

GROWTH AND CHARACTERIZATION OF GaAs_{1-x}N_x EPITAXIAL LAYERS

N. MUSAYEVA², S. ABDULLAYEVA², C. PELOSI¹, G. ATTOLINI¹, M. BOSI¹, B. CLERJAUD³,
P. BENALLOUL³, C. BARTHOUS³, R. JABBAROV², E. GAMBAROV²

¹ *Istituto dei Materiali per l'Elettronica ed il Magnetismo,*

Consiglio Nazionale delle Ricerche,

Parco Area delle Scienze 37/A, 43010 Parma, Italy.

² *academician G.M. Abdullyev Institute of Physics*

Azerbaijan National Academy of Sciences,

H. Javid avenue, 33, AZ-1143, Baku, Azerbaijan.

³ *Université Pierre et Marie Curie,*

Institut des NanoSciences de Paris,

140 rue de Lourmel 75015 Paris, France.

Metal-orqanik gaz faza epitaksial (MOGFE) üsulu ilə GaAs və Ge altlıqları üzərində yetişdirilmiş GaAs_{1-x}N_x epitaksial təbəqələrinin Raman və Fotoluminescent xasələri tədqiq olunmuşdur. Horizontal reaktorlu qurğuda Trimetilgallium, Arsin və Dimetilhidrazin element mənbəyi kimi istifadə olunmuşdur. Nümunələr atmosfer təzyiqində, 500⁰C temperaturda DMHy və başqa element mənbələrindən gələn gaz axınlarının nisbatının dəyişdirilməsi ilə yaranan müxtəlif şəraitlərdə yetişdirilmişdir.

Aşqarlanmış GaAsN –də azot (N) Raman spectrində 470 cm⁻¹ oblastda lokal vibrasiya modlarının müşahidə olunması ilə aşqarlanır. 500 və 600 cm⁻¹ arasında müşahidə olunan TO və LO kimi zəif Raman modları xəlitənin qaydasızlığı haqqında məlumat verir.

Yetişdirilmiş nümunələrin fotoluminessensiya (FL) xasələri də tədqiq olunmuşdur.

GaAs_{1-x}N_x –in tərkibində azotun (x) konsentrasiyası təxminən 2.1% təşkil etdikdə, ond 77K temperaturda fotoluminessensiya piki 1.15 eV –də müşahidə olunur.

Исследованы Рамановские и люминесцентные свойства GaAs_{1-x}N_x эпитаксиальных слоев выращенных на подложках GaAs и Ge методом металлоорганического химического газового осаждения (МОХГО). Триметилгаллий (ТМГ), Арсин (AsH₃) и диметилгидразин (DMHy) использовались в качестве источников в установке с горизонтальным реактором. Образцы выращивались в атмосферном давлении при 500⁰C в разных режимах с изменением соотношения газовых поток DMHy и других элементов источников.

Азот в легированном GaAsN обнаружен с помощью Рамановского спектра с наблюдением локальных вибрационных мод в области 470 см⁻¹. Слабые рамановские особенности второго порядка как TO и LO пики наблюдаемые между 500 и 600 см⁻¹, предупреждают о степени беспорядочности сплава.

Фотолуминесцентные (ФЛ) свойства выращенных образцов также исследованы. Когда концентрация азота (x) внутри GaAs_{1-x}N_x составляет приблизительно 2.1 %, то при температуре 77K фотолуминесцентный пик наблюдается при 1.15 эВ.

Raman scattering and photoluminescence properties of GaAs_{1-x}N_x epitaxial layers grown on GaAs and Ge substrates by means of metal-organic vapor phase epitaxy (MOVPE) have been investigated. Trimethylgallium (TMG), AsH₃ and Dimethylhydrazine (DMHy) were used as precursors in the setup with horizontal reactor. The samples were grown at atmospheric pressure at temperature 500⁰C and varying the molar ratio between DMHy and the other precursors.

Nitrogen in diluted GaAsN has been detected by Raman scattering through the observation of the nitrogen local vibrational mode at about 470 cm⁻¹. Weak GaAs second order Raman features like TO and LO peaks are observed between 500 and 600 cm⁻¹, evidencing alloy disorder.

