Warsaw, March 11, 2019

AREA OF PHYSICAL SCIENCES – **Attachment 2b**

dr Tomasz Aleksander Krajewski
Division of Physics and Technology
of Wide-Band-Gap Semiconductor Nanostructures (ON 4.2)
Institute of Physics Polish Academy of Sciences
Al. Lotników 32/46, PL-02668 Warsaw, Poland
phone: (48 22) 116-3315, fax: (48 22) 847-5223
e-mail address: krajew@ifpan.edu.pl
ResearcherID: S-2893-2016

SUMMARY OF SCIENTIFIC ACCOMPLISHMENTS

Title of the scientific achievement:

"Junction structures involving thin zinc oxide films obtained
by the Atomic Layer Deposition (ALD) technique"

(„Struktury złączowe wykorzystujące cienkie warstwy tlenku cynku
otrzymane techniką Osadzania Warstw Atomowych (ALD)")

SUMMARY OF SCIENTIFIC ACCOMPLISHMENTS

Table of contents

I. Curriculum Vitae (scientific version)

1. Personal data

dr Tomasz Aleksander Krajewski

Division of Physics and Technology
of Wide-Band-Gap Semiconductor Nanostructures (ON 4.2)
Institute of Physics Polish Academy of Sciences
Al. Lotników 32/46, PL-02668 Warsaw, Poland
phone: (48 22) 116-3315, fax: (48 22) 847-5223
e-mail address: krajew@ifpan.edu.pl

2. Education and scientific degrees

Ph.D. degree – **November 2012** for the dissertation prepared and defended in the Division of Physics and Technology of Wide-Band-Gap Semiconductor Nanostructures (ON 4.2) of the Institute of Physics Polish Academy of Sciences in Warsaw
Dissertation entitled: "Electrical properties of zinc oxide thin films obtained in the Atomic Layer Deposition (ALD) process"
Scientific supervisor: prof. nzw. dr hab. Elżbieta Guziewicz
Date of dissertation defense: October 10, 2012
Date of degree conferment: November 8, 2012

M.Sc. degree – **June 2007** for the dissertation prepared and defended at the Department of Mathematics and Natural Sciences (Faculty of Physics), College of Science Cardinal Stefan Wyszyński University in Warsaw
Dissertation entitled: "Electrical investigations of zinc oxide films obtained in the low-temperature ALD process"
Scientific supervisor: dr Elżbieta Guziewicz
Date of dissertation defense: June 27, 2007
Diploma number: WMP-494/2007

B.Sc. degree – **June 2005** for the dissertation prepared at the Institute of Geophysics and defended at the Faculty of Physics of the University of Warsaw
Dissertation entitled: "Preparation of didactic materials to the lecture on «*Fluid mechanics*»"
Scientific supervisor: dr Konrad Bajer
Date of dissertation defense: June 27, 2005
Diploma number: 1100/3944/2005

3. Employment history

December 1, 2015 – present: scientific position of **Assistant Professor** in the Division of Physics and Technology of Wide-Band-Gap Semiconductor Nanostructures (ON 4.2) at the Institute of Physics Polish Academy of Sciences in Warsaw in frames of a full-time, open-ended contract;

October 1, 2011 – November 30, 2015: position of **physicist** in the Division of Physics and Technology of Wide-Band-Gap Semiconductor Nanostructures (ON 4.2) at the Institute of Physics Polish Academy of Sciences in Warsaw in frames of a full-time, open-ended contract;

October 1, 2007 – October 10, 2012: Ph.D. studies at the Institute of Physics Polish Academy of Sciences in Warsaw (Division of Physics and Technology of Wide-Band-Gap Semiconductor Nanostructures – ON 4.2);

October 1, 2007 – September 30, 2011: position of **physicist** in the Division of Physics and Technology of Wide-Band-Gap Semiconductor Nanostructures (ON 4.2) at the Institute of Physics Polish Academy of Sciences in Warsaw in frames of the probation period followed by fixed-term contracts with the last expiry date of September 30, 2011

4. Bibliometric data according to the *Journal Citation Reports* (*JCR*) and *Web of Science* (*WoS*) database as given for January 7, 2019

Sum of the *impact factors* according to the *Journal Citation Reports* (*JCR*), corresponding to the year of publication: **IF** = **71.991**, whereas the sum of *5-year impact factors*: **IF**(**5**) = **70.152** (including **51** publications in total – see also ResearcherID: S-2893-2016);

Sum of the *impact factors* of journals in which the papers included in the habilitation series have been published according to the *Journal Citation Reports* (*JCR*), corresponding to the year of publication: **IF** = **16.911**, whereas the sum of their *5-year impact factors* **IF**(**5**) = **15.954**;

Total citations according to the *Web of Science* (*WoS*) database: **837**, including **702** (**83.87%**) without self-citations. These records take **51** publications into consideration;

Hirsch index according to the *Web of Science* (*WoS*) database: **17**

II. Achievement resulting from the art. 16 item 2 of the Act dated March 14, 2003 on academic degrees and academic title, and on degrees and title in the field of art (Journal of Laws of 2017, item 1789), constituting the basis for the application

1. Title of the scientific achievement (the series of 7 scientific publications)

“Junction structures involving thin zinc oxide films obtained by the Atomic Layer Deposition (ALD) technique”

(„Struktury złączowe wykorzystujące cienkie warstwy tlenku cynku otrzymane techniką Osadzania Warstw Atomowych (ALD)”)

2. List of publications included in the series constituting the scientific achievement (order in accordance with the summary layout)

1. [**H1**] *Tomasz A. Krajewski*, Penka Terziyska, Grzegorz Łuka, Elżbieta Łusakowska, Rafał Jakieła, Emil S. Vlakhov, Elżbieta Guziewicz
   "Diversity of contributions leading to the nominally n-type behavior of ZnO films obtained by low temperature Atomic Layer Deposition"
   Journal of Alloys and Compounds **727**, pp. 902 – 911 (2017). IF(2017): 3.779
2. [**H2**] *Tomasz A. Krajewski*, Peter Stallinga, Eunika Zielony, Krzysztof Gościński, Piotr Kruszewski, Łukasz Wachnicki, Timo Aschenbrenner, Detlef Hommel, Elżbieta Guziewicz, Marek Godlewski
   "Trap levels in the atomic layer deposition-ZnO/GaN heterojunction – Thermal admittance spectroscopy studies"
   Journal of Applied Physics **113**, 194504 (2013). IF(2013): 2.185
3. [**H3**] Dymitr Snigurenko, Krzysztof Kopalko, *Tomasz A. Krajewski*, Rafał Jakieła, Elżbieta Guziewicz
   "Nitrogen doped p-type ZnO films and p-n homojunction"
   Semiconductor Science and Technology **30**, 015001 (2015). IF(2015): 2.098
4. [**H4**] Dymitr Snigurenko, Elżbieta Guziewicz, *Tomasz A. Krajewski*, Rafał Jakieła, Yevgen Syryanyy, Krzysztof Kopalko, Wojciech Paszkowicz
   "N and Al codoping as a way to p-type ZnO without post-growth annealing"
   Materials Research Express **3**, 125907 (2016). IF(2016): 1.068
5. [**H5**] Adam J. Zakrzewski, *Tomasz A. Krajewski*, Grzegorz Łuka, Krzysztof Gościński, Elżbieta Guziewicz, Marek Godlewski
   "Role of the hafnium dioxide spacer in the ZnO-based planar Schottky diodes obtained by the low-temperature Atomic Layer Deposition method: Investigations of current-voltage characteristics"
   IEEE Trans. on Electron Devices **62** (2), pp. 630 – 633 (2015). IF(2015): 2.207
6. [**H6**] *Tomasz A. Krajewski*, Petro S. Smertenko, Grzegorz Łuka, Dymitr Snigurenko, Krzysztof Kopalko, Elżbieta Łusakowska, Rafał Jakieła, Elżbieta Guziewicz
   "Tuning the properties of ALD-ZnO-based rectifying structures by thin dielectric film insertion – Modeling and experimental studies"
   Journal of Alloys and Compounds **693**, pp. 1164 – 1173 (2017). IF(2017): 3.779
7. [**H7**] Dencho Spassov, Albena Paskaleva, *Tomasz A. Krajewski*, Elżbieta Guziewicz, Grzegorz Łuka, Tzvetan Ivanov
   "Al_2O_3/HfO_2 multilayer high-k dielectric stacks for charge trapping flash memories"
   Physica Status Solidi A 1700854 (2018). IF(2017)[1]: 1.795

The detailed list of journal publications and other scientific achievements has been included in the **Attachment 3**, which also briefly presents the role of Applicant in the papers' preparation process together with an estimation of percentage contribution. The appropriate statements of the Co-Authors of papers constituting the series are included in the **Attachment 4**, entitled *"Statements of the Co-Authors of publications constituting the scientific achievement (habilitation cycle)" („Oświadczenia Współautorów prac stanowiących osiągnięcie naukowe (cykl habilitacyjny)")*.

---

[1] For the paper [**H7**] the latest *impact factor* (from 2017) available in the *WoS* database has been taken into account.

III. Scientific aim of the publications constituting the habilitation achievement. Discussion of the possible use of their results

1. Introduction. Motivation and scientific background of the research

As stated by the Authors publishing in the magazine and at the website of *"Semiconductor Today"* *[http-semtod16]*[2], the market of optoelectronic devices based only on wide band-gap semiconductors according to the predicted expansion rate of about 33% per year will reach the total value of USD 3.7 billion till 2025[3]. This results both: from the ongoing decrease in prices of such devices as light-emitting diodes or advanced integrated circuits with a large degree of miniaturization as well as from their increasing commercial availability. The quick development of functional electronic elements imposes, in turn, severe requirements on understanding the physical phenomena occurring in different materials, aimed at their possible industrial applications. One of such perspective semiconductors is definitely zinc oxide (ZnO), which despite the large amount of literature data (due to their frequent discrepancy, stemming mainly from the sensitivity of ZnO parameters to the obtaining method and changes of process conditions itself), still appears to be attractive for numerous scientific investigations.

This particularly concerns its transport properties, closely related to the physics of defects. Here, basing on the analysis of existing reports referring to this problem, it can be noticed that a vast majority of experimental studies has been so far performed on single ZnO crystals, likely due to their high quality and attainability (*vide*: ZnO obtained by a hydrothermal method). On the other hand, a parallel interest in the structures based on thin films of this oxide (as will be shown hereafter) makes the profound investigations of the charge transport mechanisms in the ZnO layers fully justified as well.

The above stems also from the fact that the intentionally undoped zinc oxide films reveal the free electron concentration of about $10^{16} - 10^{21}$ cm^{-3} (dependently on the growth method), which is, actually, from 10 to 15 orders of magnitude higher than its intrinsic level in this compound[4]. This motivates the contemporary approaches towards involving the ZnO layers in solar cells, serving therein for the transparent electrode (provided the $n \approx 10^{20}$ cm^{-3} and high electron mobility, μ demands are both satisfied) *[Calderon PSSb05, Ellmer TSF08]* as well as in the new generation of non-volatile 3D memories built in the so-called *cross-bar* architecture. In the latter devices the antifuse (selecting) element may take an advantage of the ZnO-based Schottky junction on condition that its rectification ratio reaches the value of at least 10^6, what is possible for $n_{ZnO} \approx 10^{16}$ cm^{-3} and $\mu > 10$ cm^{2}V^{-1}s^{-1}, ensuring the necessarily low reverse and sufficiently high driving current of the diode, respectively *[Pra JCE08]*.

The reason for such a high variability of electron concentration in ZnO is, obviously, a presence of native defects and impurities, nevertheless, the influence of their given types on the electrical properties remains still quite far from being clear. As for today, there exist the papers ascribing the wide range of n values vicissitude to the hydrogen atoms located in the

---

[2] The list of references in alphabetical order has been placed in the final section of this summary. For its clarity, the reference marks throughout the text are given in square brackets consisting of the surname of publication main Author, abbreviation of the journal or book title and publication year. The references concerning web pages are preceded by *http*.

[3] According to the forecast of an *IEEE* analyst, Richard Eden, from 2016, concerning the market of optoelectronic devices based on silicon carbide (SiC) and gallium nitride (GaN). The webpage accessed on October 3, 2018.

