Chemistry: Bulgarian Journal
of Science Education
Volume 27
Number 5, 2018
Природните науки
в образованието

Education: Theory & Practice
Науката за образованието: теория и практика

Physics is an ever young science, Varna, October, 27 – 29, 2017
Физиката – вечно млада наука, Варна, 27 – 29 октомври 2017 г.

SURFACE PHOTOVOLTAGE SPECTROSCOPY CHARACTERIZATION OF GAASSBN LAYERS GROWN BY LIQUID-PHASE EPITAXY

[1]S. Georgiev, [1]V. Donchev, [2]M. Milanova
[1]University of Sofia (Bulgaria)
[2]Central Laboratory of Applied Physics – Plovdiv (Bulgaria)

Abstract. We present an experimental study of GaAsSbN layers with thickness around 1μm, grown by liquid-phase epitaxy on n-type GaAs substrates. The samples are studied by surface photovoltage (SPV) spectroscopy at room temperature. The analysis of the SPV spectra has provided information about the optical absorption and the photocarrier transport in the samples. In particular, a red shift of the energy bandgap with respect to GaAs is found. Its values are larger as compared to our previous data obtained in InGaAsN layers, grown by the same technique.

Keywords: dilute nitrides; GaAsSbN; surface photovoltage; band gap shift

Introduction

Dilute nitrides have attracted recently considerable attention from both scientific and technological perspectives. They form a novel class of semiconductor alloys, which has emerged from the conventional III – V compounds by doping with small amount of nitrogen. It has been found that the substitution of group V anions in III – V compounds with nitrogen (N) in small concentrations leads to significant change in their electronic properties, in particular bandgap narrowing and shift of the absorption edge to longer wavelengths. Their abilities, like being grown lattice-matched to GaAs and the possibility of band structure engineering makes the dilute nitrides materials of great interest for a variety of applications in advanced optoelectronic devices (Erol, 2008). The addition of indium (In) in the alloy facilitates the incorporation of N, while antimony (Sb) act as a surfactant that reduces the strain-induced defect formation, favours 2D growth and further decreases the bandgap (Fehse & Adams, 2004). Although the pentanary InGaAsSbN and quaternary InGaAsN alloys are the most intensely studied compounds, GaAsSbN shows promising properties for solar cell and photodetecting applications. The advantages of this system are absence of In-related defects and lower N composition to achieve the same bandgap. Furthermore, the conduction and valence band energies can be adjusted independently while it is latice-matched to GaAs (Braza et al., 2017, Ulloa et al., 2012). However, this quaternary system is much less investigated as compared to the pentanary InGaAsSbN and quaternary InGaAsN compounds.

The epitaxial growth of dilute nitride bulk layers remains a great challenge because of the low incorporation efficiency of N into the growing crystal, the large difference in lattice constant between nitrides and arsenides and the local high strain near N atoms. That is why the growth conditions are crucial for the quality of the epitaxial layers. Conventional fabrication methods, such as molecular beam epitaxy (MBE) and metalo-organic chemical beam deposition (MOCVD) operating at extreme nonequilibrium conditions, favour the formation of various defects responsible for many of the anomalous optical and transport properties of dilute nitride alloys (Zhang & Wei, 2004, Krispin et al., 2003, Tu, 2004). In contrast to other epitaxial methods the crystallisation at liquid phase epitaxy (LPE) is carried out under near equilibrium conditions and has recently shown promise in obtaining high-quality dilute nitride layers in terms of lifetime, mobility and freedom from defects of the epitaxial layers (Milanova et al., 2012).

The improvement of the epitaxial growth techniques and the use of modern characterization techniques have led to higher performance and quality of the dilute nitride materials and the possibility for detailed control of the interfaces at the atomic level. Such a useful method for characterization is the surface photovoltage (SPV) spectroscopy, although it has been relatively rarely applied to dilute nitrides. It provides information about the optical absorption spectrum and carrier transport in the sample (Kronik & Shapira, 1999, Donchev et al., 2010) and has proven as a good complementary technique to photoluminescence spectroscopy in investigating dilute nitrides alloys (Donchev et al. 2010; 2017).