The photoluminescence (PL) properties have also been investigated on as grown samples. The PL peak energy of a GaAs_{1-x}N_x is 1.15 eV at 77 K, when the N content (x) is about 2.1 %.

1. INTRODUCTION

Recently, intensive experimental and theoretical efforts have been directed towards the understanding of the properties of group III-V alloys in which the group V element is partially replaced by nitrogen. It has been found that the incorporation of a low concentration of nitrogen has an important effect on the electronic properties of these materials. A reduction of the band gap exceeding 0.1 eV per atomic percent of N was observed in GaAs_{1-x}N_x for x < 0.015. [1] 1.3 and 1.55 μm InGaAsN/GaAs quantum well (QW) lasers usable as light sources for optical fiber communications have been reported. [2-4]

At the same time, the introduction of nitrogen shrinks noticeably the lattice constant of the materials. Therefore for dilute nitrides, increasing the nitrogen content, it is possible to obtain a simultaneous reduction of both the band gap and the lattice constant, whereas in other III-V alloys, an inverse proportionality between these two quantities holds. Because

of these remarkable properties, a lot of works have been devoted to these materials. [5-7] However, relatively few devices involving dilute nitrides have been processed until now. The main reason is that the defects present in these materials negatively affect their characteristics (carrier mobility, minority carrier life time, minority carrier diffusion length etc.). As a matter of fact, even though the basic behaviour of dilute nitride alloys is now almost understood, [8] lot of problems remain concerning the elaboration of these alloys and the control of their defects. Most important defects are extended defects resulting from large lattice mismatches (up to about 20%) and large miscibility gap. Equilibrium thermodynamic calculations show a large immiscibility between GaAs and GaN; therefore heterogeneous materials, formed from the mixture of domains of different compositions are obtained when grown at thermodynamic equilibrium conditions. It is therefore essential to grow these materials in out of thermodynamic

equilibrium conditions, i. e. in a kinetic growth regime at low temperature; the lower the temperature, the higher the nitrogen concentration. Unfortunately, in such conditions, point defects such as antisite defects for instance appear [9]. Moreover, nitrogen, because of its free electronic doublet shows a great ability for binding to its nearest neighbours with multiple bonds and in particular triple bonds. This gives rise to specific type of defects [10,11] not observed in nitrogen free materials. In any case, these dilute nitrides are metastable materials and do not suffer thermal treatments above a certain temperature.

One of the main advantages of dilute nitride addresses the use of low cost substrates and for this reason we investigated the growth parameters for the heteroepitaxy of GaAsN on Ge. Germanium is a suitable alternative substrate to the “usual” GaAs. The lattice constant and the thermal expansion coefficient of Ge are almost identical with those of GaAs, making Ge an ideal substrate for many already existing applications such as solar cells, [12-14] electro-optic applications, LEDs [15] and laser diodes.[16] Ge has higher mechanical strength as compared to GaAs and therefore thinner Ge substrate can be used, resulting in lighter weight solar cells. Ge is also cost-efficient and available at large wafer sizes.

In this work, we have grown GaAs_{1-x}N_x epitaxial layers on GaAs and Ge substrates for comparison and analyzed the effects of the substrates on N incorporation into GaAs_{1-x}N_x layers, band gap changes and N-related local vibrational mode (LVM) Raman scattering. We have also investigated the photoluminescence (PL) properties of these layers.

2. EXPERIMENTAL PROCEDURE

The samples were grown in a MOVPE set up with a horizontal reactor (with cross section of 10.8 cm²), at atmospheric pressure using trimethylgallium (TMG), arsine (AsH₃), dimethylhydrazine (DMHy) as Ga, As and N precursors respectively; palladium-purified H₂ was used as carrier gas. The graphite susceptor was heated by IR lamps. GaAsN layers, about 350 nm thick, have been deposited at temperature 500°C on 50 nm-thick GaAs buffer layer, grown at the same temperature.

Substrates were either Si doped (1-3x10¹⁸ cm⁻³) GaAs (100) 2° off (100) or Ge (001), 6° off (110) direction.

Raman measurements were performed with a Horiba Jobin Yvon LabRam apparatus, using a He-Ne laser emitting at 632 nm and a Z(-,-)Z̄ scattering geometry. The laser spot is about 1 μm and the spectral resolution is estimated about 2 cm⁻¹.

