving rise to a dramatic increase in the electron scattering rate. As recently shown by Fahy et al. [4] by means of a tight-binding model of the electronic structure of substitutional N in GaAs, localized states associated with N clusters play a crucial role in the low carrier mobilities measured in dilute nitrides.

Raman scattering by LO phonon–plasmon coupled modes (LOPCMs) is widely used to evaluate the free charge density of polar semiconductors. Also, it provides useful information about carrier lifetimes and effective masses in these compounds [5]. While several Raman investigations on undoped GaAsN and InGaAsN have been carried out [6–9], only a few studies have used Raman scattering to study the LOPCMs in dilute nitrides [10, 11].

Here we present a Raman-scattering investigation of the LOPCMs in heavily Se-doped, *n*-type $GaAs_{1-x}N_x$ thin films grown by metal-organic molecular beam epitaxy

J. Ibáñez (✉) · E. Alarcón-Lladó · R. Cuscó · L. Artús
Institut Jaume Almera, Consell Superior d'Investigacions Científiques (CSIC), 08028 Barcelona, Catalonia, Spain
e-mail: jibanez@ija.csic.es

D. Fowler · A. Patanè
School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, UK

K. Uesugi
Faculty of Engineering, Muroran Institute of Technology, Mizumotocho, Muroran, Hokkaido 050-8585, Japan

I. Suemune
Research Institute for Electronic Science (RIES), Hokkaido University, Sapporo 060-0812, Japan

(MOMBE) with x in the 0.1–0.36% range. We find that, on account of the reduced n-type mobility in the $GaAs_{1-x}N_x$ alloy, only a heavily-damped LOPCM appears in the Raman spectra even for x as low as 0.1%. We analyze our Raman spectra with a lineshape model based on the hydrodinamical model [12]. From fits to the spectra we evaluate the lifetime (τ) of the LOPCMs as a function of x. We find that τ is strongly quenched as x increases. We compare our results with the electron mobilities determined from Hall measurements and with the calculated n-type mobilities of GaAsN reported by Fahy et al. [4].

2 Experiment

Six Se-doped $GaAs_{1-x}N_x$ epilayers, with x in the 0.1–0.36% range, were grown by MOMBE on (001) semi-insulating GaAs substrates. Details of the growth conditions can be found in Ref. [13]. The N content of the samples, which was determined by high-resolution X-ray diffraction (HRXRD) measurements, is given in Table 1. For comparison purposes, two Se-doped GaAs epilayers were also grown. The thickness of all the epilayers was evaluated from an analysis of the HRXRD curves and was found to lie between 120 and 220 nm. Hall measurements at different temperatures were performed to obtain the carrier concentrations (N_e) and Hall mobilities (μ_{Hall}) of the samples. The second and third columns of Table 1 display the corresponding values at 100 K. In the temperature range studied (4.2–300 K), both N_e and μ_{Hall} exhibit very weak temperature dependence for all the $GaAs_{1-x}N_x$ epilayers.

Raman spectra were recorded at 80 K using the high-resolution triple additive configuration of a Jobin-Yvon T64000 spectrometer equipped with a CCD detector. The 100-μm slits were used to acquire the spectra. The Raman measurements, performed in a backscattering geometry on a (001) face, were excited with the 514.5-nm line of an Ar^+ laser.

Table 1 List of Se-doped $GaAs_{1-x}N_x$ samples studied in this work. The N content (x), the carrier concentration (N_e), the electron mobility (μ_{Hall}), and the electronic damping parameter (Γ_e) as determined from a lineshape analysis of the Raman spectra, are listed

N content (x) (%)	N_e (cm^{-3})	μ_{Hall} (cm^2/Vs)	Γ_e (cm^{-1})
0	7.7×10^{18}	607	200
0	1.0×10^{19}	406	270
0.10	5.3×10^{18}	101	625
0.20	7.6×10^{18}	114	565
0.20	9.0×10^{18}	88	780
0.23	7.8×10^{18}	61	850
0.30	1.5×10^{19}	46	1,450
0.36	1.5×10^{19}	51	1,235

