Surface photovoltage and modulation spectroscopy of E₋ and E₊ transitions in GaNAs layers

R. Kudrawiec^{a), 1, 2}, P. Sitarek¹, M. Gladysiewicz¹, J. Misiewicz¹, Y. He³,
Y. Jin⁴, G. Vardar⁴, A.M. Mintarov³, J.L. Merz³, R. S. Goldman⁴, K.-M. Yu²,
and W. Walukiewicz²

¹*Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, Poland*

²*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley,
California 94720, United States*

³*Department of Electrical Engineering, University of Notre Dame, Notre Dame,
Indiana 46556, United States*

⁴*Department of Materials Science and Engineering, University of Michigan, Ann Arbor,
Michigan 48104, United States*

Surface photovoltage (SPV) spectra were measured for GaN_{0.014}As_{0.986} layers at room temperature and compared with room temperature photoreflectance (PR) and contactless electroreflectance (CER) measurements. Spectral features related to E₋ and E₊ transitions were clearly observed in SPV spectra at energies corresponding to PR and CER resonances. In this way it has been shown that SPV spectroscopy is an alternative absorption-like technique to study both the E₋ and E₊ transitions in dilute nitrides. The observation of E₊ transition in SPV spectra means that it is a direct optical transition at the Γ point of GaNAs band structure which can be explained by the band anticrossing interaction between the localized states of N and the extended conduction band states of the GaAs host.

^{a)} E-mail addresses: robert.kudrawiec@pwr.wroc.pl; rkudrawiec@lbl.gov

1. Introduction

GaNAs alloy with a few percent of nitrogen is the prominent member of a specific class of semiconductor materials known as highly mismatched alloys [1, 2]. In such alloys the band-gap engineering is achieved by strongly perturbing the host by incorporation of isovalent atoms which significantly differ from host atoms. The isovalent atom (in this case it is nitrogen) dramatically narrows the fundamental band-gap and increases the electron effective mass compared to the host material [1, 3-7]. Nitrogen is also responsible for strong carrier localization at low temperatures [8] and formation of native defects [9] in GaNAs alloys.

It has been shown that the electronic band structure of $\text{GaN}_x\text{As}_{1-x}$ with a few percent of nitrogen can be described in terms of an anticrossing interaction between the localized states of N and the extended conduction band states of the GaAs host [1, 10, 11]. This strength of the interaction is described by the off-diagonal element $V_{NM} = C_{NM}\sqrt{x}$ in the band anticrossing (BAC) Hamiltonian given by

$$H_{BAC} = \begin{pmatrix} E_M(k) & V_{NM} \\ V_{NM} & E_N \end{pmatrix} \quad (1)$$

where $E_M(k)$ is the energy dispersion of the lowest conduction band of the III-V host and E_N is the energy of N-related states, all referenced to the top of the valence band of the host (for GaNAs $E_N = 1.65\text{eV}$). x is the nitrogen concentration and C_{NM} is a coupling constant depended on the host matrix (for GaNAs $C_{NM} = 2.7\text{eV}$). The band anticrossing interaction results in formation of two subbands E_- and E_+ with dispersion relations given by

$$E_{\pm}(k) = \frac{1}{2} \left[E_N + E_M(k) \pm \sqrt{[E_N - E_M(k)]^2 + 4V_{NM}^2} \right] \quad (2)$$

These subbands are plotted by thin black line in Fig. 1. Also shown in Fig. 1 is the band structure of GaNAs obtained with a more complete 10-band ***kp*** Hamiltonian that includes 6 valence bands, 2 conduction bands and 2 localized N states, see Refs. [12, 13]. It is evident that within this band structure of GaNAs alloy an extra optical transition at the Γ point (E_+ transition) is expected besides the fundamental transition (E_- transition). It was also suggested that the E_+ transition is associated with the presence of a close lying subsidiary, indirect conduction band minimum, which is L band minimum in the GaNAs case [14].