[4] Here, it should be stressed that these data refer to the ZnO thin films. The carrier concentration in single ZnO crystals obtained, for instance, by a hydrothermal method may be additionally lowered to $n \approx 10^{14}$ cm^{-3}, owing to the presence of K and Li ions in the growth process. This is, however, still 8 orders of magnitude higher than its intrinsic level ($n_i \approx 10^6$ cm^{-3}) resulting from the bandgap width of ZnO at room temperature ($E_g \approx 3.3$eV).

interstitial positions of ZnO lattice [*Pearton S§M03, Hoffmann PRL02, VandeWalle PRL00*]. According to the other reports, neither the role of interstitial zinc (Zn_i) [*Thomas JPCS57, Gomi JJAP03*] nor of oxygen vacancies (V_O) in this issue can be omitted. Moreover, concerning the latter defect, it is claimed (see, e.g. [*Janotti RPP09*] or [*Look PRL05*]) that in spite of its relatively low formation energy, the oxygen vacancies, regarded as deep donors in ZnO may simultaneously act as efficient compensating centers, hampering the effective *p*-type doping of the oxide.

The other defect considered in the literature to be a donor in ZnO is zinc anti-site (Zn_O). However, in its case it is frequently underlined that due to the instability it frequently splits into Zn_i and V_O constituents [*Janotti RPP09, Look JEM06, Oba JAP01*]. Concerning the influence on ZnO transport properties of such defects as interstitial oxygen (O_i) or oxygen anti-site (O_{Zn}), the so far investigations indicate that the donor levels of O_i ((0/+) and (+/++)) are located below the valence band maximum, while O_{Zn} plays a role of acceptor in ZnO [*Janotti RPP09*].

Additionally, ease of some defects creation (like Zn_i or V_O) in ZnO stems also from its propensity to crystallize in the relatively “open” wurtzite structure [*Schmidt-Mende MT07*]. As demonstrated in the widely-cited paper by K. H. Tam from 2006 [*Tam JPCB06*][5], native defects in ZnO can obviously reveal different charge states dependently on the obtaining and post-obtaining treatment conditions, making their identification process more complicated.

Hence, already the rough review of literature data allows making an assertion that the issues pertaining to the electrical transport properties of ZnO thin films and the structures involving ZnO in combination with other wide band-gap materials (like e.g. GaN, HfO_2 or Al_2O_3) are complex and dependent on many factors. Taking, however, into account their cognitive aspects and practical (application-related) potential it ought to be stressed they are definitely worth studying in a possibly profound way.

* * *

The fact that a lot of the charge transport-related phenomena in semiconducting structures can be explained by discussing the behavior of rectifying junction, pointed a remarkable part of the hereafter described experimental work at the construction of good quality and stable Schottky as well as *p-n* diodes, revealing the electrical parameters that allow the realization of planned scientific goals. Although obtaining such junctions was not a fundamental problem during the investigations described in publication [**H1**] ([*Krajewski JAC17-1*]), focused mainly on optical (photoluminescent) and electrical measurements of ZnO layers, it remained one of the key tasks in case of the subsequent papers constituting the habilitation cycle [**H2**]–[**H6**]. This is due to the use in the respective research the techniques based on the study of capacitance relaxation kinetics – see [**H2**], [*Krajewski JAP13*] and the differential approach towards the theoretical analysis of current-voltage characteristics of the diodes[6] [**H6**] ([*Krajewski JAC17-2*]). From this point of view it is worth stressing that the numerous literature reports regard the problem of junction formation as a non-trivial one if referring to ZnO.

Monitoring of the released publications discussing the physics of Schottky junctions involving zinc oxide proves that in spite of the relatively simple concept of their architecture, there exists a lot of factors that ought to be considered while optimizing the diode performance with regard to the improved rectifying properties. One of the most important

---

[5] According to the *Web of Science* database (access from October 3, 2018), this paper has been cited 523 times so far.

[6] The most important aspects of selected (mentioned) measurement techniques will be briefly described in the further part of this summary, while discussing the issues related to the given paper of group of papers from the cycle.

things is the known discrepancy between the metal workfunction and Schottky barrier height φ_B stemming from the presence of additional states at the ZnO/metal interface. These tend to pin the Fermi level of ZnO resulting in $\varphi_B \approx 0.6 - 0.7\mathrm{eV}$, irrespectively to the metallization used, which enforces testing as Schottky contacts to ZnO such metals as silver[7] [*Kim SST12, Kim TEEM15*], gold [*Gu APL07*], palladium [*Kashiwaba ApSS13, Mtangi PhB09, Schifano APL07*] or platinum [*Nakamura JAP11, Yu NT10*] to overcome this problem. The other known approaches are: chemical treatment of semiconductor surface, for instance with the use of H_2O_2 [*Gu APL07, Kashiwaba ApSS13, Schifano APL07, Nakamura JAP11*] or the metallic contact oxidation [*Chasin APL12*]. These solutions usually result in the Schottky barriers as high as $0.6 - 1.2\mathrm{eV}$ accompanied by the maximal rectification ratio reaching $10^8 - 10^9$ for $\pm 2\mathrm{V}$ of applied bias [*Kashiwaba ApSS13, Schifano APL07, Nakamura JAP11*].

Apart from the Schottky structures in many cases of electrooptical research the *p*-*n* heterojunctions are used with the appropriately chosen *p*-type partner to *n*-ZnO, like *p*-CuI [*Schein APL13*], *p*-GaN [*Schuster ACSN14*] or *p*-SiC [*Guziewicz APL15*][8]. Importantly, the selected *p*-type material should have crystallographic structure as well as lattice parameters ensuring the proper band alignment on both sides of the junction. Such an approach has been examined in the paper [**H2**], discussing the *n*-ZnO/*p*-GaN diode.

Nevertheless, the kept high price of such semiconductors as gallium nitride or silicon carbide together with the above-mentioned material requirements drives the parallel search for alternative solutions involving the use of homojunction for the electrical transport measurements. However, in case of ZnO its construction still remains a kind of scientific challenge. This is because of the specificity of this material, highly preferring the *n*-type conductivity owing to the typical position of the Fermi level (E_F) usually located in the upper part of the bandgap, closely to the conduction band edge, which hampers the effective acceptor doping or conversion to the *p*-type conductivity. The most frequently considered acceptor dopants to ZnO are the elements from the group V of periodic table, like **arsenic** [*Przeździecka SactA13*] or **antimony** [*Przeździecka PRB07*], basing on the theoretical model presented in the paper by Limpijumnong *et al.* [*Limpijumnong PRL04*], according to which the appearing *p*-type conductivity in ZnO comes from the X_{Zn}–$2V_{Zn}$ complex (i.e. substitution of Zn with a dopant atom – As or Sb together with a double zinc vacancy).

The other acceptor dopant often introduced to ZnO is **nitrogen**[9]. As suggested by some Authors, for the proper activation in the doped thin films, leading to the stable homojunction behavior, it requires a carefully optimized introduction process combined with post-growth annealing [*Lee ML07, Dunlop APL08*]. Further remarks pertaining to the specificity of nitrogen introduction to ZnO will be given later, while discussing the electrical transport phenomena in ZnO homodiodes. Here, it should be mentioned that the indications included in the above-cited papers have been used while obtaining the ZnO:N/ZnO rectifying structures described in the papers [**H3**] ([*Snigurenko SST15*]) and, partially, [**H4**] ([*Snigurenko MRX16*]) from the habilitation cycle.

Next to this, a very interesting method allowing the stabilization of electrical behavior of *p*-type ZnO relies on its simultaneous doping with donor and acceptor. The advantage of so-called co-doping procedure is further simplification of the technological process through the elimination of post-growth treatment, indispensable for acceptor activation in the lack of

---

[7] Silver has also been used as a metallization in the Schottky diodes examined in frames of preparing this summary.

[8] The Applicant has also been involved in the latter experiment. However, the respective paper has not been included in the series constituting the scientific achievement.

[9] Which was also used for doping one of the ZnO layers forming the homojunctions examined in frames of the habilitation cycle.

donor co-dopant. Moreover, relevantly for the possible application of the co-doped layers, they also reveal the increased carrier mobility. As demonstrated in some theoretical papers [*Yamamoto PhB01, Yamamoto TSF02*], the appropriate candidate for ZnO codopant in pair with nitrogen to obtain *p*-ZnO is e.g. aluminum, which parallel introduction on one hand results in the increased solubility of nitrogen and on the other – causes a beneficial decrease in the Madelung energy in the deposited layer. These findings appeared to be extremely crucial regarding the experimental work presented in the article [**H4**].

* * *

The observed permanent progress in manufacturing technologically advanced semiconductor-based structures includes the improvement in their parameters via application of the various buffer layers as well. The most frequently used buffers belong to the group of wide band-gap dielectric materials – silicon dioxide (SiO_2), hafnium dioxide (HfO_2) – but likewise magnesium oxide (MgO) or ZnO playing the role of an active layer (*i*-ZnO) in the light-emitting (LED) diodes.

Hence, the paper by Sun *et al.* [*Sun ACSAMI15*] shows that due to the simultaneous use of SiO_2 as a tunneling (3.6nm) and blocking (13.5nm under the TaN contact) layer in the *n*-ZnO/*p*-NiO/SiO_2/TaN structure obtained on *n*-Si enables the substantial amendment in the electrical characteristics of such a memory device, though increasing its charge carriers' trapping ability[10].

Two more interesting examples, demonstrating the legitimacy of buffer layers application to the semiconductor devices refer to the articles by Malinkiewicz *et al.* [*Malinkiewicz RSCA12*] as well as Liu *et al.* [*Liu APL12*]. In the first of these two papers its Authors prove the effectiveness of use of buffer ZnO and MoO_3 layers in the solar cell based on organic materials, demonstrating the open-circuit voltage V_{OC} = 1V, what is, according to their statement, unique for the examined type of cells. Besides, the cell discussed therein reveals the substantially longer lifetime, comparing to the structures with the architecture modified in another way. The second work pertains to LED diode (*n*-ZnO:Al/*i*-ZnO/*p*-GaN, deposited by the *Pulsed Laser Deposition (PLD)* method. In the investigated heterostructure the buffer material (MgO with an optimized thickness of about 12nm) was placed between the active (*i*-ZnO) layer and silver nanoparticles capped with *n*-ZnO:Al, allowing the 7 – 8-fold increase in the luminescence intensity owing to the elimination of non-radiative recombination paths between Ag and *i*-ZnO.

The above reports showing a possibility of improving the electrical parameters of structures through the application to them the carefully selected dielectric buffer layers were a motivation for aiming a relevant part of the studies at verifying their role in the ZnO/Ag and ZnO:N/ZnO diodes discussed in the papers [**H5**] ([*Zakrzewski TED15*]) and [**H6**] ([*Krajewski JAC17-2*]). These issues are all the more important that finding in the literature a clear and concise theoretical description of transport phenomena occurring in these junctions due to their such modification appears hitherto to be quite difficult, despite a lot of available experimental data. In the related investigations, the two high-*k* oxides: HfO_2 and Al_2O_3 were used as a passivator of the ZnO surface in ZnO/Ag diodes and the buffer (separating) layer in ZnO:N/ZnO homojunctions, respectively.

A very important feature of this class of materials is the presence of numerous carriers' trapping states located in the bandgap. These states, highly deteriorating the performance of

---

[10] The mentioned kind of memory device – so-called *"charge trapping memory"* (CTM) – will be also considered in the paper [**H7**] referring to the structure consisting of the *n*-fold repeated HfO_2/Al_2O_3 bilayer grown by the ALD technique (see also § III.3.4).

such devices as e.g. the MOSFET[11] transistors are, however, beneficial for the above-mentioned *charge trapping memory* (CTM) elements. The recent reports devoted to this topic suggest that if based on HfO_2, such memories can reveal far better parameters than contemporarily constructed similar ones involving silicon nitride ($Si_3N_4/SiO_2/Si$) [*You APL10*]. Moreover, it is known that the electrical properties of these devices can be effectively modified, for instance through the doping or annealing processes, as well as growing multilayered structures with different high-*k* materials [*Lan JAP13, Spiga APEX12, Zhu APL10*]. These approaches still remain a large area for scientific investigations.