The PL experiments were carried out using the 488 nm line of an Ar laser, whose excitation power level was varied in the 20-200 mW range; the laser was not focused and the laser spot diameter was about 1.5 mm. The PL emission was dispersed using a HR460 monochromator and detected by a CCD detector. Emitted light was collected from the same side as the excitation by an optical fibre placed at about 1 cm from the sample surface. Temperature dependence of the emission was analyzed from 78 to 300K.

3. RESULTS AND DISCUSSION

3.1 Raman scattering

The Raman spectrum of a GaAs_{0.979}N_{0.021} sample grown on GaAs substrate evidences the TO₁ (268 cm⁻¹) and LO₁

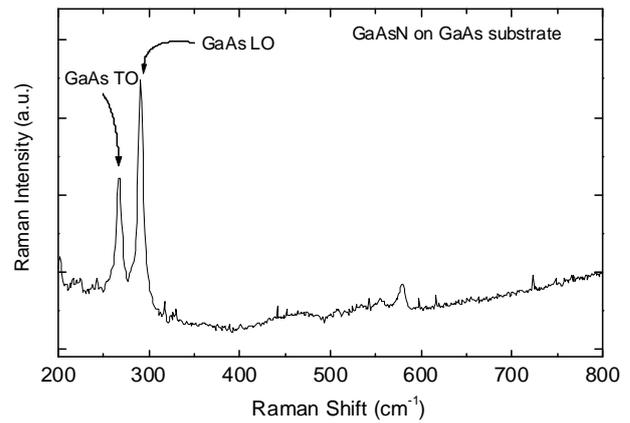


Fig. 1. Room temperature Raman spectrum GaAs_{0.979}N_{0.021} on GaAs substrate.

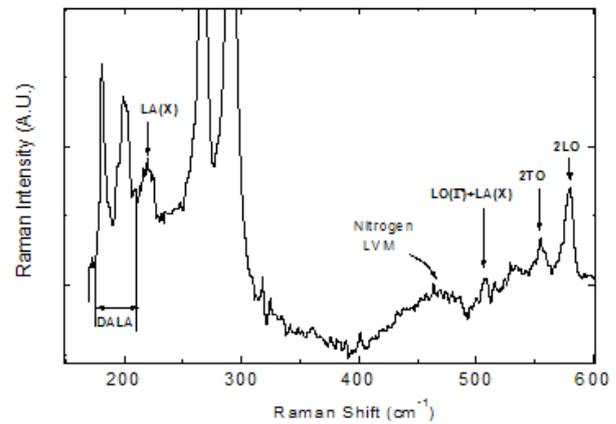


Fig. 2. Room temperature Raman spectrum GaAs_{0.979}N_{0.021} on GaAs substrate recorded during a longer acquisition time than in Fig. 1.

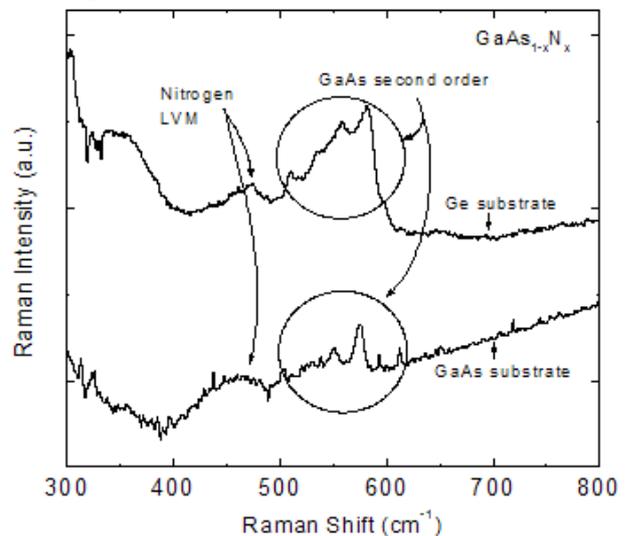


Fig.3. Comparison between room temperature Raman spectra of GaAs_{0.979}N_{0.021}/GaAs and GaAs_{0.979}N_{0.021}/Ge samples