So far the key experimental evidence for the BAC model was provided by the observation of both the E_- and E_+ transitions in photoreflectance (PR) measurements performed at high hydrostatic pressures [1]. Also measurements of energy of E_- transition as a function of the isovalent trap concentration by using photoluminescence or other technique can confirm the band anticrossing behavior for this band [15-17]. However the observation of E_+ transition seems to be the best evidence for the identification of band anticrossing interaction in the conduction band of dilute nitrides. So far, other absorption-like techniques than PR, which are sensitive to optical transitions at critical points of the band structure, were not applied to study the E_+ transition in GaNAs alloys. In this paper, we show that surface photovoltage (SPV) spectroscopy is a very good tool to study both the E_- and E_+ transitions in GaNAs alloys.

SPV spectroscopy is a well known technique to map the electronic structure of bulk semiconductors near the band edge [18-20]. This technique measures the change in surface potential induced by optically excitation with periodic illumination. The measured potential is produced by carrier redistribution and/or capture of the photoexcited carriers in the surface states. It is contactless and nondestructive method which can provide information for both the

optical absorption transitions and the electronic transport in bulk materials and nanostructures even at room temperature. Recently, SPV was extensively applied to study the band structure of low dimensional heterostructures [21-26]. Also dilute nitrides were investigated by this technique [27-29] but the observation of E_+ transition in SPV spectra was not reported so far for these materials. In this paper we applied SPV spectroscopy to study the E_+ transition in samples where this transitions was clearly observed in PR spectra.

2. Experiment

The $\text{GaN}_{0.014}\text{As}_{0.986}$ layers were grown on (001) semi-insulating GaAs substrates by molecular-beam epitaxy (MBE), using solid Ga, As_2 , Si sources and an N_2 rf plasma source. The target doping concentration for the doped sample is on the order of $\sim 5 \times 10^{17} \text{ cm}^{-3}$, as confirmed in GaAs films. The N composition in the GaNAs layers was adjusted by varying the gas flow rate monitored by partial pressure of 14 amu (active N) in the MBE chamber, as measured with a residual gas analyzer. After an initial GaAs buffer layer was grown at 580-500 °C, a series of annealing steps were performed with As overpressure, followed by the growth of 500 nm thick GaNAs:(Si) layers at 400 °C. Postgrowth annealing was performed at 760 °C for 60s in N_2 ambient, with a GaAs proximity cap to prevent As outdiffusion. Other details of the sample growth are described in Ref. [30].

The SPV measurements were performed using a contactless electrode configuration with a chopped light in air at room temperature. The light from a 250 W tungsten–halogen lamp was passed through a 0.32 m Jobin–Yvon monochromator, chopped at 180 Hz and focused onto the sample. The sample is mounted in a capacitor like sample holder on a bottom electrode (i.e. a copper plate) and covered by a top electrode (i.e., a metal grid). The induced SPV signal on the metal grid was measured with a copper bottom as the ground electrode, using a buffer circuit and a lock-in amplifier [26].

A “bright configuration” of experimental set-up was used to measure the PR and contactless electroreflectance (CER) spectra [31]. A single grating 0.55 meter focal-length monochromator and a Si *pin* photodiode were used to disperse and detect the reflected light from the samples. A 150W halogen lamp was used as the probe beam and a YAG laser (532nm line) was used as the pump source. The probe and pump beams were focused onto the sample to the diameter of ~3 mm and the power of laser beam was reduced to 10 mW using a neutral density filter. The pump beam was modulated by a mechanical chopper at a frequency of 280 Hz. For CER measurements samples were mounted in a capacitor with the top electrode made from a copper-wire mesh which is semi-transparent to light. This electrode was kept at a distance of ~0.5 mm from the sample surface while the sample itself was fixed on the bottom copper electrode. A maximum peak-to-peak alternating voltage of ~3.0 kV with the frequency of 285 Hz was applied. Phase sensitive detection of the PR and CER signal was accomplished using a lock-in amplifier. Other relevant details of CER and PR measurements are described in Refs. [31, 32].