3 Results and discussion

Figure 1 shows $z(xy)\bar{z}$ Raman spectra of two of the samples investigated in this work. Curve A corresponds to a Se-doped GaAs epilayer with $N_e = 1.0 \times 10^{19}$ cm^{-3}, while curve B corresponds to a Se-doped $GaAs_{1-x}N_x$ epilayer with $x = 0.2\%$ and $N_e = 9.0 \times 10^{18}$ cm^{-3}. Curve A is a typical spectrum of heavily-doped n-type GaAs. This spectrum is dominated by a strong peak at $\sim$271 cm^{-1} that can be attributed to a L^- coupled mode arising from the coupling between the LO phonons and the collective excitations of the free carriers (plasmons) [5]. The corresponding L^+ coupled mode [5] for this sample appears as a broad band centered at around 1,150 cm^{-1} (see the inset of Fig. 1). The frequency at which the L^+ mode is observed is in good agreement with the results of previous Raman studies on heavily doped n-GaAs [14]. The weaker peak at $\sim$294 cm^{-1} corresponds to the LO phonon mode of GaAs

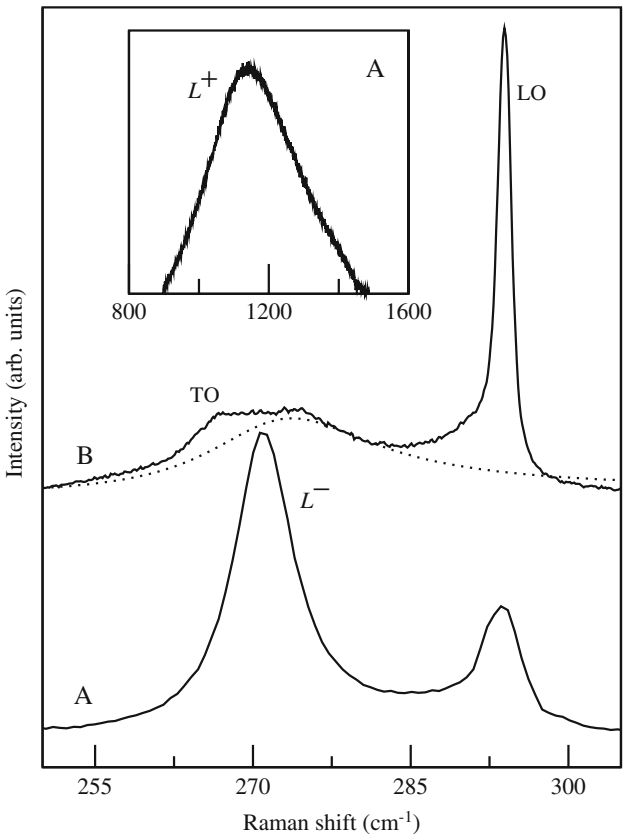

Fig. 1 Raman spectra of n-type GaAs with $N_e = 1.0 \times 10^{19}$ cm^{-3} (curve A) and of a n-type $GaAs_{1-x}N_x$ epilayer with $x = 0.2\%$ and $N_e = 9.0 \times 10^{18}$ cm^{-3} (curve B). The inset shows the L^+ band that is observed in the case of the n-GaAs epilayer. No L^+ band is observed in any of the spectra of the n-$GaAs_{1-x}N_x$ samples

arising from the surface depletion region, which is well-known to exist in the (100) surface of GaAs [5, 15].

In the case of the $GaAs_{1-x}N_x$ epilayer with $x = 0.2\%$ and $N_e = 9.0 \times 10^{18}$ cm^{-3} (curve B), three features can be observed. Similar spectra are obtained for the rest of $GaAs_{1-x}N_x$ samples. The most intense peak, located at $\sim$294 cm^{-1}, corresponds to the GaAs-like LO mode of $GaAs_{1-x}N_x$ from the surface depletion region. Note that the thickness of these epilayers is large compared to $1/2\alpha$ [16], where α is the absorption coefficient of GaAs for the 514.5-nm radiation. As a consequence, the contribution of the GaAs substrate to the Raman signal is negligible. As discussed in Refs. [6] and [9], the frequency of the GaAs-like LO mode of $GaAs_{1-x}N_x$ is progressively redshifted with increasing x due to strain, N alloying and disorder. However, for the N contents involved in our samples, such shifts can be neglected. The peak located at $\sim$268 cm^{-1} corresponds to the forbidden TO mode of $GaAs_{1-x}N_x$. The frequency of this mode is barely shifted with respect to GaAs [6, 9]. Besides these two peaks, an additional broad feature emerges between the TO and LO phonons of $GaAs_{1-x}N_x$. As occurs in p-type GaAs [17, 18], where the LOPCMs are heavily damped owing to the low mobility of the free holes, this feature can be assigned to a heavily-damped LOPCM [19]. The strong damping of this mode can be attributed to the disorder introduced by N. We observe this heavily-damped coupled mode in all samples, even in the epilayer with x as low as 0.1%.