The mentioned facts motivated Applicant for the involvement in the respective studies focused on the properties of CTM elements, realized in cooperation with the dedicated research group from the Institute of Solid State Physics of Bulgarian Academy of Sciences (ISSP-BAS) in Sofia, during the series of research stays between 2015 and 2017. Conclusions from the to date works have been described in the paper [**H7**] ([*Spassov TSF18*]), devoted to the analysis of the CTM (Al_2O_3/HfO_2) structure behavior . According to the view of Applicant, their significance enables a deeper insight into the transport phenomena taking place in the above-mentioned rectifying structures containing passivating and buffer dielectric layers.

From the presented introduction to this summary it can be unambiguously seen that a diversity of factors possibly affecting the electrical transport phenomena in the junction structures (e.g. a degree of construction complexity or thermal treatment) allows regarding the related issues to be a distinct scientific problem. Not only pertains this remark to the structures based solely on ZnO (which parameters exhibit a remarkable sensitivity to the material obtaining method and the process conditions itself), but also to the related structures, with other wide bandgap materials (such as HfO_2 or Al_2O_3), involved therein to receive the substantial improvement of their electrical parameters. The complexity and timeliness of these problems, which are significant e.g. taking into account the modern electronics, as well as the importance of the gained new results have made these problems a good base for the presented habilitation achievement.

To conclude, the basic goals of scientific research presented in this summary can be therefore formulated as follows:

- ✧ Identification of the main types of native defects in intentionally undoped zinc oxide thin films grown in the temperature range of 100°C – 200°C and their influence on electro-optical properties of ZnO through the photoluminescence and electrical measurements carried out at room temperature (article [**H1**]). Use of the drawn conclusions as indispensable for the construction of *n*-ZnO/*p*-GaN heterojunction revealing the electrical parameters suitable for its defect structure examination with the techniques involving the study of capacitance relaxation kinetics at the temperatures between 77 K and 330K (see paper [**H2**]);
- ✧ Identification of the factors influencing the rectification effect in the two types of ZnO:N/ZnO homojunctions – with the ZnO layer doped with nitrogen subsequently undergoing the thermal treatment as well as involving the ZnO film co-doped with nitrogen and aluminum allowing the further annealing step elimination (papers [**H3**] and [**H4**]);
- ✧ Description of the influence of passivating HfO_2 layer on the charge transport mechanisms in the ZnO/HfO_2/Ag Schottky structures constructed according to the planar and vertical architectures. Defining the reason for the observed changes in

---

[11] Abbrev.: Metal Oxide Semiconductor Field Effect Transistor.

the transport properties of ZnO-based junctions equipped with the dielectric (HfO_2 or Al_2O_3) interlayers by applying the theoretical *differential approach* to the experimentally measured current-voltage (*I*-*V*) characteristics of the modified junctions. Demonstration that such an approach describes their electrical behavior adequately, allowing the identification of electrical transport mechanisms (see paper [**H5**] as well as [**H6**]);

✧ Demonstration (with reference to the articles [**H5**] and [**H6**] an alternative possibility of use of the dielectric material-based structures as the charge trapping memory elements (as shown in the publication [**H7**]). Aim – to shed more light on the role of dielectric interlayers applied to the Schottky diodes and homojunctions involving the thin ZnO films.

2. Thin films and structures growth method. *Atomic Layer Deposition (ALD)*

Considering the fact that all the films and semiconducting structures investigated in frames of this summary were obtained by the Atomic Layer Deposition (ALD) method, its short characteristics as a technique nowadays widely used for many scientific purposes as well as involved in the modern electronics will be fully justified.

The origin of this deposition method reaches the 20th century (turn of the seventies and eighties) when it was described and patented by Dr. Tuomo Suntola [*Suntola USP-1, Suntola USP-2*]. Its key feature is a self-limiting growth process and sequentiality of a layer deposition. The required material can be obtained on the selected substrate basing on the additive , single– or double[12] exchange chemical reaction between the reagents. In such a case, every of the reagents, introduced alternately to the growth chamber, supplies one kind of atoms forming the final compound, uniformly deposited on the substrate.

The thickness of deposited layer is, in turn, determined by a number of ALD growth cycles, while a single ALD cycle can be schematically presented as below (see also Fig. 1.):

$$precursor\ I \rightarrow chamber\ purging \rightarrow precursor\ II \rightarrow chamber\ purging \rightarrow precursor\ I \rightarrow \ldots .$$

In the presented scheme, a particular attention should be paid on the purging of a reaction chamber with a neutral gas following every introduced precursor dose, due to which a contact between the partners of chemical reaction is limited to the substrate surface only[13]. This is the main feature distinguishing ALD e.g. from the *Chemical Vapor Deposition (CVD)* process. Besides, due to the elimination of the possibility of reaction taking place in the chamber's volume it enables the use of very reactive, organic precursors allowing the additional decrease in the growth temperature. As will be demonstrated further on, this ALD capability was of fundamental importance regarding the carried out experimental work.

Ensuring the proper ALD growth temperature is a key factor for several reasons, among which one of the most relevant are the chemical stability of the used precursors as well as the full saturation of chemical reactions. Furthermore, this is also a precondition for supplying the adequate energy to start a given reaction and assure the effective desorption of its byproducts from the substrate surface right before introducing the next precursor dose to the chamber. This explains the crucial role of *ALD growth window*, that is influenced not only by the deposition temperature, but also by the purging times and precursor doses. Some further details concerning the ALD growth window the Reader can find in [*Suntola HCG94*].

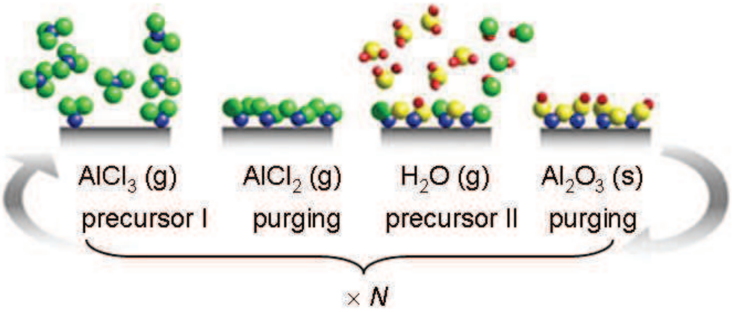

Fig. 1. The scheme of a double exchange reaction between aluminum chloride and water leading to the growth of aluminum(III) oxide by ALD. The figure depicting a single ALD cycle reprinted basing on [*Pakkala HDT10 p. 365*].

---

[12] For obtaining all the films and structures examined within this summary, the double exchange chemical reaction has been used.

[13] In the ON4.2 IP PAS team laboratory this is ensured by the use of gaseous nitrogen.

The not very high (when compared to the other techniques) growth rate of ALD method is, however, compensated if combined with the possibility of a large-scale deposition (even on the sizeable surfaces of about 1.4m^2). Such a possibility makes the ALD technique industrially applicable, e.g. for the fabrication of flat panel displays or various protective coatings (see also [*Pakkala HDT10*]).

For the investigations the thin films and structures obtained with the following precursors have been used: diethylzinc (DEZn, $Zn(C_2H_5)_2$), trimethylaluminum (TMA, $Al(CH_3)_3$), tetrakis(dimethylamido)hafnium(IV) (TDMAH, $Hf[(CH_3)_2N]_4$), deionized water (H_2O), ammonia water (NH_4OH)[14], serving simultaneously for the source of oxygen and nitrogen source in case of ZnO:N as well as ZnO:(N, Al) films. The ALD growth was performed in the *Savannah100 Cambridge NanoTech* and *BENEQ TFS-200* reactors, according to the following double exchange reactions (to preserve the summary clarity, temperature ranges of the respective ALD processes will be given while discussing the particular research issue):

ZnO films:

$$Zn(C_2H_5)_2 + H_2O \rightarrow ZnO + 2C_2H_6, \tag{1}$$

HfO_2 layers:

$$Hf[(CH_3)_2N]_4 + 2H_2O \rightarrow HfO_2 + 4HN(CH_3)_2, \tag{2}$$

Al_2O_3 layers:

$$2Al(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4. \tag{3}$$

The following part of the summary will be devoted to the discussion of the key results from the papers [**H1**]–[**H7**], constituting the habilitation cycle. The discussed problems will be focused on the influence of native defects on the transport phenomena in the thin films and structures containing the undoped ALD-ZnO material, possibility of the ZnO-based homodiode construction involving the ZnO layers doped with nitrogen and co-doped with nitrogen and aluminum as well as the description of transport processes in the rectifying junctions containing ZnO and dielectric interlayers (HfO_2, Al_2O_3). In the end, the characteristics of multi-layered HfO_2/Al_2O_3 CTM elements will be presented together with a description of optimization possibilities of their electrical performance.

3. Junction structures involving thin zinc oxide films obtained by the Atomic Layer Deposition (ALD) technique – series of publications [H1]–[H7] constituting the scientific achievement

3.1. Identification and control of native defects in undoped ALD-ZnO films. The defect structure of *n*-ZnO/*p*-GaN heterojunction in the temperature range 77 – 330K ([H1], [H2])

In order to understand the influence of native defects on the transport of charge carriers at room temperature, a series of intentionally undoped ZnO layers deposited between 100°C and 200°C was discussed in frames of paper [**H1**]. Here, it ought to be stressed that growth temperature was the only parameter undergoing the changes within the given series, while the rest (i.e. precursors' doses and chamber purging times) remained constant – 20ms/8s for DEZn and 20ms/20s for H_2O. The growth of zinc oxide on silicon, quartz (SiO_2) and glass

---

[14] Being a 25 – 30% aqueous solution of ammonia, $(NH_3)_{aq}$.

substrates, always consisting of 1000 ALD cycles, proceeded according to reaction (1), resulting in the polycrystalline ZnO films of about 135 – 180nm thick.

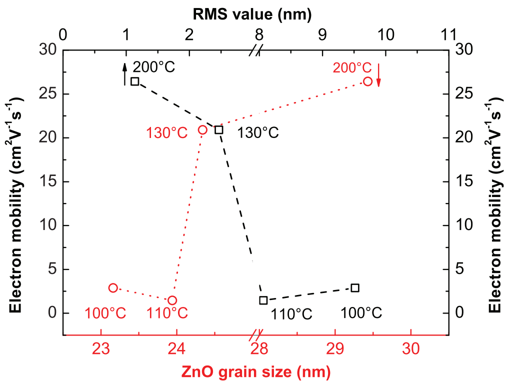

Fig. 2. Dependence between the electron mobility in the intentionally undoped ZnO layers and the grain size calculated from the X-Ray Diffraction (XRD) measurements – lower scale – as well as the RMS parameter derived from the AFM studies – upper scale. Figure reprinted from paper [**H1**].

As it was observed at the initial stage of experimental work, the surface roughness of these layers derived from the Atomic Force Microscopy (AFM) measurements and described by the Root Mean Square (RMS) parameter decreased from about 9 nm to 1 nm with increasing growth temperature (from 100 to 200°C). Noteworthy, the layers obtained at higher temperatures revealed an evident tendency to grow with the *c* axis oriented perpendicularly to the substrate surface (thus, according to the (00.2) crystallographic orientation), what is consistent with the earlier findings, reported i.a. by Kowalik *et al.* [*Kowalik JCG09*]. Relations between the grain size, surface roughness and electron mobility (μ)[15], presented in Fig. 2. incline to the statement that the crystallite size in case of the discussed ZnO films is not the dominating factor limiting the μ parameter. As can be noticed, the increase of 1nm in the grain size, between the layers obtained in 110°C and 130°C, respectively, results in the increase in electron mobility that reaches one order of magnitude (~2 → 20 cm^{2}V^{-1}s^{-1}). Such a behavior suggests a relation between the layers, electrical properties and their chemical composition (including the Zn-to-O ratio) [*Guziewicz SST12*]. Besides, the carrier scattering mechanisms, influencing the transport processes, are also strictly related to their concentration in the material. Namely, if the carrier concentration in semiconductor exceeds the given critical value n_C (the so-called *Mott criterion*), above which the *insulator-metal* transition occurs, it should be assumed that the grain boundary-related potential barriers are sufficiently low (usually few Å) to activate the carrier tunneling processes. According to the literature data concerning ZnO, the value of n_C for this compound is approximately 9.4×10^{18} cm^{-3} at room temperature (see, e.g. [*Roth PRB82*]). This means that the phenomena described here should be taken into account while considering the transport processes in ZnO films grown at the temperature in the vicinity of 200°C, which revealed the electron concentration $n \approx 8.6\times10^{19}$ cm^{-3}.