3. Results and discussion

Figure 2 shows room temperature SPV and PR spectra measured for GaAs layer (reference sample) and as-grown and annealed GaNAs layers. For the reference sample, the strong SPV signal appears near the GaAs absorption edge. This signal starts at lower energy than the GaAs energy gap since the probing beam in the transparency region ($E < 1.42\text{eV}$) penetrates the whole sample including GaAs substrate which gives a large contribution to SPV signal below energy gap due to a significant tail of density of states (DOS) in this material. GaAs substrate is not probed by PR since the main contribution to PR signal originates from the sample region near the sample surface. Thus, the narrow PR resonance at 1.42eV is associated with the absorption in the GaAs epitaxial layer. SPV signal from the

GaAs epitaxial layer is also visible in SPV spectrum as the sharp spectral feature at 1.42 eV in Fig. 2 (a). It is worth noting that the tail of DOS in GaAs substrate is present due to large concentration of impurities which are typical for the bulk growth method. For epitaxial layers, the impurity concentration is at least two orders of magnitude lower than for bulk substrates. As is seen in Fig. 2 (b)-(e) a SPV signal related to absorption edge in GaNAs is observed ~ 0.25 eV below the GaAs energy gap. This signal correlates very well with the PR resonance associated with the E. transition shown by the red arrow in Fig. 1. This transition shifts to blue upon annealing for both undoped and Si-doped GaNAs films. Such a shift is often observed for GaNAs layers [33] and can be attributed to a passivation of N atoms. Beside the E. transition, the E_+ transition is clearly observed in PR spectra at the energy of ~ 1.85 eV, see the blue arrow in Fig. 1. This transition is also observed in SPV spectra, see SPV signal in this spectral range in Fig. 2 (b)-(e). Such a signal is not observed in SPV spectra of the reference sample, see Fig. 2(a). For the GaAs sample the spin-orbit transition ($E_0 + \Delta_{SO}$) is observed in this region of the PR spectrum. However its energy of 1.78 eV differs significantly from the energy of E_+ transition (~ 1.85 eV) that can be only attributed to GaNAs layer. A SPV signal related to GaAs buffer/substrate layer is also observed for GaNAs samples since the thickness of GaNAs layers is 500 nm that is partially transparent in this spectral range. Despite the contribution of GaAs-related signal to SPV spectra of GaNAs samples, the two optical transitions related to E. and E_+ subbands can be identified in these spectra.

A detailed analysis of modulated reflectance (PR and CER) and SPV spectra for one GaNAs sample is shown in Fig. 3. It is important to note that the probing depth in CER spectroscopy is much smaller than in PR spectroscopy [34] and therefore the GaAs-related signal, which is associated with the optical transition in GaAs buffer layer, is not observed in CER spectrum. Except this difference, CER and PR spectra look very similar and the same

optical transitions are observed in these spectra. These spectra have been fitted by Aspnes formula [35]

$$\frac{\Delta R}{R}(E) = \text{Re} \left[C e^{i\vartheta} (E - E_j + i\Gamma)^{-m} \right], \quad (3)$$

where $\frac{\Delta R}{R}(E)$ is the energy dependence of PR (or CER) signal, C and ϑ are the amplitude and phase of the resonance, and E_j and Γ are the energy and the broadening parameter of the optical transition, respectively. The exponent m depends on the type of optical transition. For an inhomogeneous system, it can be assumed that $m = 3$. The fitting curves are shown as thick grey lines in Fig. 3 together with the moduli of PR (CER) resonances, which are shown as dashed lines. The modulus of PR (CER) resonance (ρ) was obtained according to Eq.(4) with parameters taken from the fit.

$$\Delta \rho(E) = \frac{|C|}{\left[(E - E_j)^2 + \Gamma^2 \right]^{\frac{m}{2}}} \quad (4)$$

Comparing energies of optical transitions observed in modulated reflectance shown by the vertical dashed lines, with spectral features observed in SPV spectrum and its derivative form shown in Fig. 3(d) it is clear that these spectral features correlate very well with the E_- and E_+ transition. A signal related to the $E_- + \Delta_{SO}$ transition is not observed in the SPV spectrum because of an interference with GaAs-related features. An interesting feature of the spectra is that the shape of SPV signal related to E_- transition is similar to that observed for an edge absorption whereas the shape of SPV signal related to E_+ transition is significantly different.

