Proceedings of the 42th "Jaszowiec" International School and Conference on the Physics of Semiconductors, Wisła 2013

Characterization of n-ZnO/p-GaN Heterojunction for Optoelectronic Applications

L. Wachnicki[a], S. Gieraltowska[a], B.S. Witkowski[a], S. Figge[b], D. Hommel[b], E. Guziewicz[a] and M. Godlewski[a,c]

[a]Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warszawa, Poland
[b]University of Bremen Institute of Solid State Physics Semiconductor Epitaxy, Otto-Hahn-Allee NW1 D-28359 Bremen, Germany
[c]Cardinal Stefan Wyszyński University, College of Science, Department of Mathematics and Natural Sciences Warszawa, Poland

An important feature of zinc oxide and gallium nitride materials are their similar physical properties. This allows to use them as a p–n junction materials for applications in optoelectronics. In earlier work we presented use of ZnO as a transparent contact to GaN, which may improve external efficiency of LED devices. In this work we discuss properties of a n-ZnO/p-GaN heterostructure and discuss its optimization. The heterostructure is investigated by us for possible applications, e.g. in a new generation of UV LEDs or UV light detectors.

DOI: 10.12693/APhysPolA.124.869
PACS: 85.30.Kk, 61.05.cp, 81.05.Dz

1. Introduction

Zinc oxide (ZnO) and gallium nitride (GaN) are two semiconductor materials, which are investigated for many possible applications in electronics, optoelectronics, biology, and medicine. Physical and chemical properties of both GaN and ZnO mean that these materials can be used as light emitting diodes (LEDs), sensor devices, in transparent electronics, and as solar cells [1–3].

In recent years the research concentrates on ZnO properties, due to many expected advantages of devices based on this material. For example, in envisioned ZnO-based laser diodes, lasing would likely occur via excitonic UV transitions. Thus, if realized, it would lead to much lower threshold currents, as compared to the ones in GaN-based devices. Moreover, ZnO-based diodes constructed by us and others are characterized by low reverse-leakage currents of 10^{-7} A observed at room temperature, which is important in point of view of some electronic applications. Regarding heterostructures, GaN/ZnO heterostructures are also very interesting, since heavily doped ZnO can be also used as a top conductive contact to GaN-based LEDs, as demonstrated recently [4, 5].

Both semiconductors are characterized by a large band gap energy of about 3.4 eV at room temperature [6, 7]. Their similar physical properties allow creation of LEDs emitting in a short wavelength spectral region [6–8]. ZnO/GaN heterostructures are also investigated for this application [9, 10]. This is highly interesting, since both materials in normal conditions (room temperature, atmospheric pressure) are crystallized in the wurtzite structure [11, 12]. Moreover, due to the relatively small lattice mismatch (about 1.6%) between ZnO and GaN it is possible to achieve an epitaxial growth of zinc oxide using a gallium nitride template. In fact, we demonstrated that we can grow zinc oxide of a high crystalline quality on top of GaN, with a reduced concentration of imperfections [11, 13]. In most of the cases the imperfections are related to the use of a substrate with a large lattice mismatch (for example silicon for ZnO or GaN epitaxy).

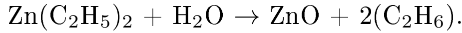
Short-wavelength UV detectors based on n-GaN/p-GaN homojunctions [13, 14] have been widely studied. Despite the fact that GaN-based LEDs, laser diodes and detectors are commercialized, some of their properties need further improvements. In particular, our first investigations show that ZnO-based UV detectors cannot only be more sensitive, but much cheaper, as well. This fact motivated us to study various versions of possible UV detectors, including the ones discussed in the present work.

In the present work we confirmed that zinc oxide layers grown on GaN are characterized by a relatively small number of defects. This is an important finding, since such material properties are required for optoelectronic or sensors and detectors applications. We present characterization and optimization of n-ZnO/p-GaN heterostructures, investigated for possible application in a new generation of UV detectors. We conclude that the simplicity and low costs of technology we use, combined with a relatively high quality of obtained monocrystalline ZnO films at relatively low temperature ($< 350\,^{\circ}$C), makes our approach attractive for a fabrication of modern semiconducting devices.