Concerning the measurements of optical absorption edge in the discussed layers[16], they lead to the conclusion that the increase in carrier concentration observed for higher growth temperatures (from $n \approx 1.7\times10^{17}$ cm^{-3} for ZnO obtained at 100°C up to $n \approx 8.6\times10^{19}$ cm^{-3} for the layer grown at 200°C) finds the reflection in the remarkable Burstein-Moss shift that reaches approximately 70 meV. Interestingly, there exists an evident anti-correlation between the carrier concentration in the layer and the intensity of wide emission band in the photoluminescence (PL) spectra ascribed to the presence of deep defects in ZnO (see Fig. 3., presenting the respective PL data collected at room temperature in the energy range of 1.6 – 3.4 eV). This observation, in combination with increasing carrier mobility in ZnO grown at higher temperatures (see Fig. 2.) may suggest that at lower growth temperatures the compensation effects in ZnO play a relevant role [*Wu APL01, Vanheusden APL96*]. An increase

---

[15] Estimated from the Hall effect measurement carried out in the Van der Pauw configuration on the square (10mm×10mm) ZnO samples.

[16] Performed in collaboration and due to the courtesy of the researchers from the Institute of Solid State Physics of the Bulgarian Academy of Sciences (ISSP-BAS) in Sofia, Bulgaria.

in the near-band-edge (NBE) luminescence intensity indicates, in turn, the better crystallographic quality of the films deposited closer to 200°C.

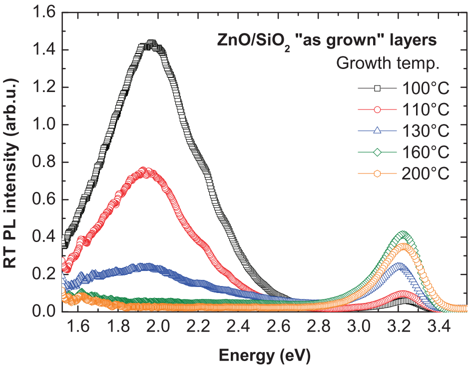

Fig. 3. Room temperature PL spectra acquired on the ALD-ZnO films deposited on quartz substrates. The visible quenching of luminescence attributed to the presence of deep defects (at lower energies) for the layers grown at higher temperatures as well as its anti-correlation with the electron concentration indicate on the influence of compensation effects. Figure reprinted from paper [**H1**].

In the further part of investigations, aimed at the deeper analysis of the described phenomena, a series of PL measurements has been carried out on the ZnO layers. Prior to theses studies the ZnO films were annealed with the RTP[17] technique at 700°C (within 60s) in the nitrogen– and oxygen-rich atmosphere.

As noticed, influence of annealing procedure on the ALD-ZnO PL spectra of the layers grown at the temperatures up to 130°C in comparison with the "as grown" films is qualitatively similar to the one presented in Fig. 4a. In case of ZnO obtained at higher temperatures, the behavior (shape) of PL intensity attributed to the deep defects changes fundamentally upon annealing (see, Figs. 4b., 4c.), as will be discussed underneath. Getting back to the annealing results for the films deposited below 130°C, it is visible that for both types of atmosphere the RTP process causes a decrease in intensity of emission in the energy range of 1.5 – 2.4 eV, however, this effect is slightly more evident after RTP carried out in oxygen-rich conditions. Besides, annealing in O_2 shifts this emission (likely consisting of two dominating subbands peaked at about 1.9 eV and 2.3 eV) towards the lower energies, when compared to the respective maximum registered for the "as grown" layers. This is, according to the literature reports [*Gomi JJAP03, Tam JPCB06*], related to the defects present in the zinc sublattice of ZnO (mainly vacancies). The simultaneous quenching of "green" emission (at 2.25 – 2.30 eV; 540 – 550 nm) indicates the effective diminishing of the optical activity of defects involving oxygen vacancies. Moreover, very similar behavior is observed in the ZnO layers after exposing them to the nitrogen-rich atmosphere, however, in this case the described effect is not so remarkable (particularly for the subband with a maximum at $E \approx 2.3$ eV).

The substantial enhancement of defect-related emission in the vicinity of $E \approx 2.3$ eV was, in turn, observed in the ZnO layers grown at 130°C and subjected to the RTP process in nitrogen (see Fig. 4b.). This fact gives an argument confirming the above assumptions

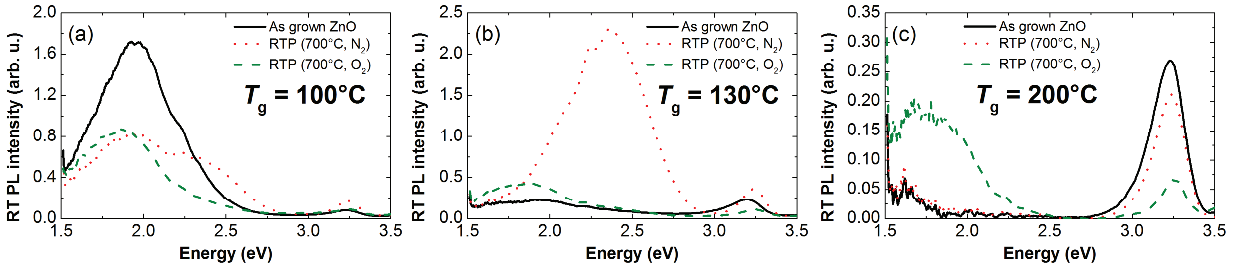

Fig. 4. Room temperature photoluminescence spectra acquired on the ZnO layers deposited on quartz substrates at 100°C (a), 130°C (b) and 200°C (c), respectively. The illustration depicts the influence of RTP annealing (700°C, 60s.) in nitrogen-rich (red dotted line) and oxygen-rich (green dashed line) conditions on the shape of RT PL spectra in comparison to the PL response obtained from the as grown ZnO films (black solid line). Figure reprinted from the paper [**H1**].

---

[17] Abbrev.: Rapid Thermal Processing.

concerning the contribution of oxygen vacancy-related defects (as invulnerable to the compensation effect in N_2 atmosphere) to the ZnO emission in this energy range. Additionally, as seen in Fig. 4c., depicting the RT PL spectra acquired on the films deposited at 200°C, as a result of their annealing in O_2, a characteristic maximum in the red emission area can be again observed, whereas the luminescence in the energies from the visible range of the spectrum remains quenched.

These conclusions find a supplementary confirmation in the earlier investigations of the objective ZnO films using the XPS[18] and RBS[19] methods (see the paper by Guziewicz *et al.* [*Guziewicz SST12*]). As inferred from these studies, the layers grown at about 100°C contain more oxygen than the ones deposited at 130°C. This partially explains the reason, for which somewhat weaker luminescence was noticed close to E = 2.3 eV in ALD-ZnO obtained at 100°C after subjecting it to the RTP process in nitrogen. Similar conclusions were also drawn in the publications by Murmu *et al.* [*Murmu JAP11*] as well as Kennedy *et al.* [*Kennedy JAC14*], devoted to the Gd-implanted single ZnO crystals prepared by the hydrothermal (HT) method. As stated therein, the annealing at 650 – 750°C carried out in vacuum and oxygen-rich ambient quenched a "green" luminescence in HT-ZnO:Gd with a simultaneous PL response shift towards yellow and red emission area, that can be ascribed to the thermally-induced modification of the oxygen and zinc sublattices in the ZnO matrix, respectively.

Obviously, annealing processes affect the electrical parameters of ALD-ZnO layers as well. As noticed, the RTP treatment in O_2 leads to the radical drop in the electron concentration, reaching three orders of magnitude when compared to the "as grown" ZnO films (n: ~$10^{19} \rightarrow 10^{16}$ cm^{-3}). The same concerns the electron mobility, which does not exceed 6.5 cm^{2}V^{-1}s^{-1} in the annealed layers. Interestingly, annealing in the nitrogen-rich atmosphere does not result in such an evident carrier concentration drop (maximally 1.5 order of magnitude); in the layers obtained at 130°C the substantial increase in mobility up to 25 cm^{2}V^{-1}s^{-1} after annealing in N_2-rich ambient has been observed. As suggested in the papers by Kennedy *et al.* [*Kennedy ApSS16, Kennedy CAP06*], there exists a possible dependence between such a behavior and diminished (as a result of annealing) content of interstitial hydrogen (H_i) or its complexes with oxygen vacancy (H_i–V_O) in the ZnO films. This remains consistent with the total hydrogen percentage contribution, which decreases about one order of magnitude.

Additionally, the above-mentioned increase in the carriers' mobility accompanied by the simultaneous decrease in its concentration and supported by the RT PL behavior noticed for the ZnO layer grown at 130°C after its annealing in nitrogen (see Fig. 4b.) allows making an assertion that there exists a defect in the analyzed films showing a tendency to be active in the zinc sublattice and introducing acceptor states [*Hamad TSF05*]. In order to get a better view on this problem, a more detailed analysis of the RT PL subband located between $1.53 \leq E \leq 2.75$ eV has been carried out, basing on its deconvolution to the Gaussian contributions. As can be noticed in Fig. 5., presenting such a step made for the spectrum gathered from the layer deposited at 100°C, the deconvolution in this case reveals a quite complicated character, resulting from the necessity of using from three to five Gaussian components every time. As it is seen on the middle panel of Fig. 5., annealing of the ZnO films in nitrogen-rich conditions causes a remarkable percentage increase (comparing to the as grown layer) in the luminescence intensity between 2.23 and 2.38 eV (~20.1 → 37.6%[20]). According to the literature

---

[18] Abbrev.: X-ray Photoelectron Spectroscopy.

[19] Abbrev.: Rutherford Backscattering Spectrometry.

[20] For the ZnO grown at 130°C this change is even as high as ~30% → 96.4%. The percentage contribution of a given Gaussian component has been estimated taking the integral value from the envelope (orange in Fig. 5.) as 100%.

reports [*Nikitenko ZnO05, Lin APL01, Xu NIMB03*], emission in this energy range is ascribed to such defects as V_O or O_{Zn}. Here, it is worth-noting that very similar feature of the RTPL spectra deconvolutions was also observed for the case of ZnO films obtained at 110°C, 130°C as well as 160°C. Relating the above to the earlier-described behavior of free carrier concentration, it can be stated that the oxygen vacancies, despite their deep donor-like character, may partially affect the ZnO conductivity. Concerning the role of the O_{Zn} defect – due to its high formation energy it is assumed that its influence on the electrical parameters of ZnO remains rather limited [*Janotti RPP09*].

While analyzing the RTP-O_2 annealing influence on the defect-related luminescence in ZnO, it should be underlined that on the contrary to the effect observed after thermal treatment in the nitrogen ambient, in this case the energetic shift of the dominating PL maximum towards 1.71 – 1.72 eV has been registered, whereas the previously discussed "green" luminescence undergoes the effective diminishing or even quenching. This is, as widely described in the paper [**H1**], particularly visible for the case of ALD-ZnO layers obtained at 130°C, for which a decrease of the "green" luminescence was noticed from 30% down to 14.7%. In parallel, for the film grown at 100°C (see, the bottom panel of Fig. 5.) the contribution of luminescence with the peak at 1.71 eV takes approximately 49.5% of the whole energy range between 1.53 and 2.75 eV. The observed behavior is often attributed in the literature to the V_{Zn}-related states in ZnO [*Nikitenko ZnO05, Anantachaisilp JL15*]. Besides, it proves that the RTP annealing process performed in oxygen-rich conditions remarkably reduces the influence of oxygen vacancies on the electrical compensation in ZnO as well as affects the emission from the defect levels related to some of the ionized states (like V_O^+ [*Lima JIM01, Vlasenko PRB05*]) in this material.