This difference can be attributed the difference in the nature the E_+ and E_- subband edges. The E_+ subband edge lies closely to the N-derived level and thus it is a more localized nature whereas the edge of the E_- subband is further removed from the N-level and more closely resembles extended states of GaAs matrix.

4. Conclusions

In conclusion, spectral features related to both the E_- and E_+ transitions were clearly observed in SPV spectra of GaNAs layers. These features correspond very well to optical transitions observed in PR and CER spectra. It means that SPV spectroscopy is an alternative absorption-like technique to study both the E_- and E_+ transitions in dilute nitrides. The observation of E_+ transition in SPV spectra can be explained by the band anticrossing interaction between the localized states of N and the extended conduction band states of the GaAs host.

Acknowledgments

The authors acknowledge support from the NCN (grant No. 2012/07/E/ST3/01742) and the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. DOE under Contract No. DE-AC02-05CH11231. In addition, R.K. was supported within the grant “Mobilnosc Plus” from the MNiSzW, GV was supported in part by the Fulbright Foreign Student Fellowship, YJ, GV, and RSG were supported in part by NSF DMR Grant No. 1006835.

References

- [1] W. Shan, W. Walukiewicz, J.W. Ager III, E.E. Haller, J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz, Band Anticrossing in GaInNAs Alloys, *Phys. Rev. Lett.* 82 (1999) 1221-1224.
- [2] J. Wu, W. Walukiewicz, E. E. Haller, Band structure of highly mismatched semiconductor alloys: Coherent potential approximation, *Phys. Rev. B* 65 (2001) 233210.
- [3] M. Weyers, M. Sato, H. Ando, Red Shift of Photoluminescence and Absorption in Dilute GaAsN Alloy Layers, *Jpn. J. Appl. Phys., Part 2* 31 (1992) L853-L855.
- [4] J.D. Perkins, A. Mascarenhas, Y. Zhang, J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz, Nitrogen-Activated Transitions, Level Repulsion, and Band Gap Reduction in $\text{GaAs}_{1-x}\text{N}_x$ with, *Phys. Rev. Lett.* 82 (1999) 3312-3315.
- [5] C. Skierbiszewski, P. Perlin, P. Wisniewski, W. Knap, T. Suski, W. Walukiewicz, W. Shan, K.M. Yu, J. W. Ager, E.E. Haller, J.F. Geisz, J.M. Olson, Large, Nitrogen-Induced Increase of the Electron Effective Mass in $\text{In}_y\text{Ga}_{1-y}\text{N}_x\text{As}_{1-x}$, *Appl. Phys. Lett.* 76 (2000) 2409-2411.
- [6] P.N. Hai, W.M. Chen, I.A. Buyanova, H.P. Xin, C.W. Tu, Direct determination of electron effective mass in GaNAs/GaAs quantum wells, *Appl. Phys. Lett.* 77 (2000) 1843-1845.
- [7] T. Dannecker, Y. Jin, H. Cheng, C. F. Gorman, J. Buckeridge, C. Uher, S. Fahy, C. Kurdak, R. S. Goldman, Nitrogen composition dependence of electron effective mass in $\text{GaAs}_{1-x}\text{N}_x$, *Phys. Rev. B* 82 (2010) 125203.
- [8] W. Shan, W. Walukiewicz, K.M. Yu, J.W. Ager III, E.E. Haller, J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz, H.P. Xin, C.W. Tu, Band Anticrossing in III–N–V Alloys, *Phys. Stat. Sol. (b)* 223 (2001) 75-85.
- [9] J. Wu, W. Shan, W. Walukiewicz, Band anticrossing in highly mismatched III–V semiconductor alloys, *Semicond. Sci. Technol.* 17 (2002) 860-869.