2. Experimental details

Undoped zinc oxide films with a high crystalline quality were deposited by the atomic layer deposition (ALD) method. Test samples were deposited first on a glass, and only then after optimizing the growth parameters, on gallium nitride template and zinc oxide (bulk material).

Before a growth substrates were chemically cleaned. ZnO layers, with thickness in the range from 0.5 to 2 μm, were obtained by a double exchange reaction, using diethylzinc and deionized water as precursors



$$Zn(C_2H_5)_2 + H_2O \rightarrow ZnO + 2(C_2H_6).$$

The details on the growth parameters (pulse time precursors, purging time) are given in our recent work [11].

After the process optimization, ZnO films were deposited at temperature of 300 °C on GaN/sapphire templates, with a GaN layer grown by the metalorganic chemical vapor deposition (MOCVD). On zinc oxide and gallium nitride surfaces were evaporated ohmic contacts, consisting of Au/Ti for ZnO and Au/Ni for GaN. Contacts were annealed at high temperature about 400 °C in RTP system for 5 min.

The structure and the crystallographic orientation of ZnO layers were measured with a high resolution (HRXRD) X'Pert MRD diffractometer equipped with the X-ray mirror, a four-bounce monochromator at the incident beam and a three bounce analyzer at the diffracted beam. Optical properties of zinc oxide nanostructures have been characterized by the spectrofluorimeter CM2203, with a xenon lamp used as the excitation source. The surface morphology was investigated by the atomic force microscopy (AFM, Bruker Dimension Icon) using the PeakForce Tapping and silicon nitride probes with sharp tips (a tip radius: 2 nm). Surface roughness was characterized by the root mean square (RMS) value. Films cross-section images were obtained by scanning electron microscopy (SEM, Hitachi SU-70) at the operation voltage of 15 kV. The Hall effect measurements were performed with a RH2035 system produced by PhysTech GmbH, with a permanent magnet giving a magnetic field of 0.426 T. The Hall measurements were done in the van der Pauw configuration with four contacts mechanically pressed to a square sample of ZnO thin film in its corners. I–V electrical characterizations were performed using a Keithley 2601A electrometer.

3. Result and discussion

In this paper we analyze properties of the ZnO/GaN diode with a monocrystalline zinc oxide layer deposited by the ALD.

Figure 1 shows a SEM cross-section image of ZnO (0.5 μm thick)/GaN (3 μm thick) heterostructure obtained by us, confirming a sharp interface between the two semiconductors. The SEM investigations allow us to trace how dislocations from gallium nitride template pass to zinc oxide layer. SEM and the following XRD investigations indicate that the two compounds adjust to each other.

HRXRD measurements confirm that the obtained ZnO layers are of a high crystalline quality. A full width at half maximum (FWHM) of the rocking curve of 00.6 reflection equals 0.07° (Fig. 2). This value of the rocking curve is identical to the one measured for the gallium nitride template, which means that quality of the ZnO

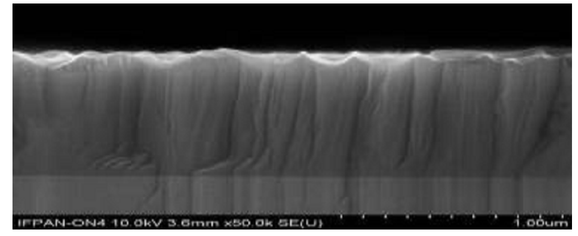


Fig. 1. The cross-sectional SEM image of the ZnO (0.5 μm thick) on GaN (3 μm thick) thin film grown by the ALD at temperature of 300 °C.

film is limited by imperfections in a GaN layer. The perpendicular lattice constant c was determined from the HRXRD measurements of the symmetrical 00.2 reflection as (5.1978 ± 0.0001) Å, while the parallel constant was determined from the asymmetrical reflection $(-1) - 1.4$ as (3.2569 ± 0.0005) Å. These results only slightly differ from the lattice constants of a bulk ZnO (at room temperature), which are 5.2069 Å and 3.2495 Å [4], respectively. From the lattice parameter results we can conclude that obtained layers are slightly tensile strained, which is due to the small lattice mismatch between ZnO and GaN.