The above considerations convince unambiguously that the problem of physics of native defects and their influence on the charge transport properties of zinc oxide still remains, despite the appreciable (and continuously increasing) number of literature reports, quite

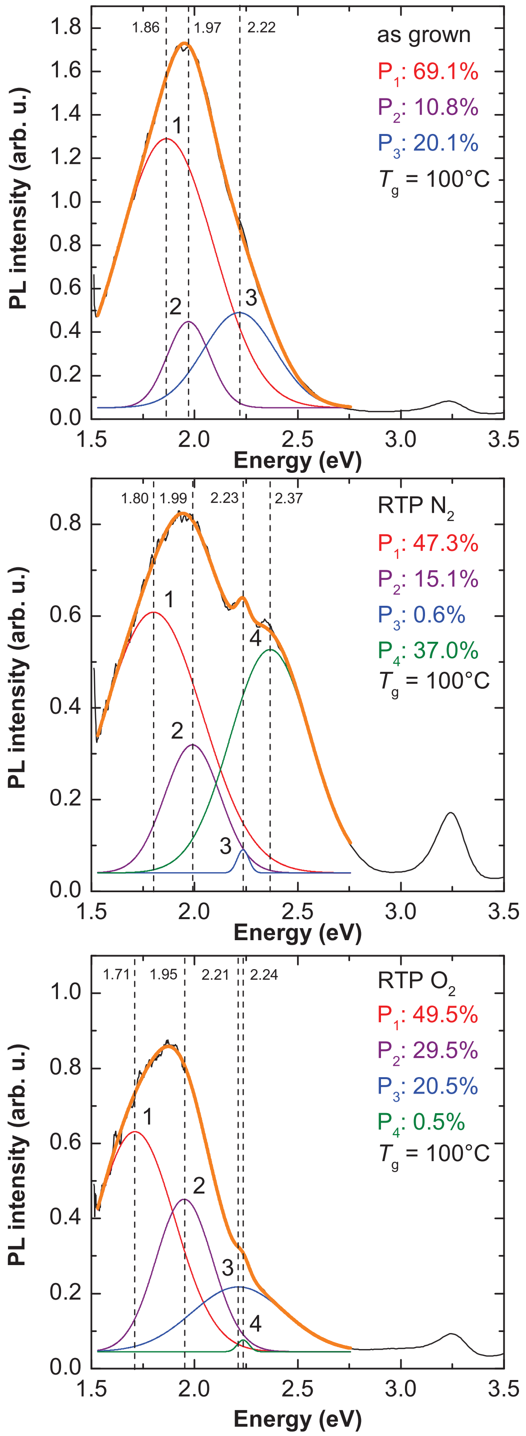

Fig. 5. Deconvolution of the RT PL spectrum acquired on the ALD-ZnO film obtained at 100°C without the thermal treatment (top panel). Comparison with the spectra measured after RTP annealing of ZnO layer in nitrogen (700° C, 1 min.) – middle panel – and oxygen (700° C, 1 min.) – bottom panel shows the shifts of the defect-related PL maximum ascribed to the changes in contribution coming from different defects to the spectrum (see description in the text). Similar deconvolutions were performed for the other layers from the discussed series, deposited at 110, 130, 160 and 200°C. Figure reprinted from the paper [**H1**].

intricate. Therefore, the respective investigations frequently require the use of advanced experimental methods. Among these, the particularly useful ones involve the measurement and analysis of capacitance transient kinetics, which can be influenced e.g. by the adequately chosen voltage pulses. Such experiments, provided the good quality and stable rectifying junction is used, allow to have an insight into the defect structure of a given material in the wide range of temperatures. The further part of this summary will be focused on the concise description of the related studies performed on the *n*-ZnO/*p*-GaN heterostructure.

Junction, being the subject of considerations presented in the paper [**H2**], has been obtained by the ALD deposition of undoped *n*-ZnO film (~1100 nm thick) carried out at 100°C on the GaN substrate (~500 nm) grown at 1050°C by the MetalOrganic Vapor Phase Epitaxy technique at the University of Bremen. To obtain a p-type conductivity in GaN doping with Mg has been used resulting in $p \approx 5\times10^{18}$ cm^{-3}. Further details referring to the GaN growth process the Reader can find in the related publication by Figge *et al.* [*Figge APL02*].

It should be stressed that regarding the severe requirements imposed on the electrical parameters of the materials forming the junction as well as the specificity of the used experimental methodology, the measurements involving analysis of capacitance transient kinetics are nowadays performed (in the vast majority of cases) on the structures involving single ZnO crystals (grown e.g. by the already mentioned hydrothermal method). This is for the fact that they reveal sufficiently low free electron concentration. Having this in mind, the above remarks pertaining to the influence of native defects on the electrical parameters of ZnO thin films and the possibility of their efficient regulation, particularly through the adjustment of growth temperature, gather the additional significant meaning.

Importantly, growing the ZnO film at 100°C enabled getting the "as grown" free electron concentration at the level of $n \approx 7\times10^{17}$ cm^{-3}, confirmed independently by both: Hall effect measurements carried out on the reference ZnO/glass sample and the respective calculations stemming from the analysis of capacitance-voltage (*C*-*V*) behavior of the *n*-ZnO/*p*-GaN diode as will be shown later on. As a starting point to the more advanced investigations of the topical rectifying structure, involving some elements of the thermal admittance spectroscopy technique (for the principles, see e.g. [*Kanai JJAP90*]), its current-voltage (*I*-*V*) as well as capacitance-voltage characteristics were acquired at room temperature (see Figs. 6a. and 6b.). As observed, the obtained diode revealed a stable rectification ($I_{\mathrm{ON}}/I_{\mathrm{OFF}}$) ratio reaching three orders of magnitude while polarized with ±2 V, making it promising for further studies. Far more important was, however, the information contained in Fig 6b., which depicts the results of C-V measurements, demonstrating that the low frequency probing voltage (*ac*) signal ought to be used for the experiments. This is because of the existence of "*cut-off* frequency", above which the observation of any changes in the junction capacitance under the applied bias becomes impossible. Such a phenomenon can be explained taking an advantage of the equivalent circuit scheme presented in the inset to Fig. 6b. It consists of two *RC* loops, referring to the depleted region of ZnO/GaN junction (exhibiting R_{d} and C_{d}) and to the whole (bulk) structure (with R_{b} and C_{b}), respectively. In typical conditions one has : $R_{\mathrm{d}} >> R_{\mathrm{b}}$ as well as $C_{\mathrm{d}} >> C_{\mathrm{b}}$. Taking into account the low frequency probing signal, this results in the capacitance C_{d} and resistance R_{d} measured. Otherwise, the sum of $C_{\mathrm{d}} + C_{\mathrm{b}}$ should be considered, yielding the *C*-*V* response, in which no capacitance changes can be seen.

The described problem is clearly visible in Fig. 6c., demonstrating the way of the junction built-in (V_{bi}) voltage estimation, basing on the C^{-2} (V) dependence. For the structure being discussed the V_{bi} = 0.92 V has been obtained, what was feasible with the use of low-frequency (f = 10kHz) probing signal only. At higher frequency (e.g. 1 MHz) the charge carriers lag behind the electric field changes in the junction, yielding the meaningless *C*-*V* response (see the black dashed line in Fig. 6c.). One of the reasons for such behavior could undoubtedly be a quite low mobility of electrons in thin ALD-ZnO films (about $\mu_{\mathrm{ZnO}} \approx 50$ cm^{2}V^{-1}s^{-1}).

Significance of the above-mentioned cut-off frequency in frames of presently considered *n*-ZnO/*p*-GaN diode is well illustrated in Fig. 7a., showing the measurements of capacitance (C) and loss[21] (L) parameters of the structure as a function of the probing signal frequency. As can be seen in the figure, the diode capacitance is reliably high and responds properly to the applied bias changes within the range of -0.48 V to +0.2 V only if the probing voltage frequency is lower than 100 kHz.

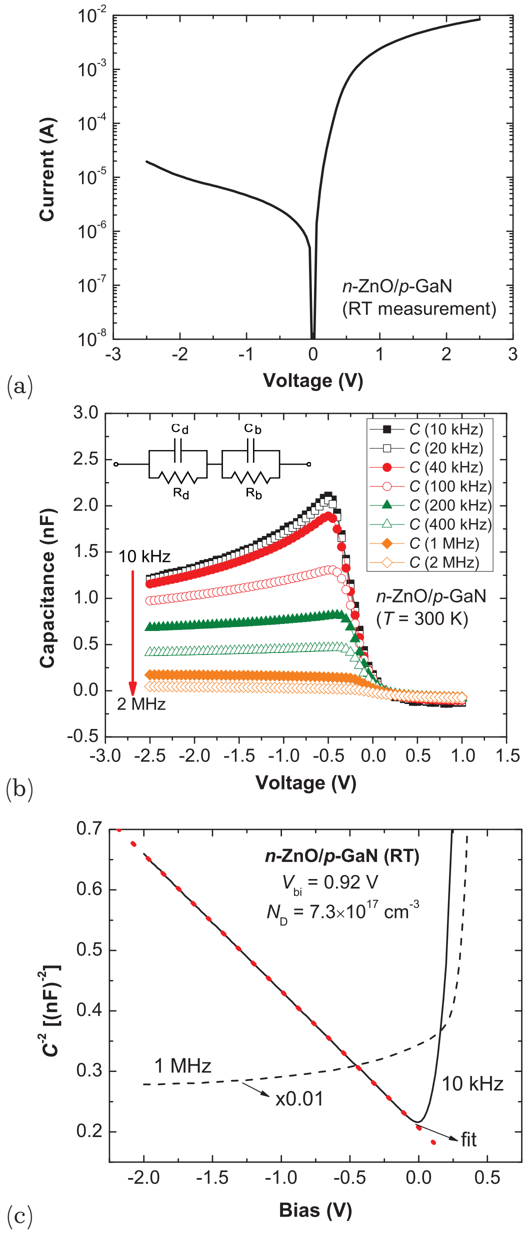

Fig. 6. (a) Room temperature current-voltage (I-V) characteristics of the *n*-ZnO/*p*-GaN junction, discussed in the paper [**H2**]. (b) The capacitance-voltage (C-V) characteristics of this junction acquired for different frequencies of the *ac* probing voltage signal within the range of 10 kHz – 2 MHz together with the respective equivalent circuit scheme (see the inset). (c) The way of calculating built-in (V_{bi}) potential of the diode based on the C-V measurements, explaining the necessity of carrying out the experiment with the low-frequency probing voltage signal. Figures reprinted from the paper [**H2**].

Regarding this fact, further electrical investigations enabling the localization and quantitative description of defect levels in the *n*-ZnO/*p*-GaN junction at the temperature range 77 – 330 K were carried out with the use of $f = 10$ kHz signal. Such a frequency in combination with the carrier concentration on both junction sides meeting the criterion of $n_{\mathrm{ZnO}} < p_{\mathrm{GaN}}$ ensured probing the depleted region shifted towards the zinc oxide, which was crucial for the discussed case. The value of trap filling pulse within the experiment has been set as $V_{\mathrm{fill}} = 0$ V, whereas the $V_{\mathrm{empty}} = -2$ V. The capacitance transient was measured within $t = 300$s after the one second long filling pulse. The exact description of defect levels (apart from their energetic localization E_{T} in the bandgap with regard to the conduction band edge E_{C}) took into account the traps' concentration N_{T} and the estimation of capture cross-section (σ_n) value as well. This was possible taking an advantage of the dependences given e.g. in [*Dyba APPA09, Kanai JJAP90, Stallinga OEM09*]. Moreover, for the capture cross-section calculations one dominating minimum of the ZnO conduction band was assumed, located in the Γ-point of Brillouin zone, after [*Albrecht JAP99*].

For the levels depicted in Fig. 7b. the following values of E_{T}, N_{T} and σ_n were obtained:

$$E_{\mathrm{T1}} = (0.57 \pm 0.03)\ \mathrm{eV},\ N_{\mathrm{T1}} = 4.4\times10^{15}\ \mathrm{cm}^{-3},\quad \sigma_{\mathrm{n}}^{\mathrm{T1}} = 4.4\times10^{-16}\ \mathrm{cm}^2;$$

$$E_{\mathrm{T2}} = (0.20 \pm 0.03)\ \mathrm{eV},\ N_{\mathrm{T2}} = 4.4\times10^{14}\ \mathrm{cm}^{-3},\quad \sigma_{\mathrm{n}}^{\mathrm{T2}} = 1.0\times10^{-18}\ \mathrm{cm}^2;$$

$$E_{\mathrm{T3}} = (0.73 \pm 0.24)\ \mathrm{eV},\ N_{\mathrm{T3}} = 8.8\times10^{14}\ \mathrm{cm}^{-3},\quad \sigma_{\mathrm{n}}^{\mathrm{T3}} = 8.3\times10^{-17}\ \mathrm{cm}^2;$$

$$E_{\mathrm{T4}} = (0.65 \pm 0.29)\ \mathrm{eV},\ N_{\mathrm{T4}} = 8.8\times10^{14}\ \mathrm{cm}^{-3},\quad \sigma_{\mathrm{n}}^{\mathrm{T4}} = 6.3\times10^{-19}\ \mathrm{cm}^2.$$

---

[21] Defined as the junction conductance G to the probing signal frequency ω ratio.