- [10] R. Kudrawiec, G. Sęk, J. Misiewicz, F. Ishikawa, A. Trampert, K.H. Ploog, Localized and delocalized states in GaNAs studied by microphotoluminescence and photoreflectance, *Appl. Phys. Lett.* 94 (2009) 011907.
- [11] R. Kudrawiec, M. Latkowska, M. Welna, J. Misiewicz, M. Shafi, R. H. Mari, M. Henini, W. Walukiewicz, Correlations between the band structure, activation energies of electron traps, and photoluminescence in n-type GaNAs layers, *Appl. Phys. Lett.* 101 (2012) 082109.
- [12] S. Tomic, E.P. O'Reilly, R. Fehse, S.J. Sweeney, A.R. Adams, A.D. Andreev, S.A. Choulis, T.J. Hosea, H. Riechert, Theoretical and experimental analysis of 1.3- μm InGaAsN/GaAs lasers, *IEEE J. Selected Topics in Quantum Electron.* 9 (2003) 1228-1238.
- [13] M. Gladysiewicz, R. Kudrawiec, J.M. Miloszewski, P. Weetman, J. Misiewicz, M. Wartak, Band structure and the optical gain of GaInNAs/GaAs quantum wells modeled within 10-band and 8-band kp model, *J. Appl. Phys.* 113 (2013) 063514.
- [14] T. Mattila, S.-H. Wei, A. Zunger, Localization and anticrossing of electron levels in $\text{GaAs}_{1-x}\text{N}_x$ alloys, *Phys. Rev. B* 60 (1999) R11245.
- [15] I. A. Buyanova, M. Izadifard, W. M. Chen, Y. G. Hong, C. W. Tu, Modeling of band gap properties of GaInNP alloys lattice matched to GaAs, *Appl. Phys. Lett.* 88 (2006) 031907.
- [16] J. A. H. Coaquira, M.-A. Pinault, A. P. Litvinchuk, L. Bhusal, A. Freundlich, Near band-edge luminescence and evidence of the weakening of the N-conduction-band coupling for partially relaxed and high nitrogen composition $\text{GaAs}_{1-x}\text{N}_x$ epilayers, *J. Appl. Phys.* 102 (2007) 073716.
- [17] D. Serries, T. Geppert, P. Ganser, M. Maier, K. Kohler, N. Herres, J. Wagner, Quaternary GaInAsN with high In content: Dependence of band gap energy on N content, *Appl. Phys. Lett.* 80 (2002) 2448-2450.
- [18] J. Lagowski, Semiconductor surface spectroscopies: the early years, *Surf. Sci.* 299/300 (1994) 92-101.

- [19] L. Kronik, Y. Shapira, Surface photovoltage phenomena: theory, experiment, and applications, *Surf. Sci. Rep.* 37 (1999) 1-206.
- [20] M. A. Reshchikov, M. Foussekis, A. A. Baski, Surface photovoltage in undoped n-type GaN, *J. Appl. Phys.* 107 (2010) 113535.
- [21] N. Bachrach-Ashkenasy, L. Kronik, Y. Shapira, Y. Rosenwaks, M. C. Hanna, M. Leibovitch, P. Ram, Surface photovoltage spectroscopy of quantum wells and superlattices, *Appl. Phys. Lett.* 68 (1996) 879-881.
- [22] Y.S. Huang, C.J. Lin, C.H. Wang, N.Y. Li, C.C. Fan, P.W. Li, Photoreflectance and surface photovoltage spectroscopy characteristics of an InGaP/InGaAsN/GaAs NPN DHBT structure, *IEE Proc. Optoelectron.* 150 (2003) 99-101.
- [23] Ts. Ivanov, V. Donchev, Y. Wang, H. S. Djie, B. S. Ooi, Interdiffused InAs/InGaAlAs quantum dashes-in-well structures studied by surface photovoltage spectroscopy, *J. Appl. Phys.* 101 (2007) 114309.
- [24] Ts. Ivanov, V. Donchev, K. Germanova, P. F. Gomes, F. Iikawa, M. J. S. P. Brasil, M. A. Cotta, A surface photovoltage spectroscopy study of GaAs/AlAs complicated nanostructures with graded interfaces, *J. Appl. Phys.* 101 (2007) 124305.
- [25] C. H. Chan, C. W. Kao, H. P. Hsu, Y. S. Huang, J. S. Wang, J. L. Shen, K. K. Tiong, Surface photovoltage and photoluminescence excitation spectroscopy of stacked self-assembled InAs quantum dots with InGaAs overgrown layers *J. Appl. Phys.* 103 (2008) 084303.
- [26] P. Sitarek, H. P. Hsu, Y. S. Huang, J. M. Lin, H. H. Lin, K. K. Tiong, Optical studies of type-I GaAs_{1-x}Sb_x/GaAs multiple quantum well structures, *J. Appl. Phys.* 105 (2009) 123523.
- [27] Gh. Dumitras, H. Riechert, H. Porteanu, F. Koch, Surface photovoltage studies of In_xGa_{1-x}As and In_xGa_{1-x}As_{1-y}N_y quantum well structures, *Phys. Rev. B* 66 (2002) 205324.