The energy of the L^+ coupled mode detected in n-type III–V semiconductors such as n-GaAs or n-InP is very sensitive to N_e variations. In contrast, the heavily-damped LOPCM observed in p-GaAs or in n-$GaAs_{1-x}N_x$ does not show such high sensitivity. These heavily-damped LOPCM peaks, however, can still be used to obtain relevant information about the investigated materials. For instance, Limmer et al. [18] performed a full lineshape analysis of the Raman spectra of p-GaMnAs layers to evaluate hole concentrations and mobilities. These type of analyses necessarily rely on the Lindhard–Mermin (LM) dielectric function, since only this model allows one to include finite-temperature and nonparabolicity effects as well as Landau damping effects [12, 20]. In the case of $GaAs_{1-x}N_x$, the LM model cannot be used because the dispersion of the conduction band of this compound is not well known. In contrast, simpler models such as the hydrodynamical (HD) model do not have this limitation. The HD approach neglects important effects, but it still allows one to take into account the spatial dispersion of plasmons (i.e., wave-vector effects) through a wave-vector dependent electric susceptibility [12]. The HD model can be extended to include temperature effects and the dependence on N_e of the electron effective mass provided that the conduction-band dispersion is known [20].

Here, we perform a lineshape analysis of the Raman spectra based on the conventional HD model with the aim of evaluating the lifetime, τ, of the free carriers. For this purpose, we calculate LOPCM lineshapes using a fluctuation–dissipation formalism and the HD susceptibility for the free electrons [12, 21]. The calculated lineshapes are then fitted to the experimental Raman spectra. For the sake of simplicity, we neglect the nonparabolicity of the conduction band of dilute nitrides for the present analysis and we use the electron effective-mass values recently measured by Masia et al. [22] with magnetophotoluminescence spectroscopy in $GaAs_{1-x}N_x$. In the composition range $0.2\% \leq x \leq 0.36\%$ the effective mass can be well approximated by a constant value $m^* = 0.13m_e$, whereas for $x = 0.1\%$ we take $m^* = 0.1m_e$ [22]. For the samples with $x = 0\%$ we take $m^* = 0.09m_e$ from Ref. [23].

For the fits, it would be in principle possible to treat the carrier concentration N_e and the phenomenological electronic damping parameter Γ_e, both of which enter the electric susceptibility of the electron gas [12], as free parameters. However, in the case of heavily-damped LOPCMs this yields some degree of ambiguity in the lineshape analysis, since different combinations of N_e and Γ_e may lead to satisfactory fits (see the discussion in Ref. [18]). To avoid this problem, here we use the N_e values obtained from Hall measurements (Table 1) for the fitting procedure and we leave Γ_e as the only fitting parameter. The lifetime of the LOPCMs can then be derived via the energy-time uncertainty relation, $\tau^{-1} = 2\pi c\Gamma_e$, where c is the speed of light in vacuum and Γ_e is expressed in wavenumber units (cm^{-1}).

As mentioned above, nonparabolicity effects are neglected throughout this work. This is expected to yield increased Γ_e values as extracted from the fits, which can be shown by comparing LOPCM lineshapes calculated with different values of m^* and Γ_e. Nevertheless, for the low N composition of the samples studied in this work, the m^* values that we take from Ref. [22] are not too different from the values predicted by the BAC model for n-GaAsN with 5×10^{18} cm^{-3} $< N_e <$ 1.5×10^{19} cm^{-3} [24]. Consequently, bearing in mind the controversial nature of the conduction band of GaAsN [25] and the lack of electron effective-mass measurements in this compound as a function of N_e, for the present analysis we rely on the experimental data of Ref. [22].

In Fig. 1 (dashed line), we show the fit of the theoretical LOPCM lineshapes to the experimental spectrum for the n-$GaAs_{1-x}N_x$ epilayer with $x = 0.2\%$ and $N_e = 9.0 \times 10^{18}$ cm^{-3}. A value of $\Gamma_e = 780$ cm^{-1}, corresponding to $\tau = 6.8 \times 10^{-15}$ s, was extracted from this fit. Prior to the fits, the Raman peaks from the TO and LO modes were fitted by Lorentzian lineshapes and substracted from the Raman spectra.