When compared to the available literature data, a certain ambiguity was noticed in ascribing the trap levels existing in the examined structure to the given type of native defect in ZnO. For instance, in the paper by Lajn *et al.* [Lajn JEM10], the level of E_T = 0.24 eV below the conduction band edge (thus, close to E_{T2}) is discussed, attributed by Liu *et al.* [Liu SCTS11] to the presence of doubly-ionized interstitial zinc (Zn_i^{2-}) in ZnO, in its neutral state introducing the level located 30 – 40 meV below E_C [Look PRL05, Lajn JEM10, Krajewski AM14]. It is, however, worth-noting that despite the further confirmation of the conclusions from [Liu SCTS11] by the studies described by [Blatter PRB86], [Han MChP02] and [Shohata JJAP80], Auret *et al.* [Auret APL02] do not exclude the link between this energy and the existing oxygen vacancy-related defects in zinc oxide.

On the other hand, far more frequently to the V_O defect the level of E_T = 0.54 – 0.60 eV is ascribed, actually located in the vicinity of E_{T1}, mentioned in this summary. Such an interpretation one can find e.g. in the publications by Auret *et al.* [Auret APL01], Fernández-Hevia *et al.* [Fernández-Hevia APL03], Frank *et al.* [Frank APA07] as well as Van de Walle [VandeWalle PhB01]. Noteworthy, the latter paper, based on theoretical investigations gainsays the role of V_O as a defect influencing the charge transport properties of ZnO.

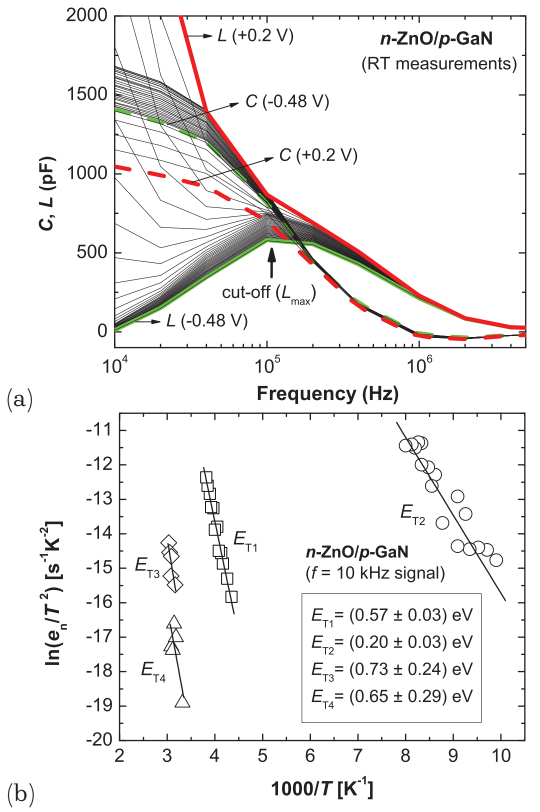

Fig. 7. (a) Reaction of the capacitance *C* and loss *L* of the *n*-ZnO/*p*-GaN junction to the changes in frequency of the probing voltage signal and the bias applied to the structure, illustrating the physical sense of cut-off frequency. Red curves refer to the junction biased with *V* = +0.2V (dashed one for capacitance *C*, solid one for loss *L*), while green curves pertain to the structure biased with *V* = -0.48V (dashed one for capacitance *C*, solid one for loss *L*). The respective measurements were made at RT. (b) Trap levels detected in the *n*-ZnO/*p*-GaN heterostructure (Arrhenius plots), obtained under the bias conditions of V_{fill} = 0V, V_{empty} = -2V. The acquisition time of a single capacitance transient *t* = 300s. Figures reprinted from the paper [**H2**].

Concerning the levels marked in Fig. 7b. as E_{T3} and E_{T4}, it should be stressed that the uncertainty of their estimation reaches 30 – 40 % of the energy value, making the assignment to a given defect disputable and thus requiring further experimental confirmation. Nevertheless, there exist the papers, for instance by Wang *et al.* [Wang APL96] suggesting that they might be related to the different charge state of oxygen vacancy. The Authors motivate such a view i.a. with the possible decoration of ZnO grain boundaries by oxygen atoms.

To conclude, the above-described optical and electrical investigations of the defect structure of intentionally undoped thin ZnO films point at the presence and significant role played in such layers by mainly three types of native defects, i.e. zinc vacancies, zinc interstitials as well as oxygen vacancies. Considering the lively literature discussion pertaining to their influence on the oxide transport properties (see, the mentioned polemic referring to V_O), the following part of the summary will be devoted to the analysis of the possibility of using the examined films to the construction of ZnO homojunctions. In this context, the approach focused on influencing the carriers' flow mechanisms in ZnO through the controllable introduction of nitrogen acceptor dopant during the layer growth will be discussed, based on the papers [**H3**] and [**H4**] from the habilitation cycle.

3.2. ZnO:N/ZnO and ZnO:(N,Al)/ZnO homojunctions obtained by the ALD method – problem of the electrical parameters' optimization ([H3], [H4])

Direct reason for the doping asymmetry in ZnO (as mentioned in the *Introduction* section) that causes difficulties in obtaining *p*-type conductivity in this material lies in the specific location of the Fermi level (E_F) situated in the upper part of the bandgap, close to the conduction band (CB) edge. Nevertheless, the constantly high price of such semiconductors as GaN:Mg, which could serve as a *p*-type partner, forming the *p*-*n* junction with *n*-ZnO, makes the search for stable *p*-type dopant in zinc oxide a live issue. Moreover, finding a method of effective acceptor doping in ZnO, could pave the way to its wider application in the modern electronics, e.g. due to the construction of ZnO-based homodiode, being a very interesting alternative to the currently used *p*-*n* structures. The rectifying junction involving only ZnO would ensure a proper lattice match, band alignment and interface quality, enabling this way a more effective control and comprehension of the native defects' role in ZnO (see also the papers [**H1**] and [**H2**]).

Apart from the elements from group V of periodic table, like arsenic or antimony, such alkali metals as lithium [*Lee AdvM, Tsai JCG11*], potassium [*Jun ML08*] or sodium [*Lin JAP09, Lin SSC08*] are also tested as possible candidates for *p*-type dopants in ZnO. Observing, however, the available literature data, it can be seen that one of the most popular element used for this purpose, partially due to the ionic radius similar to the one of oxygen, is nitrogen.

In the paper [**H3**], discussing the possibility of ZnO *p*-type doping aimed at the homojunction construction, the efficient nitrogen introduction was achieved through the use of ammonia water (NH_4OH) as an oxygen precursor in the ALD process. Growth of the ZnO layers constituting the homojunction parts has been carried out at 100°C as well as 130°C. This ensured – apart from the well-balanced Zn-to-O ratio [*Guziewicz SST12*] – also the easier control of the introduced amount of nitrogen dopant.. As can be deduced from the SIMS profiles of the doped films, the amount of introduced nitrogen scales perfectly with the number of ALD cycles involving the NH_4OH precursor against the number of ALD cycles with H_2O. Such an approach can yield the ZnO films with nitrogen contribution as high as 10^{19} – 10^{21} at..cm^{-3}.

Focused at the initial stage of experimental work on obtaining the lowest possible electron concentration in the ZnO:N films, the four ways of nitrogen introduction to ZnO were tested, replacing H_2O with an NH_4OH precursor in every fourth, two out of four, three out of four and each ALD cycle, respectively. This resulted in the lowest electron concentration of $n = 5.4\times10^{15}$ cm^{-3} achieved for the situation with 2:4 ALD cycles with NH_4OH. According to the SIMS investigations, in this case the nitrogen contribution was at the level of ~10^{20} at./cm^{-3}.

To obtain the *p*-type conversion, the ZnO:N films were subsequently subjected to the thermal treatment (RTP annealing) in oxygen-rich conditions (3 min. at 800°C) as well as – for comparison – in nitrogen ambient (10 minutes at 325, 350, 375 and 400°C). Here, it should be stressed that such a way of acceptor dopant activation in ZnO is successful not only for the case of nitrogen, as demonstrated in the publications [**H3**] and [*Bian APL04, Chao SCT13, Wang SM14*] but also for ZnO doped with group I elements, e.g. lithium [*Tsai JCG11*]. Interestingly, in frames of the paper [**H3**] it was noticed that after annealing in oxygen at 800°C, the conversion effect in may be achieved only these doped ZnO layers, which contain lower amount of nitrogen (i.e. $p = 1.5\times10^{17}$ cm^{-3} with a hole mobility $\mu = 6.1$ cm^{2}V^{-1}s^{-1} for N ~ 10^{18} at./cm^{-3} as well as $p = 4.5\times10^{16}$ cm^{-3} with a hole mobility $\mu = 17.3$ cm^{2}V^{-1}s^{-1} for N ~ 10^{19} at./cm^{-3}), whereas for higher dopant contribution the RTP annealing makes ZnO:N a highly resistive material.

Comparing to the above, slightly different situation has been observed in the case of ZnO:N layers annealed in nitrogen. For these films the conductivity type conversion occurred only as a result of RTP process carried out at 400°C, which yielded p ~ 9.0×10^{14} cm^{-3}.

The phenomenon of conductivity type conversion stemming from the RTP annealing of ZnO:N films may be explained by the occurring dissociation of N_O-H complex [*Monakhov APL05*], which is created during the ZnO:N growth as a result of the dopant introduction combined with the passivation of substitutional nitrogen by hydrogen[22] [*Li APL05*]. Besides, annealing in oxygen-rich conditions enables the conversion process due to the reduction of the compensating influence of V_O donors in ZnO:N (see also paper [**H1**] and [*Kolkovsky SST14*].

Noteworthy, results of the above-described investigations were successfully used while constructing the ZnO homojunctions. Pursuing the suppression of the role that might be played by the highly resistive Si (100) substrate in terms of their electrical parameters, at the initial stage it was covered by a 40 nm thick ALD-ZnO buffer layer subsequently capped with thin (8 nm) film of ALD-Al_2O_3. These two steps were made prior to the deposition of topical ZnO-based homodiodes. Within these particular studies two types of rectifying structures were investigated. In type I the 80nm thick ZnO:N film was grown at 100°C at the bottom, followed by the undoped ZnO deposited at 130°C, in order to ensure the free electron concentration at the level of n~10^{18} cm^{-3}. The whole diode was terminated with the ohmic Ti/Au metallization.

For comparison, in the structure of type II the order of homojunction partners has been reversed, i.e. n-ZnO preceded the ZnO:N film. In both cases the ZnO:N material contained from 10^{19} to 10^{21} at./cm^{-3} of nitrogen. Concerning the nitrogen dopant activation, indispensable annealing processes in nitrogen (10 min. at 350°C and 400°C) as well as oxygen (3 min. at 800°C) atmospheres in case of the junction of type I were performed prior to n-ZnO deposition, whereas for the case of type II – after terminating the whole homojunction.

The preliminary measurements of I-V characteristics of the obtained structures made after oxygen-rich annealing have revealed for type I the I_{ON}/I_{OFF} ratio from 1.5 to 15 when polarized with ±2 V, while for type II the rectification effect was not observed, presumably because of the nitrogen diffusion from the ZnO:N layer to the whole homojunction as a result of annealing.