- [28] M. Galluppi, L. Geelhaar, H. Riechert, Nitrogen and indium dependence of the band offsets in InGaAsN quantum wells, *Appl. Phys. Lett.* 86 (2005) 131925.
- [29] B. Bansal, A. Kadir, A. Bhattacharya, B. M. Arora, R. Bhat, Alloy disorder effects on the room temperature optical properties of $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ quantum wells, *Appl. Phys. Lett.* 89 (2006) 032110.
- [30] M. Reason, Y. Jin, H. A. McKay, N. Mangan, D. Mao, R. S. Goldman, X. Bai, C. Kurdak, Influence of N on the electronic properties of GaAsN alloy films and heterostructures, *J. Appl. Phys.* 102 (2007) 103710.
- [31] R. Kudrawiec, J. Misiewicz, Photorefectance and contactless electroreflectance measurements of semiconductor structures by using bright and dark configurations, *Rev. Sci. Instr.* 80 (2009) 096103.
- [32] J. Misiewicz, R. Kudrawiec, Contactless electroreflectance spectroscopy of optical transitions in low dimensional semiconductor structures, *Opto-Electron. Rev.* 20 (2012) 101-119.
- [33] R. Kudrawiec, G. Sek, J. Misiewicz, L.H. Li, J.C. Harmand, Investigation of recombination processes involving defect-related states in (Ga,In)(As,Sb,N) compounds, *Eur. Phys. J. Appl. Phys.* 27 (2004) 313-316.
- [34] R. Kudrawiec, Application of contactless electroreflectance to III-nitrides, *Physica Status Solidi (b)* 247 (2010) 1616-1621.
- [35] D. E. Aspnes, Third-derivative modulation spectroscopy with low-field electroreflectance, *Surf. Sci.* 37 (1973) 418-442.

Figure Captions:

FIG. 1. Band structure of $\text{GaN}_{0.014}\text{As}_{0.986}$ calculated within the BAC model (thin black lines) and 10-band *kp* model (dashed black lines).

FIG. 2. Room temperature SPV and PR spectra of the reference sample (a), as-grown (b) and annealed $\text{GaN}_{0.014}\text{As}_{0.986}$ (c) samples, and as-grown (d) and annealed $\text{GaN}_{0.0135}\text{As}_{0.9865}\text{:Si}$ (e) samples.

FIG. 3. Room temperature PR (a) and CER (b) spectra of annealed $\text{GaN}_{0.014}\text{As}_{0.986}$ sample together with the fitting curves (thick grey lines) and modulus of individual resonances (thin solid lines). Room temperature SPV spectrum of annealed $\text{GaN}_{0.014}\text{As}_{0.986}$ sample (c) and its derivative (d).

FIG. 1.

(R. Kudrawiec et al.)

FIG. 2.

(R. Kudrawiec et al.)

FIG. 3.

(R. Kudrawiec et al.)