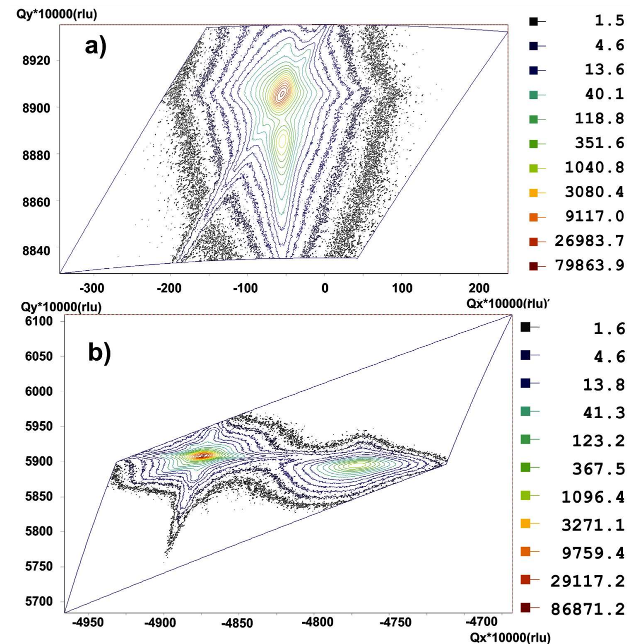


Fig. 2. (a) 00.2 symmetrical and (b) −1–14 asymmetrical reflection reciprocal space maps collected with antiscattered slit 1/8° before the XRD detector.

Electrical parameters and surface morphology measurements of the ZnO layers were then performed. For these measurements ZnO thin films were grown at the temperature range between 100 and 300 °C (see Table I) on GaN (carrier concentration $\approx 10^{17}$ cm^{-3} and mobility ≈ 20 cm^2/(V s)), ZnO and glass substrates. ZnO films

(0.5–2 μm thick) are characterized by free electron concentrations of about 10^{18} cm^{-3}. One can notice that we investigated junctions with relatively thick ZnO layers, done on purpose to limit gallium nitride substrate on the results of electrical investigations of ZnO.

TABLE I

Surface roughness defined by the RMS and carrier concentration vs. growth temperature of ZnO layers with thickness of 0.5 μm obtained in the ALD processes on GaN template.

Growth temperature [°C]	RMS [nm]	Carrier concetration [cm^{-3}]
300	6	3.88×10^{18}
250	7	4.80×10^{18}
200	9	6.32×10^{18}
150	28	8.25×10^{18}
100	17	3.16×10^{18}

For junctions (see schematic in Fig. 3) investigations we selected ZnO layers grown at temperature of 300 °C. These films exhibited the highest carriers' mobility at room temperature. The increase of the mobility of carriers was observed for films grown at a higher growth temperature and for thicker zinc oxide layers. Mobility of about 150 cm^{-2}/(V s) was obtained for the best structures. ZnO films were monocrystalline with a very flat surface morphology (see Tables I and II). Similar quality films were deposited on ZnO substrate, as discussed in the recent paper [13]. Test samples deposited on a glass were polycrystalline.

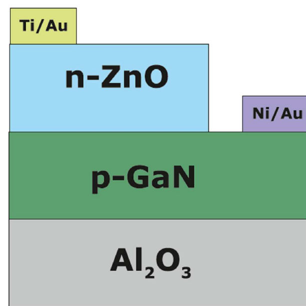


Fig. 3. Schematic presentation of the n-ZnO/p-GaN heterojunction with deposited ohmic contacts.

The optimized ZnO/GaN structure was characterized by a smooth interface, but by a relatively roughness surface (6 nm as compared to 1 nm of GaN template). For not optimized films the RMS value of 20 nm was obtained (see Fig. 4).