Focusing in the next stage of research on the further optimization of electrical parameters of type I structure, it was noticed that the highest I_{ON}/I_{OFF} ratio (of about 2×10^2 for ±2 V – see, the red curves in Fig. 8a., b.) was obtained when the ZnO:N film with N ~ 10^{21} at./cm^{-3} annealed in nitrogen (10 min. at 400°C) was applied to its construction. Taking into consideration the necessity of preventing nitrogen diffusion to the second homojunction partner (i.e., top n-ZnO film) with the lapse of time, the additional technological solution was introduced, relying on the insertion of thin (4 nm) aluminum(III)oxide[23] (Al_2O_3) dielectric interlayer between the ZnO films forming the diode. It is worth-mentioning that the choice of

---

[22] As demonstrated in the paper by Guziewicz *et al.* {Guziewicz SST12], contribution of hydrogen in the ZnO films obtained in the temperature range of 100 – 130°C is about 0.4 – 0.6 %, thus sufficiently high for the N_O-H complex formation during the growth.

[23] The Al_2O_3 film was obtained in the ALD process at 100°C according to the reaction (3), involving TMA and H_2O as aluminum and oxygen precursor, respectively.

dielectric material was motivated by the respective literature data, according to which Al, acting as donor in ZnO, in case of its diffusion to the upper homojunction part would ensure its stable *n*-type conductivity, while if migrated to the lower part (ZnO:N) would protect (as a nitrogen co-dopant) the desired *p*-type [*Yang AM12, Chou ApSS08*] (further aspects of electrical transport properties of the co-doped ZnO:(N, Al) layers will be presented below, while considering the results included in the paper [**H4**].

As derived from the measurements of current-voltage characteristics of such a modified structure, the change introduced to its architecture resulted in the further enhancement of the I_{ON}/I_{OFF} parameter, up to the level of 2×10^2 for the polarizing voltage of ±2 V (see, the blue *I-V* curves in both parts of Fig. 8.), proving the effectiveness of applied approach.

The more profound studies on the role played by the dielectric interlayer in terms of charge transport processes occurring in the rectifying junctions will be presented in paragraph 3.3. of this summary, while discussing the papers [**H5**] and [**H6**] from the habilitation cycle.

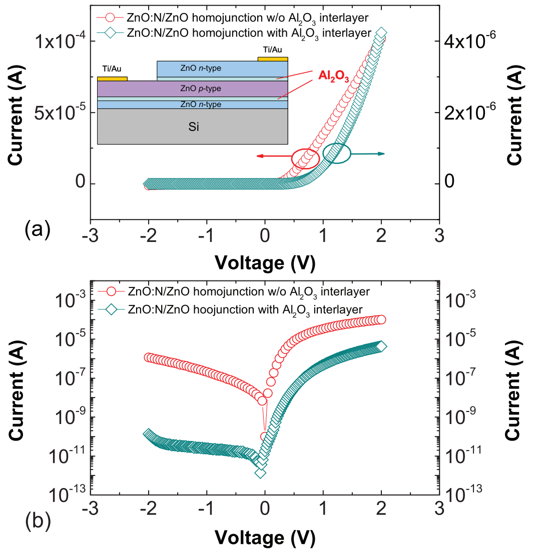

Fig. 8. Comparison of *I-V* characteristics of the ZnO:N/ZnO homojunction without Al_2O_3 dielectric interlayer (the red curves in both parts of illustration) with the characteristics of an analogous structure containing the Al_2O_3 interlayer placed between the homojunction parts (see, the blue curves in both parts of the illustration and the inset in panel (a)). For the better view on a remarkable improvement of the diode rectification ratio occurring after the dielectric film application, the graph in panel (b) is presented in the semi-logarithmic scale. Figure reprinted from the paper [**H3**].

* * *

Discussion of the electrical parameters of ZnO:(N, Al) films as well as ZnO:(N, Al)/ZnO homojunctions should be started from somewhat wider presentation of ZnO codoping method. It ought to be mentioned that similarly to ZnO:N films, also the ZnO:(N, Al) layers were deposited at 100°C, however, in their case the nitrogen dopant was introduced in three manners, i.e. replacing H_2O with NH_4OH in 1:4, 2:4 and 3:4 ALD cycles, while the aluminum (TMA) precursor was applied alternately to DEZn. This led to the effective control of N:Al ratio in the examined ANZO material. The number of ALD cycles was set to be between 1000 and 5000, resulting in the ANZO layers of 150 – 800 nm thick.

As it can be deduced from the SIMS depth profiles of ANZO films, presented in the paper [**H4**], the procedure of ZnO codoping with donor and acceptor allows obtaining the layers, which contain a remarkably higher concentration of acceptors when compared to the material with only acceptor dopant applied in analogous growth conditions : the difference in acceptor concentration can, in such a case, reach even one order of magnitude. In the described situation the nitrogen contribution to the ZnO:(N, Al) films was about $\sim 2\times10^{21}$ at./cm^3, in ZnO:N being estimated at the level of $\sim 1.2\times10^{20}$ at./cm^3. According to the theoretical model included in the ealier-mentioned papers [*Yamamoto PhB01, Yamamoto TSF02*], this fact is a direct consequence of the occurring attractive interaction between nitrogen and aluminum leading to the N-Al complexes formation, in which the Al atom is able to bind from two to three atoms of nitrogen.

The Al-N clusters, similarly to the smaller grain size derived from the XRD measurements of ANZO layers can, in turn, be both responsible for their fairly decreased surface roughness, when compared to the ZnO:N material (2.6 versus 5.9 nm for the layers of about 180 nm thick as well as 7.7 nm versus 41.3 nm when concerns the thickness of about 800 nm, respectively). This is particularly beneficial for the possible application of codoped ZnO films in the electronic devices, where the good quality of interface is of fundamental importance. Besides, regarding the polycrystalline nature of ANZO, combined with its grain size between 20 – 40 nm and the dominating growth with the *c* axis parallel to the substrate, the grain boundaries can be expected to be the main scattering factor in the codoped zinc oxide films.

In order to verify the influence of N:Al ratio on the electrical conductivity type of the codoped layers, according to the suggestion published in [*Duan PRB09*], a series of ZnO:(N, Al) films has been obtained with N:Al relation varying from 2 to 4, pointing that that an increase in Al contribution in comparison to the nitrogen results in the stabilization of ANZO hole conductivity. (Here, it should be added that either for too decreased aluminum contribution or inappropriately chosen N:Al ratio, an electron conductivity type was observed in these layers, despite the performed acceptor doping.) The maximal hole concentration of $p = 8.93 \times 10^{17}$ cm^{-3} in ANZO was, in turn, noticed for N:Al = 2.4:1. This made obvious a question about the chemical nature of nitrogen dopant in ZnO and its role in the *p*-type conductivity activation.

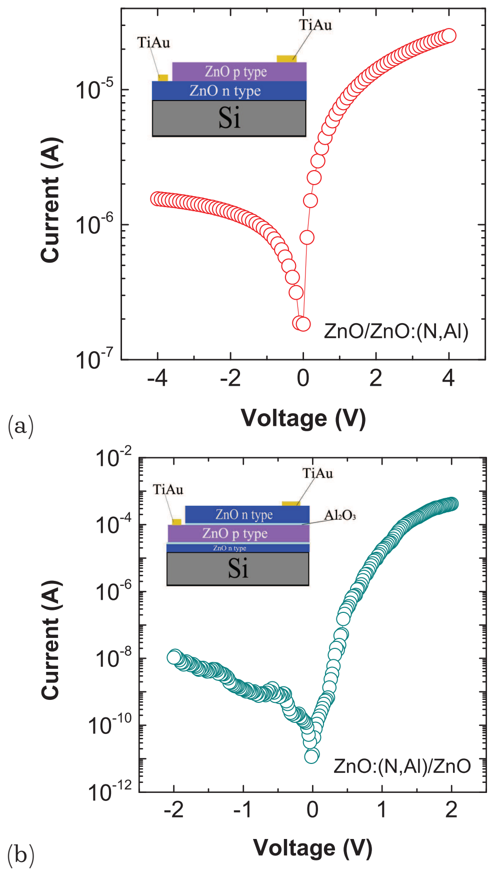

Fig. 9. Comparison of the *I-V* behavior of ZnO/ZnO:(N, Al) homojunction deprived of the dielectric (Al_2O_3) interlayer (panel (a)) with the characteristics of the modified structure, containing the ultrathin Al_2O_3 layer placed between the homojunction parts (b) – see the schemes in both panels of the illustration. For the enhancement of rectification ratio, in the diode from panel (b) the order of constituting layers has been reversed, by placing the codoped (ANZO) film at the bottom. Figure reprinted from the paper [**H4**].

Aiming at the explanation of the above issue, the two XPS spectra (*N1s* level) of ANZO films with similar N:Al ratio, however, revealing different conductivity type were acquired. Due to the deconvolution of these spectra into the Gaussian components (see, paper [**H4**]), the three main contributions with binding energies equal to (396.1 ± 0.1) eV, (397.4 ± 0.1) eV as well as about 399 – 399.5 eV were, respectively, found, being qualitatively ascribed to the presence of nitrogen in oxygen substitutional positions (N_O, [*Perkins JAP05*]), Al-N bonds ([*Wang TSF97*]) and N-H bonds ([*Ozawa SRL02, Perkins JAP05*]). Noteworthy, the latter ones might be the consequence of applying NH_4OH as an oxygen precursor and dopant source in the ALD process. As deduced based on the XPS investigations, the *p*-type conductivity occurs in the ANZO films with more intensive response coming from the N_O substitution. Importantly, the lack of XPS signal in the vicinity of binding energy of 404 eV (attributed to the N-N pairs [*Perkins JAP05*]), proves that the nitrogen used for purging the ALD reactor chamber does not affect the dopant behavior itself. What has to be particularly stressed, the stable *p*-type conductivity of ANZO films with an appropriate N:Al ratio (2.4:1, resulting in $p = 8.93 \times 10^{17}$ cm^{-3}, $\mu = 5.79$ cm^{2}V^{-1}s^{-1}) was obtained without the necessity of post-growth annealing, contrarily to the reports of Kalyanaraman *et al.* ([*Kalyanaraman JPCS13*]) or Xia *et al.* ([*Xia ML12*]). This, in combination with the low growth temperature (100°C), makes the discussed ANZO layers perspective ones if considered for applications in hybrid structures, for instance involving the high temperature-sensitive organic materials.

Promising results of the related investigations have pushed further studies towards the ZnO:(N, Al)/ZnO homojunction construction (fully obtained by ALD at 100°C), focusing them on the comparison of its electrical properties with the ones of a very similar structure, described in the paper [**H3**].

Similarly to the diode based on the ZnO:N layers, also in the rectifying structure relying on the codoped ZnO:(N, Al) films two types of its architecture on the Si substrate have been examined – with the codoped zinc oxide at the top (type I – see the scheme depicted in Fig. 9a.) as well as at the bottom (type II – see Fig. 9b.). While measuring the *I-V* characteristics of the junction of type I, the rectifying effect slightly exceeding one order of magnitude (~15 under the polarizing bias of ± 4V, see Fig. 9a.) was noticed. However, the electrical behavior was not sufficiently stable, likely because of the exposition of codoped ZnO film to the atmospheric influence, leading to the loss of the demanded electrical properties in the lapse of time.

The three modifications introduced to the structure of type II – application of the buffer *n*-ZnO layer, covered with Al_2O_3 aimed at the substrate's influence separation, deposition of ZnO:(N, Al) film as the bottom part of the diode as well as the growth of thin (4 nm) Al_2O_3 dielectric interlayer detaching the top (*n*-ZnO) homojunction partner resulted in the substantially enhanced I_{ON}/I_{OFF} ratio (up to about 4×10^4 for ±2 V – see Fig. 9b.). The obtained parameters are proximate to the ones achieved in the case of ZnO:N/ZnO diode (see, the paper [**H3**]), however, while assessing the complexity of both structures' preparation procedure, a particular attention should be paid on the fact that the additional post-growth annealing of the ZnO:(N, Al) film (indispensable for ZnO:N) may be eliminated due to its successful codoping, leading to the comparable improvement of the diode transport properties.