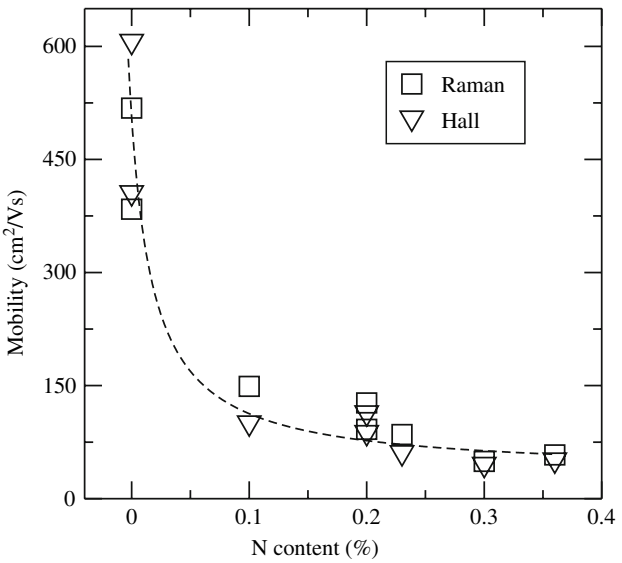

Fig. 2 Mobility versus N content for the samples studied in this work as determined by Hall measurements and from a lineshape analysis of the LOPCM peaks

In the last column of Table 1 we display the value of Γ_e obtained from the lineshape fits for all the samples studied in this work. Clearly, the coupled-mode lifetime tends to decrease with increasing N content as occurs with the Hall mobility. To compare Γ_e with μ_{Hall}, we plot in Fig. 2 the value of $\mu_{\text{Raman}} = e/(2\pi c\Gamma_e m^*)$ as a function of x for all our samples (open squares). In the last expression, e denotes the electron charge. For the n-GaAs samples ($x = 0\%$), the Raman mobilities were determined by fitting the L^- and L^+ coupled mode peaks. In Fig. 2, we also plot the electron mobility as determined from Hall measurements (open triangles). As can be observed in the figure, good agreement is found between the Hall measurements and our Raman analysis. Both techniques show that the electron mobility (and therefore the electron lifetime) is abruptly reduced with the addition of just 0.1% of N in GaAs, which may be mainly attributed to electron scattering by localized electron states associated with N impurities and clusters [4]. An additional contribution to the observed mobility reduction may also arise from the increased electron effective mass in the $GaAs_{1-x}N_x$ alloy, which is expected to be more important in the degenerate limit [26]. Owing to the increased amount of N-related disorder in the samples, a progressive reduction of the mobility is observed with increasing x for $x > 0.1\%$.

With regard to the results of Fig. 2, we would like to remark that intrinsic differences exist between the optical and the transport measurements. While the former probe the lifetime of the LOPCMs (i.e., the lifetime of the collective excitations of the conduction electrons) through a lineshape analysis of the Raman spectra, the Hall mobilities are derived from the transport properties of free electrons. Note also that the presence of N-related localized electronic states in n-$GaAs_{1-x}N_x$ modifies the scattering rate of the free carriers, leading to a more complex picture in which the electron mobility shows a $1/\sqrt{m^*}$ dependence [4]. While the lifetime of the LOPCMs is expected to be affected by the N localized states, the evaluation of such effect is clearly beyond the scope of this work.

Finally, we note that the Hall mobilities measured in our $GaAs_{1-x}N_x$ samples (< 120 cm^2 V^{-1} s^{-1}) are sizeably lower that those predicted in Ref. [4]. Also, the mobilty of our n-GaAs samples is already below the predictions of Ref. [4]. Thus, we conclude that other scattering mechanisms not related to the N impurities are present in these epilayers. In particular, the high density of ionized Se donors may be greatly responsible for the low electron mobilities of our samples. As reported by Fowler et al. [27], the conductivity is significantly enhanced in modulation-doped $GaAs_{1-x}N_x$ heterostructures. In such type of structures, the electron mobility has also shown to be strongly limited by N-related scattering [27], in agreement with the considerations of Ref. [4] and with the Hall and Raman data obtained in our samples.