In this work we present an experimental study of the optical properties of LPE grown GaAsSbN layers based on SPV spectroscopy. The results are compared to the findings for InGaAsN layers from our previous study.

Experimental details

A series of $GaAs_{1-x-y}Sb_yN_x$ epitaxial layers were grown by the horizontal graphite slide-boat technique for LPE on (100) n-type GaAs:Si ($\sim 10^{18} cm^{-3}$) substrates. A flux of Pd- membrane purified hydrogen at atmospheric pressure was used for the experiments. No special baking of the system was carried out before epitaxy. The starting materials for the solutions consisted of 6N pure solvent metals Ga, Sb and of polycrystalline GaAs and GaN with purity of 5N. The N content in the melt was 0.5 at. % for all grown layers. Epitaxial layers with thickness of 1 µm were grown in a temperature range 570 – 558˚C at a cooling rate of 0.8˚C/min.

SPV spectra were recorded at room temperature using the metal-insulator-semiconductor operation mode of the SPV technique (Kronik & Shapira, 1999). The sample was illuminated by means of a 250 W halogen lamp along with a SPEX grating monochromator (f = 0.25 m, 600 gr/mm) and an optical chopper (94 Hz). The probe electrode was a semitransparent SnO_2 film evaporated on the bottom surface of a quartz glass. It was separated by a sheet of mica (15 µm) from the sample, which was positioned on a copper platform. The probe signal with respect to the ground was fed to a high-impedance unity gain buffer and then measured by a SR830 lock-in amplifier. The photon flux was kept constant ($\approx 1.5\times 10^{14}$ $cm^{-2}s^{-1} \pm 1$ %) for all wavelengths, by positioning a neutral density filter with variable optical density driven by a step motor. More details about the SPV measurement procedure can be found in (Donchev et al., 2010).

An original sample holder was specially designed and fabricated for this study. It contains a bridge, a vertical stick and a screw positioned on a massive platform (Fig.1). The stick and the screw pass through openings in a plastic arm, which holds the quartz glass with the probe electrode by means of a clip with a tightening screw assuring electrical contact with the electrode. A spring loaded on the screw pushes the plastic arm upward, while a another screw passing through the bridge can push it downward. This way a better control of the height and angle of the electrode with respect to the sample can be achieved as compared to the vertical sample holder used in our previous experiments (Donchev et al., 2010; 2016; 2017). The new arrangement eliminates the surface pressure and the wedge between the planes of the glass and the sample, which can influence the SPV signal. In addition, it allows easier and faster exchange of the samples under study and can accommodate larger samples. A metallic box with an opening for the excitation light covers all the elements of the sample holder to screen unwanted electromagnetic fields.