(291 cm⁻¹) modes as shown in Fig. 1. In addition, a Raman mode of the Ge substrate at 300 cm⁻¹ is also present in the spectra of the samples grown on Ge. The presence of the TO mode in these spectra is due both to a breakdown of the Raman selection rules that occur because of both alloy disorder and spectra acquisition at near-resonance. The violation of the selection rules, induced by the absence of long-range order in the crystal, has been attributed to the

presence of nitrogen.[17] As shown in Fig. 2, in the spectral region ranging from 180 to 230 cm⁻¹, disorder-activated longitudinal acoustic (DALA) phonons and LA(X) phonon at 223 cm⁻¹ are observed that confirms the absence of long range order.

In order to study the transitions exhibiting low scattering intensities between 400 and 600 cm⁻¹, longer acquisition time measurements were performed (see Fig. 3), saturating the intense peaks between 260 and 300 cm⁻¹. N related LVM at about 470 cm⁻¹ is observed in both layers grown on GaAs and Ge substrates. This mode is attributed to the stretching vibration associated with isolated N atoms each bonding to four Ga neighbours.[18]

The spectra collected on GaAs substrate were much noisier than the ones obtained on Ge substrate, probably because of the strong luminescence excited in the substrate. The structures that appear between 500 and 600 cm⁻¹ are due to second order GaAs LO and TO modes. The N mode around 470 cm⁻¹ is also more evident in the samples grown on Ge than in those grown on GaAs substrates as it can be seen in Fig. 3.

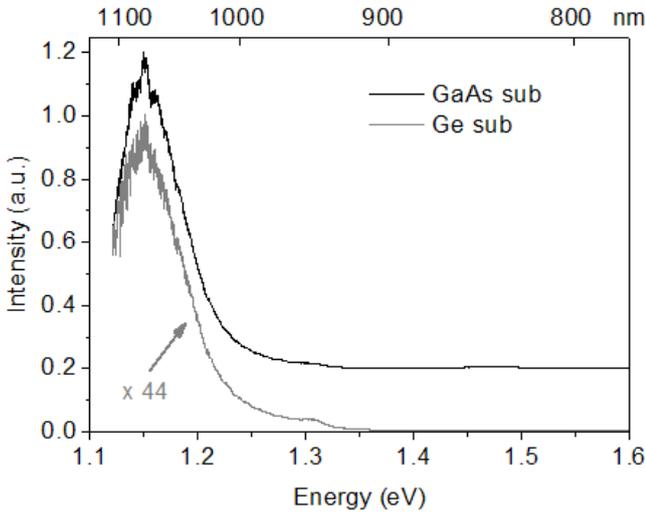


Fig. 4 PL spectra at 78 K of two samples grown in the same run on GaAs and Ge substrates. The PL is excited by 150 mW (unfocused) of the 488 nm line of an argon laser.

The gain for the sample grown on Ge substrate is 44 times larger than for the sample grown on GaAs substrate. For clarity, the spectrum of the sample grown on GaAs substrate has been shifted up by 0.2 with respect to the spectrum of the sample grown on Ge substrate.

3.2 Photoluminescence (PL) properties

Fig. 4 shows the PL spectra at 78 K of two samples grown in the same run, one on a GaAs substrate and the other one on a germanium substrate. The maximum intensity has been normalized for both spectra; it has to be noted that the intensity of the photoluminescence of the sample on germanium substrate has been multiplied by a factor 44 with respect to the one on the GaAs substrate. Apart from the intensities, the two spectra are very similar, both peaking at 1.15 ± 0.01 eV. This means that both samples have the same composition: GaAs_{0.979}N_{0.021} and a good crystalline quality. The PL spectra seem to have in fact three components. The fact that the luminescence is much less intense in the samples grown on germanium substrate is most probably due to the presence of extra non-radiative centres in these samples, the physical nature of which is presently not clear.