4 Conclusion

The LO-plasmon coupled modes (LOPCMs) in dilute $GaAs_{1-x}N_x$ are heavily damped, which is attributed to carrier scattering by N-related localized electronic states. We have carried out a lineshape analysis based on the hydrodynamical model to evaluate the lifetime of the free carriers. Our calculations show that in the high damping regime a single LOPCM is expected between the TO and LO modes of GaAsN. The lifetimes of the LOPCMs as obtained from our analysis are in good agreement with the measured Hall mobilities. The introduction of only a 0.1% of N into GaAs dramatically reduces both the lifetime and the Hall mobility of the free carriers.

Acknowledgements Work funded by the Spanish Ministry of Education and Science under Contracts Ref. MAT2004-0664, MAT2007-63617 and by the Ramon y Cajal Program.

References

1. Special issue III-V-N Semiconductor alloys, Semicond. Sci. Technol. **17** (2002)
2. A.R. Adams, Elec. Lett. **40**, 1086 (2004)
3. A. Ignatov, A. Patanè, O. Makarovsky, L. Eaves, Appl. Phys. Lett. **88**, 032107 (2006)
4. S. Fahy, A. Lindsay, H. Ouerdane, E.P. O'Reilly, Phys. Rev. B **74**, 035203 (2006)
5. Abstreiter et al., in *Light Scattering in Solids IV*, ed. by M. Cardona, G. Güntherodt (Springer-Verlag, Berlin, 1984)

6. T. Prokofieva, T. Sauncy, M. Seon, M. Holtz, Y. Qiu, S. Nikishin, H. Temkin, Appl. Phys. Lett. **73**, 1409 (1998)
7. A. Mascarenhas, M.J. Seong, Semicond. Sci. Technol. **17**, 823 (2002)
8. H.F. Liu, N. Xiang, S. Tripathy, S.J. Chua, J. Appl. Phys. **99**, 103503 (2006)
9. J. Ibáñez, E. Alarcón-Lladó, R. Cuscó, L. Artús, M. Hopkinson, J. Appl. Phys. **102**, 013502 (2007)
10. T. Tite, O. Pagès, M. Ajjoun, J.P. Laurenti, D. Bormann, E. Tournié, O. Maksimov, M.C. Tamargo, Solid State Electr. **47**, 455 (2003)
11. P.A. Grandt, A.E. Griffith, M.O. Manasreh, D.J. Friedman, S. Dogan, D. Johnstone, Appl. Phys. Lett. **85**, 4905 (2004)
12. L. Artús, R. Cuscó, J. Ibáñez, N. Blanco, G. González, Phys. Rev. B **60**, 5456 (1999)
13. I. Suemune, K. Uesugi, T.Y. Seong, Semicond. Sci. Technol. **17**, 755 (2002)
14. M. Ramsteiner, J. Wagner, P. Hiesinger, K. Köhler, U. Rössler, J. Appl. Phys. **73**, 5023 (1993)
15. H. Shen, F.H. Pollak, R.N. Sacks, Appl. Phys. Lett. **47**, 891 (1985)
16. D.E. Aspnes, A.A. Studna, Phys. Rev. B **27**, 985 (1983)
17. K. Wan, J.F. Young, Phys. Rev. B **41**, 10772 (1990)
18. W. Limmer, M. Glunk, S. Mascheck, A. Koeder, D. Klarer, W. Schoch, K. Thonke, R. Sauer, A. Waag, Phys. Rev. B **66**, 205209 (2002)
19. J. Ibáñez et al., in *Physics of Semiconductors*, ed. by J. Menendez, C.G. VanDeWalle (Aip Conference Proceedings, New York 2005), pp. 293–294
20. J. Ibáñez, R. Cuscó, L. Artús, Phys. Stat. Sol. (b) **223**, 715 (2001)
21. R. Cuscó, J. Ibáñez, L. Artús, Phys. Rev. B **57**, 12197 (1998)
22. F. Masia et al., Phys. Rev. B **73**, 073201 (2006)
23. H.R. Chandrasekhar, A.K. Ramdas, Phys. Rev. B **21**, 1511 (1980)
24. C. Skierbiszewski et al., Appl. Phys. Lett. **76**, 2409 (2000)
25. A. Lindsay, E.P. O'Reilly, Phys. Rev. Lett. **93**, 196402 (2004)
26. M.P. Vaughan, B.K. Ridley, Phys. Rev. B **75**, 195205 (2007)
27. D. Fowler, O. Makarovsky, A. Patanè, L. Eaves, L. Geelhaar, H. Riechert, Phys. Rev. B **69**, 153305 (2004)