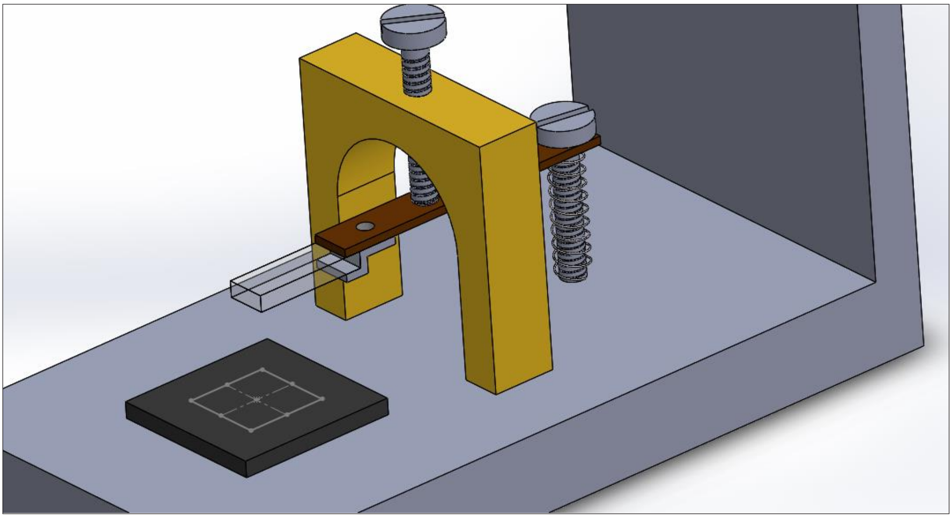

Figure 1. Schema of the sample holder

Results and discussions

Fig. 2 represents the normalized SPV amplitude spectra of a GaAsSbN sample compared with that of the GaAs substrate and an InGaAsN sample. The small undulations in the SPV spectra are due to interference effects caused by the mica sheet. The spectra reveal steep jumps of the signal, which are related to the absorption edge of the semiconductor materials. A clear red shift of the absorption edge with respect to GaAs is observed for the dilute nitride layers. This shift is larger in the case of GaAsSbN.

To assess the band gap energies, we have used two methods. Assuming that the SPV is proportional to the absorption coefficient, we have plotted the square of the SPV amplitude vs. the photon energy. In the ideal case, there should be a straight line, resulting from the shape of the 3D joint density of states. In the present case we have considered the linear part of the obtained curve and have extrapolated it to find its intersection point with the abscissa, which is assumed to be the band gap energy, E_g. We have obtained the same result (within the experimental error) for the band gap energy by using Tauc plot. These results for the GaAsSbN sample are shown in Fig. 3. In this case the obtained value of E_g is 1.24 eV, which means that the red shift of the absorption edge with respect to GaAs (E_g = 1.423 eV) is ΔE_g = 0.183 eV. For the other sample (InGaAsN) E_g = 1.311 eV and therefore ΔE_g = 0.112 eV, which is by 71 meV smaller than the values for GaAsSbN. Decreasing of the bandgap is expected due to the presence of nitrogen, but in the case of GaAsSbN it is larger than in InGaAsN. This is explained by the replacement of indium with antimony in the growth process. The main role of the antimony in dilute nitrides is as a surfactant, but it also moves the edge of the valence band toward higher energies (Ulloa et al., 2012) this way further decreasing the band gap.

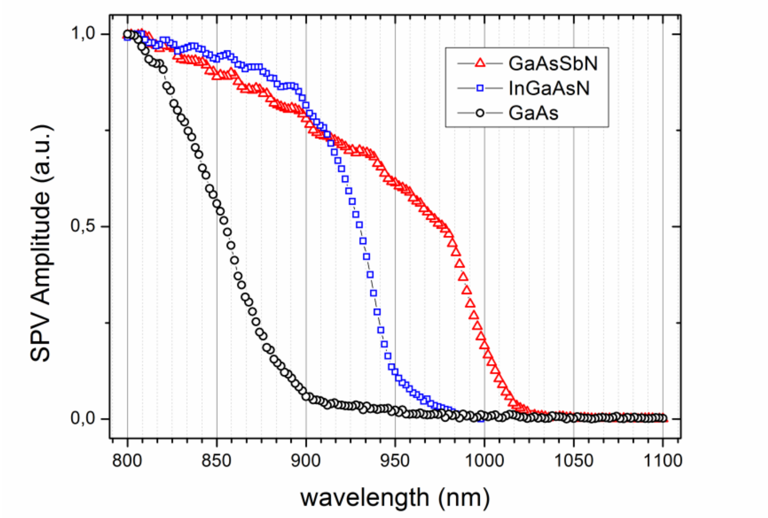

Figure 2. Normalized SPV amplitude spectra of the GaAsSbN and InGaAsN layer samples compared to that of the GaAs substrate

Fig. 4 shows the SPV phase spectra of the GaAsSbN, InGaAsN samples and the GaAs substrate. The phase spectral behaviour is associated with the alignment of the energy bands across the structure (Donchev et al., 2010). The phase values are in the IV quadrant and their spectral behaviour is typical for the case of upwards energy band bending in the direction towards the surface (Donchev et al., 2010). This indicates an n-type doping of the layers, which is in accordance with the Hall measurements results and with our previous results on InGaAsN layers (Donchev et al., 2016). In addition, the phase values show that the energy band bending at the interface layer/substrate is also upwards. Such interface bending is expected from the following considerations. There is a downward shift of the conduction band edge in the dilute nitride alloys with respect to GaAs (Shan et al., 1999). In addition, the Hall effect measurements have revealed a lower free electron concentration in the layer samples as compared to the substrate sample, indicating a lower Fermi level (measured with respect to the conduction band edge) in the layer. All this leads to an electron flow from the substrate to the layer and therefore to an upward band bending at the interface.