Current–voltage characteristic of the heterojunction, shown in Fig. 5, was investigated to determine the rectification ratio of the junction, defined as the ratio of forward to reverse currents. This ratio is mostly determined by a barrier height seen by electrons and holes. To account for the deviation from the ideal structure

TABLE II

Electrical properties of ZnO layers with thickness of about 2 μm deposited at temperature of 300 °C on three different substrates.

Substrate	Mobility [cm^2/(V s)]	Carrier concentration [cm^{-3}]
GaN	150	4×10^{18}
ZnO	80	5×10^{18}
glass	50	3×10^{18}

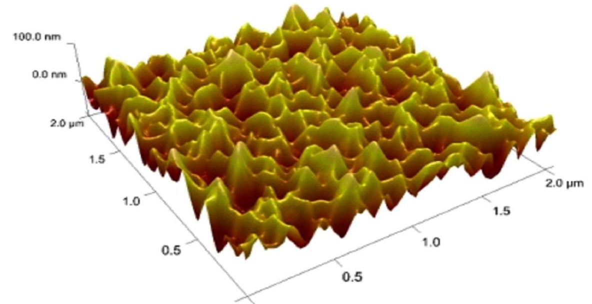


Fig. 4. Surface morphology AFM image (2×2 μm^2) of not optimized ZnO layer grown by the ALD at temperature 300 °C (2 μm thick) on a GaN template. ZnO layer is characterized by the RMS of about 20 nm. For GaN template RMS value is below 1 nm.

the so-called ideality factor is introduced. For most of ZnO structures investigated by us this factor deviates from 1 and is quite big (equal to 5) in the present case. The rectification ratio of our test n–p junction is $I_{\rm on}/I_{\rm off} = 1.8 \times 10^3$ for a voltage of 2 V. This result favourably compares to e.g. 10^2 reported for n-GaN/p-GaN junctions based on layers or nanowires as well as to e.g. 10^3 and 10^2 obtained for n-ZnO/p-GaN junctions based on layers and nanowires, respectively [15–18].

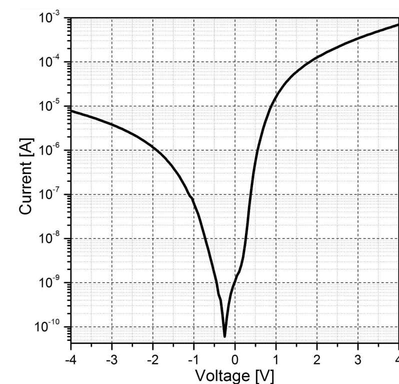


Fig. 5. I–V characteristic of ZnO/GaN heterojunction with $I_{\rm on}/I_{\rm off} = 1.8 \times 10^3$ for 2 V and $I_{\rm on} = 1.3 \times 10^{-2}$ A/cm^2.

The $I(V)$ characteristics of the junctions are strongly affected by UV illumination. Importantly, no response

was observed (or quite weak) in case of the visible light illumination. At present we optimize the structures for UV detector applications. These results will be a subject of forthcoming publication.

4. Conclusions

In this work we discuss properties of n-ZnO/p-GaN heterostructures, investigated for possible application in optoelectronic and detector devices. ZnO layers with a high crystalline quality and good electrical properties (carrier concentration $\approx 10^{18}$ cm^{-3} and mobility ≈ 150 cm^2/(V s)) were deposited by the ALD method at temperature of 300 °C on GaN/sapphire templates. On zinc oxide and gallium nitride surfaces there were evaporated ohmic contacts consisting of Au/Ti for ZnO and Au/Ni for GaN. Current–voltage properties of the heterojunction are fairly favourably, with the rectification factor of $I_{\mathrm{on}}/I_{\mathrm{off}} = 1.8 \times 10^3$ for a voltage of 2 V. Our first investigations indicate a great potential for application of the heterojunction as UV detectors, in particular in "Solar Blind" detectors.

Acknowledgments

The research was supported by the European Union within European Regional Development Fund through grant Innovative Economy (POIG.01.01.02-00-008/08).