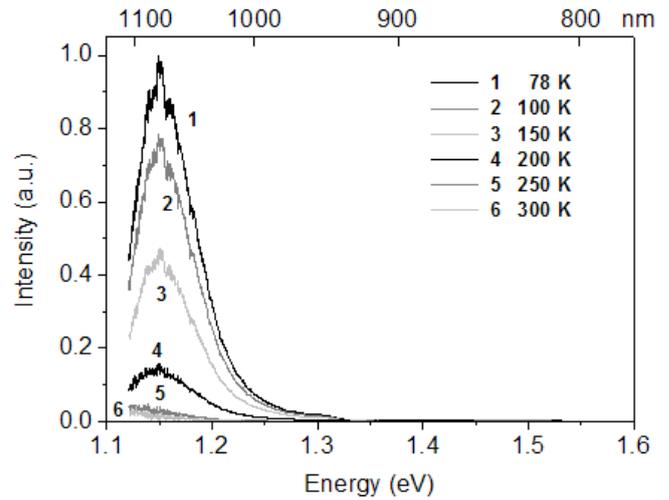


Fig. 5 PL spectra of the same sample grown on GaAs substrate as in Fig. 4 at various temperatures. The PL is excited by 150 mW (unfocused) of the 488 nm line of an argon laser.

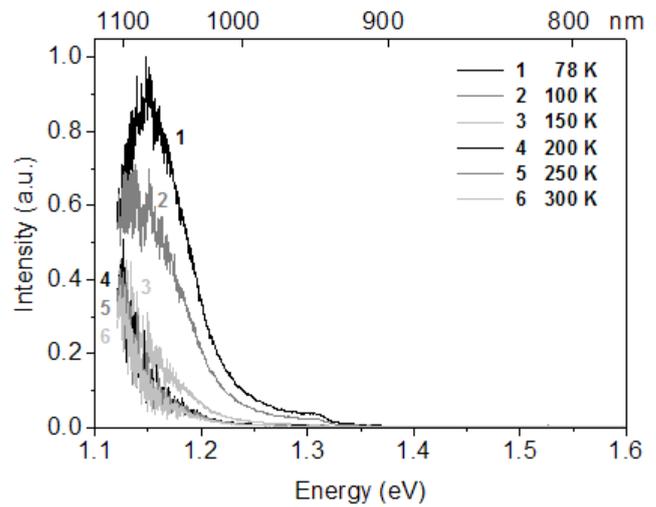


Fig. 6 PL spectra of the same sample grown on GaAs substrate as in Fig. 4 at various temperatures. The PL is excited by 150 mW (unfocused) of the 488 nm line of an argon laser.

Fig. 5 shows the variation of the PL spectra of a sample grown on GaAs substrate at different temperatures between liquid nitrogen and room temperatures. The position of the maximum of the PL spectra does not seem to shift noticeably between 78 and 200 K; at higher temperature, it shifts towards low energy when temperature increases following the bandgap narrowing of the material. It has to be noted that the apparent absence of shift of the PL maximum between 78 K and 200 K is not in line with some published reports on GaAsN alloys, [19,20] but that a very small peak shift at low temperatures, much smaller than the bandgap shift, has already been reported. [21].

The situation with the samples grown on Ge substrates contrasts with the one of the samples grown on GaAs as shown in Fig. 6. The PL peak shifts strongly towards low energies for the samples grown on Ge even between 78 and 100 K; unfortunately, the spectral limit of the CCD detector we are using impedes following this peak at temperatures above 100 K. However looking at the high energy tail of the emission, it seems clear that the line continue to broaden

when temperature increases over 100 K and that its maximum continues to shift towards low energy.

The difference of the PL behaviours of the samples grown on GaAs and Ge substrates is striking. On the one hand, as the PL band shapes at 78 K are quite similar, one has the impression that the larger lattice mismatch between the germanium substrate and the layers does not play an important role; on the other hand, the much stronger shifts and broadenings of the photoluminescence of the samples grown on germanium when temperature increases suggest that the substrate plays an important role in the processes governing the luminescence. As the lattice expansion coefficients are not very different for germanium and GaAs in the temperature range 78-300 K, the variation of the strains, induced by the lattice mismatch, with temperature can hardly be invoked for explaining the very different behaviours of the PL depending on which substrate the samples have been grown.

4. CONCLUSION

The growth of good quality GaAs_{1-x}N_x layers by MOVPE is possible on both GaAs and Ge substrates. The observation of the nitrogen related LVM around 470 cm⁻¹ by Raman

scattering spectroscopy evidences the proper location of nitrogen surrounded by four gallium nearest neighbours.