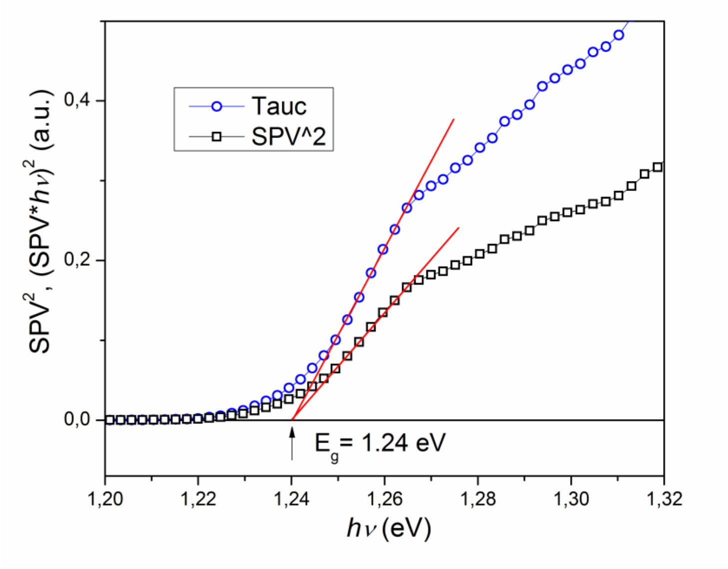

Figure 3. Determining the bandgap of the GaAsSbN sample using the squared SPV spectrum and Tauc plot

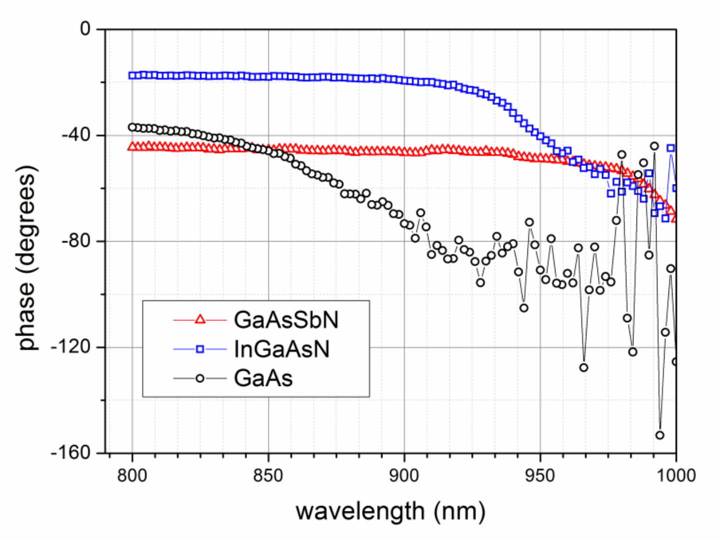

Figure 4. SPV phase spectra of the GaAsSbN and InGaAsN layer samples and the GaAs substrate

Conclusion

An original study is presented of the optical properties of thick LPE grown GaAsSbN layers. The absorption features, measured by SPV spectroscopy, are compared with previous results obtained by the same method for our InGaAsN samples. In this way, we showed that the addition of antimony instead of indium during the growth process further reduces the band gap energy (≈ 0.07 eV) of the dilute nitrides. The bending of the energy bands determined by the SPV phase spectra is found to be upward both at the surface and at the interface layer/substrate. This work demonstrates the applicability of the SPV technique as an alternative of the optical absorption spectroscopy for studying dilute nitride materials. The results obtained contribute to the better understanding of the physical properties of dilute nitrides grown by LPE and their potential for optoelectronic applications.

Aknowledgements. This work was supported by the Cost Action MP1406 "Multiscale in modelling and validation for solar photovoltaics (MultiscaleSolar)" and the Bulgarian National Science Fund (contract ДКОСТ 01/16). B. Arnaudov is acknowledged for the Hall effect measurements.