References

[1] C. Skierbiszewski, M. Siekacz, H. Turski, G. Muziol, M. Sawicka, P. Wolny, G. Cywiński, L. Marona, P. Perlin, P. Wiśniewski, M. Albrecht, Z.R. Wasilewski, S. Porowski, *Appl. Phys. Expr.* **5**, 2103 (2012).

[2] M. Godlewski, E. Guziewicz, K. Kopalko, G. Łuka, M.I. Łukasiewicz, T. Krajewski, B.S. Witkowski, S. Gierałtowska, *Low Temp. Phys.* **37**, 235 (2011).

[3] S. Gierałtowska, L. Wachnicki, B.S. Witkowski, M. Godlewski, E. Guziewicz, *Thin Solid Films* **520**, 4694 (2012).

[4] S. Grzanka, G. Łuka, T.A. Krajewski, E. Guziewicz, R. Jachymek, W. Purgal, P. Perlin, *Acta Phys. Pol. A* **119**, 672 (2011).

[5] Y.I. Alivov, E.V. Kalinina, A.E. Cherenkov, D.C. Look, B.M. Ataev, A.K. Omaev, D.M. Bagnall, *Appl. Phys. Lett.* **83**, 4719 (2003).

[6] C. Klingshirn, *Phys. Status Solidi B* **244**, 3027 (2007).

[7] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Superlatt. Microstruct.* **34**, 3 (2003).

[8] D.C. Look, B. Claflin, Y.I. Alivov, S.J. Park, *Phys. Status Solidi A* **201**, 2203 (2004).

[9] Y. Chen, D.M. Bagnal, H.-J. Koh, K.-T. Park, K. Hiraga, Z. Zhu, T. Yao, *J. Appl. Phys.* **84**, 3912 (1998).

[10] Ya.I. Alivov, J.E. van Nostrand, D.C. Look, M.V. Chukichev, B.M. Ataev, *Appl. Phys. Lett.* **83**, 4719 (2003).

[11] L. Wachnicki, T. Krajewski, G. Luka, B. Witkowski, B. Kowalski, K. Kopalko, J.Z. Domagala, M. Guziewicz, M. Godlewski, E. Guziewicz, *Thin Solid Films* **518**, 4556 (2010).

[12] D.J. Rogers, F.H. Teherani, A. Yasan, K. Minder, P. Kung, M. Razeghi, *Appl. Phys. Lett.* **88**, 141918 (2006).

[13] L. Wachnicki, A. Duzynska, J.Z. Domagała, B. S. Witkowski, T.A. Krajewski, E. Przeździecka, M. Guziewicz, A. Wierzbicka, K. Kopalko, S. FIügge, D. Hommel, M. Godlewski, E. Guziewicz, *Acta Phys. Pol. A* **120**, (2011).

[14] T. Suntola, in: *Handbook of Crystal Growth*, Part 3b *Growth Mechanisms and Dynamics*, Ed. D.T.J. Hurle, Elsevier, Amsterdam 1994, p. 605.

[15] R. Hickman, J.M. Van Hove, P.P. Chow, J.J. Klaassen, A.M. Wowchak, C.J. Polley, D.J. King, F. Ren, C.R. Abernathy, S.J. Pearton, K.B. Jung, H. Cho, J.R. La Roche, *Solid-State Electron.* **44**, 377 (2000).

[16] A. de Luna Bugallo, M. Tchernycheva, G. Jacopin, L. Rigutti, F.H. Julien, S.T. Chou, Y.T. Lin, P.H. Tseng, L.W. Tu, *Nanotechnology* **21**, 315201 (2010).

[17] J.Y. Lee, J.H. Lee, H. Seung Kim, C.H. Lee, H.S. Ahn, H.K. Cho, Y.Y. Kim, B.H. Kong, H.S. Lee, *Thin Solid Films* **517**, 5157 (2009).

[18] S. Jha, J.C. Qian, O. Kutsay, J. Kovac Jr, C.Y. Luan, J.A. Zapien, W. Zhang, S.T. Lee, I. Bello, *Nanotechnology* **22**, 245202 (2011).