PL measurements evidence the similar composition of samples grown in the same run on GaAs and Ge substrates. However great differences are observed depending on the substrate. The PL of samples grown on Ge substrates is much less intense than the one of samples grown on GaAs substrates indicating the presence of extra non-radiative centres in samples grown on Ge substrates. The maximum of the PL of samples grown on GaAs substrates practically does not shift when temperature increases from 78 to 200 K; this contrasts with the behaviour of the layers grown on Ge substrates that show a strong shift of the PL maximum when temperature increases.

In future works, further efforts should be devoted to the elaboration of the buffer layers with different growth conditions in order to decrease the differences between the layers grown on both types of substrates.

ACKNOWLEDGMENT

This work is supported by the INTAS co-operation agreement N° 06-1000017-8536.

-
- [1]. *M. Weyers, M. Sato, and H. Ando*: Jpn. J. Appl. Phys. 31 (1992) L853.
- [2]. *G. Y. Plaine, C. Asplund, P. Sundgren, S. Mogg and M. Hammar*: Jpn. J. Appl. Phys. 41 (2002) 1040.
- [3]. *N. Tansu, A. Guandt, M. Kanskar, W. Mulhearn and L. J. Mawst*: Appl. Phys. Lett. 83 (2003) 18.
- [4]. *M. Kondow, K. Uoni, A. Niwa, T. Kitatani, S. Watahiki and Y. Yazawa*: Jpn. J. Appl. Phys. 35 (1996) 1273.
- [5]. *Special issue on III-V-N semiconductor alloys*: Semicond. Sci. Technol. 17 (2002) N°8.
- [6]. *Special issue on dilute nitrides*: J. Phys.: Condens. Matter 16 (2004) N°31.
- [7]. *C. Pelosi, G. Attolini, M. Bosi, M. Avella, M. Calicchio, N. Musayeva, J. Jimenez*: J. Cryst. Growth. 287 (2006) 625.
- [8]. *P. J. Klar, J. Teubert, M. Güngerich, T. Niebling, H. Grüning, W. Heimbrod, K. Volz, H. Riechert and S. Tomic*: Phys. Status Solidi B 244 (2007) 24.
- [9]. *I. A. Buyanova, W. M. Chen and C. W. Tu*: J. Phys.: Condens. Matter 16 (2004) S3027.
- [10]. *W. Ulrici and B. Clerjaud*: Phys. Rev. B 72 (2005) 045203.
- [11]. *W. Ulrici and B. Clerjaud*: Physica B 376-377 (2006) 560.
- [12]. *J. C. Chen, M. Ladle Ristow, J. I. Cabbage and J. G. Werthen*: Appl. Phys. Lett. 58 (1991) 20.
- [13]. *S. K. Agarwal, R. Tyagi, M. Singh and R. K. Jain*: Sol. Energy Mater. Sol. Cells 59 (1999) 19.
- [14]. *R. R. King, D. C. Law, K. M. Edmonson, C. M. Fetzer, G. S. Kinsey, H. Yoon, R. A. Sherif and N. K. Karam*: Appl. Phys. Lett. 90 (2007) 183516.
- [15]. *J. Derluyn, K. Dessein, G. Flamand, Y. Mols, J. Poortmans, G. Borghs and I. Moerman*: J. Cryst. Growth 247 (2003) 237.
- [16]. *P. Modak, M. D'Hondt, P. Mijlemans, I. Moerman, P. Van Daele and P. Demeester*: J. Electron. Mater. 29 (2000) 80.
- [17]. *G. Y. Yu, Z. X. Shen, L. Liu and W. X. Sun*: Mat. Sci. Semicond. Process. 4 (2001) 581.
- [18]. *A. Mascarenhas and M. J. Seong*: Semicond. Sci. Technol. 17 (2002) 823.
- [19]. *J. Salzmann and H. Temkin*, Mater. Sci. Eng. B 50 (1997) 148.
- [20]. *S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishin and H. Temjin*, Appl. Phys. Lett. 72 (1998) 1857.
- [21]. *K. Onabe, D. Aoki, J. Wu, H. Yaguchi and Y. Shiraki*, Phys. Stat. Sol. A 176 (1999) 231.