REFERENCES

Braza, V., Reyes, D.F., Gonzalo, A., Utrilla, A.D., Ben, T., Ulloa, J.M., & González, D. (2017). Sb and N incorporation interplay in GaAsSbN/GaAs epilayers near lattice-matching condition for 1.0 – 1.16-eV photonic applications. *Nanoscale Res. Lett.*, *12*, art. no. 356.

Donchev, V., Ivanov, T., Germanova, K. & Kirilov, K. (2010). Surface photovoltage spectroscopy – an advanced method for characterization of semiconductor nanostructures. *Trends Appl. Spectroscopy, 8,* 27 – 66.

Donchev, V., Milanova, M., Lemieux, J., Shtinkov, N. & Ivanov, I.G. (2016). Surface photovoltage and photoluminescence study of thick Ga(In)AsN layers grown by liquid-phase epitaxy. *J. Phys.: Conf. Ser.*, *700*, art. no. 012028.

Donchev, V., Asenova, I., Milanova, M., Alonso-Álvarez, D., Kirilov, K., Shtinkov, N., Ivanov, I.G., Georgiev, S., Valcheva, E. & Ekins-Daukes, N. (2017). Optical properties of thick GaInAs(Sb)N layers grown by liquid-phase epitaxy. *J. Phys.: Conf. Ser.*, *794*, art. no. 012013.

Erol, A. (2008). *Dilute III – V nitride semiconductors and material systems: physics and technology.* Berlin: Springer.

Fehse, R & Adams, A.R. (2004). Recombination processes in GaInNAs long-wavelength lasers (pp. 339-370). In: Buyanova, I.A. & Chen, W.M. (Eds.). *Physics and applications of dilute nitrides*. New York, Taylor & Francis.

Krispin, P., Gambin, V., Harris, J.S. & Ploog, K.H. (2003). Nitrogen-related electron traps in Ga(As,N) layers (≤ 3% N). *J. Appl. Phys., 93*, 6095 – 6099.

Kronik, L. & Shapira, Y. (1999). Surface photovoltage phenomena: theory, experiment, and applications. *Surf. Sci. Rep/*, *37*, 1–206.

Milanova, M., Vitanov, P., Terziyska, P., Popov, G. & Koleva, G. (2012). Structural and electrical characteristics of InGaAsN layers grown by LPE. *J. Crystal Growth*, *346*, 79 – 82.

Shan, W., Walukiewicz, W., Ager III, J.W., Haller, E.E., Geisz, J.F., Friedman, D.J., Olson, J.M. & Kurtz, S.R. (1999). Band anticrossing in GaInNAs alloys. *Phys. Rev. Lett*, *82*, 1221 – 1224.

Tu, C.W. (2004). Growth, caracterization, and band-gap engineering of dilute nitrides (pp. 301 – 329). In: Buyanova, I.A. & Chen, W.M. (Eds.). *Physics and applications of dilute nitrides*. New York: Taylor & Francis.

Ulloa, J.M., Reyes, D.F., Montes, M., Yamamoto, K., Sales, D.L., González, D., Guzman, A. & Hierro, A. (2012). Independent tuning of electron and hole confinement in InAs/GaAs quantum dots through a thin GaAsSbN capping layer. *Appl. Phys. Lett.*, *100*, art. no. 013107.

Zhang, S.B. & Wei, S.-H. (2004). Theory of defects in dilute nitrides (pp. 239-270). In: Buyanova, I.A. & Chen, W.M. (Eds.). *Physics and applications of dilute nitrides*. New York: Taylor & Francis.

✉ **Mr. S. Georgiev**
Faculty of Physics
University of Sofia
5, James Bourchier Blvd.
1164 Sofia, Bulgaria
E-mail: stefangg1@live.com

✉ **Dr. V. Donchev**
Faculty of Physics
University of Sofia
5, James Bourchier Blvd.
1164 Sofia, Bulgaria
E-mail: vtd@phys.uni-sofia.bg

✉ **Dr. M. Milanova**
Central Laboratory of Applied Physics
59, St. Petersburg Blvd
4000 Plovdiv, Bulgaria
E-mail: milanovam@yahoo.com