3.3. Influence of technological modifications on charge transport in ZnO/Ag Schottky junctions – the role of HfO_2 dielectric interlayer. Comparison with the ZnO-based homojunctions containing Al_2O_3 interlayer ([H5], [H6])

To obtain the possibly full view on transport mechanisms, existing in the semiconducting junctions modified by placing a dielectric interlayer therein, the current subsection will be fully devoted to the analysis of ZnO/Ag metal-semiconductor (also: *m-s*, Schottky) structures, in which as an interlayer between semiconductor and a metal contact a thin HfO_2 film was used. The ALD growth processes of ZnO and HfO_2 have been carried out according to the reactions (1) and (2), at the temperatures of 80°C as well as 135°C, respectively. In the series of ZnO/HfO_2/Ag Schottky diodes, discussed hereafter, the HfO_2 interlayers of various thickness were tested (i.e. 0 nm, 1.25 nm, 2.5 nm, 5.0 nm and 7.5 nm). Appropriate studies included the verification of the influence of diodes' construction (planar or vertical) on their electrical performance as well.

In the case of **planar architecture**, both types of metallic electrical contacts – ohmic Ti/Au and rectifying Ag were placed on the 100 nm of ZnO film, uniformly covered with HfO_2 exhibiting the thicknesses from the above-mentioned range (see, the inset to Fig. 10.). The contact layout with respect to the rest of the structure distinguished this junction from the one built according to the **vertical approach**, involving the indium-tin-oxide (ITO) substrate as an ohmic electrode.

The runs of room temperature *I-V* characteristics of planar ZnO/HfO_2/Ag junctions clearly indicate (see, Fig. 10.) that the reverse current in this type of structures strictly depends on the thickness of dielectric layer covering ZnO, which obviously suggests the necessity of its optimization focused on yielding the highest possible rectification ratio. This is because, as can be easily seen in Fig. 10., too thick dielectric leads to the weakening of the diode rectifying properties. The reason for such a behavior may be related to the progressive diffusion of hafnium into the ZnO layer, where it can act as a donor and thus cause an increase in the semiconductor free electron concentration.

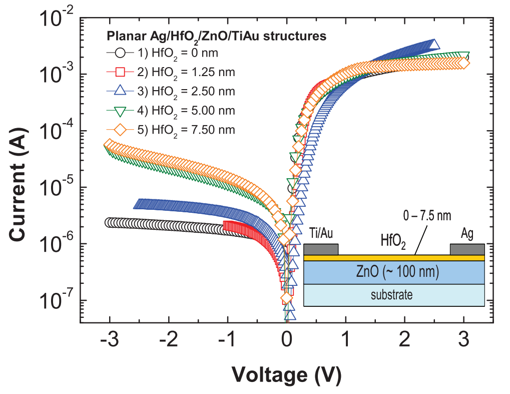

Fig. 10. Comparison of current-voltage characteristics of the planar ZnO/HfO$_2$/Ag junctions (see the inset), showing the influence of HfO$_2$ dielectric interlayer thickness on the diode reverse current for the polarizing voltages up to ± 2.5 V. The structure with HfO$_2$ interlayer as thick as 1.25 nm exhibited the instability of a reverse current behavior, resulting in impossibility of its parameters estimation within the whole range of applied voltages. Figure reprinted from the paper [**H5**].

The starting point for theoretical analysis of the electrical behavior of ZnO/HfO$_2$/Ag junctions built in the planar architecture was the Shockley equation describing the current I, flowing through the junction as:

$$I = I_0 \left\{ \exp\left[\frac{q\,(V - I\,R_S)}{\eta\,k\,T} \right] - 1 \right\}. \qquad (4)$$

This dependence takes into account the basic junction parameters, i.e. saturation current I_0, series resistance R_S and ideality factor η (the other symbols stand, respectively, for: q – elementary charge, k – Boltzmann constant and T – temperature). Relevantly, from I_0 value the Schottky barrier height, φ_B, can be derived.

Nevertheless, quite frequently the implicit (with regard to the current I) form of equation (4) induces the use of its simplified version referring only to the quasi-linear part of the junction I-V characteristics (thus considering the initial range of forward bias only and omitting the resistance R_S – see Fig. 10.).

On the other hand, such parameters as η or often subjected to the mentioned simplification IR_S reflect by their behavior the influence of *a priori* unknown, though interesting physical effects explaining various deviations from the "ideal" shape of I-V dependence.

Regarding this, in order not to lose the deeper insight into the characteristics of the structures described in paper [**H5**], their analysis has been based on the modified (via introduction of the Lambert W-function) equation (4), which after such approach can be rewritten as follows [*Ortiz-Conde SSE00*] (5):

$$I = \frac{\eta\,kT}{q\,R_S} W\left\{ \frac{I_0\,R_S\,q}{\eta\,kT} \exp\left[\frac{q\left(V + I_0\,R_S\right)}{\eta\,kT} \right] \right\} - I_0\,. \qquad (5)$$

The values of ideality factor, saturation current and series resistance can be then found treating η, I_0 and R_S as fitting parameters minimizing the following sum of squares (6):

$$\sum_{i=1}^{n} \left(I_i - \frac{\eta\,kT}{q\,R_S} W\left\{ \frac{I_0\,R_S\,q}{\eta\,kT} \exp\left[\frac{q\left(V_i + I_0\,R_S\right)}{\eta\,kT} \right] \right\} - I_0 \right)^2 , \qquad (6)$$

where V_i and I_i stand for the values of polarizing voltage and respective junction current in the total number of n measurement points.

Such theoretical fits to the experimental data of I-V characteristics of ZnO/HfO$_2$/Ag Schottky junctions (see Figs. 11a – e.) lead to numerous conclusions concerning the justness of

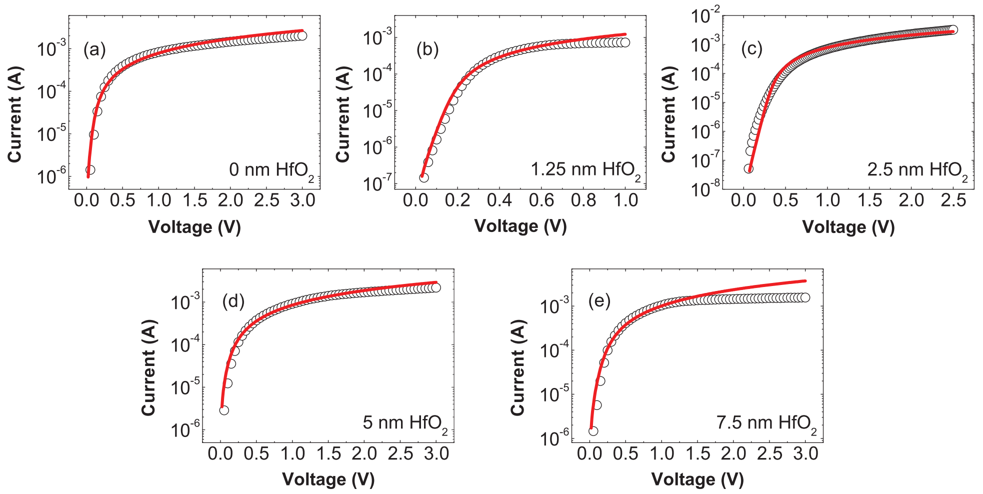

Fig. 11. Theoretical fits of the experimental *I–V* characteristics of planar ZnO/HfO$_2$/Ag junctions with various thickness of HfO$_2$ dielectric interlayer, from 0 to 7.5 nm (panels (a) – (e)) obtained using Eqs. (5) and (6). The fits of forward part of *I*-V data illustrate beneficial influence of 2.5 nm thick HfO$_2$ dielectric film on the properties of modified diode (see the numerical values from Table 1.). Figure reprinted from the paper [**H5**].

HfO$_2$ interlayer application in terms of the diodes' parameters improvement. In the case of structures constructed according to the planar architecture, the highest Schottky barrier, about $\varphi_B \approx 0.7$ eV, was observed for the junctions with the interlayer as thick as ~2.5 nm. Interestingly, these diodes exhibit the noticeably low reverse current density (8.92×10^{-4} Acm^{-2}). This, together with the rectification ratio reaching 6.7×10^{2} achieved for the diode biased with ± 1 V confirms the statement that regarding the specificity of junction's architecture[24], such dielectric thickness satisfactorily influences its properties. Comparing these data with the ones included in the papers by Allen *et al.*, Sheng *et al.* as well as Young *et al.* [*Allen APL06, Sheng APL02, Young SST08*], reporting the comparable or slightly higher Schottky barriers ($0.7 \le \varphi_B \le 1$ eV) one should take into account both: the different ZnO growth method (the single crystal due to the decreased electron concentration is more favorable with regard to the thin film) and the electrical contacts' preparation technology. During the here-described experiments, it has been noticed that for the optimal performance of the junction an amorphous form of HfO$_2$ is indispensable, as beneficial for the interface quality and ensuring the elimination of undesired recombination channels. Moreover, the role of adequately chosen dielectric interlayer relies on the semiconductor surface protection from the negative atmospheric influence, proper regulation of band bending in the structure as well as blocking the unwanted increase in the diode reverse current. The latter is achieved through preventing the creation of electron accumulation layer located directly under the rectifying electrical contact.

The selected parameters of ZnO/HfO$_2$/Ag rectifying structures built according to the planar architecture are gathered in Table 1., reprinted from the publication [**H5**].

Interestingly, ideality factor of the examined junctions increases with the augmentation of dielectric interlayer thickness (reaching 2 for 7.5 nm of HfO$_2$) indicating that the thermionic emission is not the only mechanism governing the carrier transport phenomena.

---

[24] As will be demonstrated in the further part of this summary, the rectifying properties of ZnO/HfO$_2$/Ag junction are strictly dependent on its architecture, undoubtedly influencing the carrier transport in the structure. In the analogous diode built in vertical configuration (described below) the values of rectification ratio are considerably higher, in exchange for e.g. the increased (i.e. worse) ideality factor.

HfO_2 thickness (nm)	Schottky barrier height (φ_B) (eV)	Series resistance R_S (Ω)	Reverse current density (at -1V) (Acm^{-2})	Reverse current density (at -2.5V) (Acm^{-2})	Rectification ratio I_{ON}/I_{OFF}
0	0.56	1.15×10^{3}	1.01×10^{-3}	1.33×10^{-3}	767 (±2.5V)
1.25	0.65	7.50×10^{2}	4.49×10^{-4}	unstable	345 (± 1.0V)
2.50	**0.70**	$\mathbf{7.20\times10^{2}}$	$\mathbf{8.92\times10^{-4}}$	$\mathbf{1.24\times10^{-3}}$	**672 (± 2.5V)**
5.00	0.54	9.50×10^{2}	2.27×10^{-3}	6.00×10^{-3}	65 (± 2.5V)
7.50	0.56	7.10×10^{2}	2.73×10^{-3}	6.99×10^{-3}	40 (±2.5V)

Table 1. Set of the basic parameters of planar ZnO/HfO_2/Ag junctions. The appropriate theoretical modeling was made using Eqs. (5) and (6) (see the related description in the text). Parameters of the junction with optimally adjusted thickness of HfO_2 interlayer have been marked in half-bold. The uncertainty of calculated values has been estimated to be around 10%.

Therefore, the ZnO/HfO_2/Ag diodes in vertical configuration have also been constructed, aimed at getting a closer look into this issue. This purpose can be achieved due to the theoretical modeling of their *I-V* characteristics using the *differential approach* (described in details in [**H6**]). In frames of this publication same analysis was applied with regard to the earlier-discussed ZnO-based homojunctions, which will help in gaining the possibly clear and full answer to the question about the dominating factors influencing the charge transport mechanisms in the discussed structures.

* * *

Differential approach towards the analysis of junctions' current-voltage characteristics, considered in frames of the article [**H6**], can be applied to the structures involving a wide range of materials (also organic ones). It is based on the observation of behavior of two dimensionless parameters: α and γ that can be defined in each local point of the examined *I-V* characteristics. They are given by the following equations (see, e.g. [*Smertenko ACIS05*]):

$$\alpha(V)=\frac{d(\lg I)}{d(\lg V)}=\frac{V}{I}\times\frac{dI}{dV}, \qquad (7)$$

$$\gamma(V)=\frac{d(\lg\alpha)}{d(\lg V)}=\frac{V}{\alpha}\times\frac{d\alpha}{dV}. \qquad (8)$$

Taking into account that during the measurements the polarizing bias exhibited only discrete values, changed every time within a constant step, the dependences (7) and (8) can be reformulated as below:

$$\alpha\left(\frac{V_n+V_{n+1}}{2}\right)=\frac{V_{n+1}+V_n}{V_{n+1}-V_n}\times\frac{I_{n+1}-I_n}{I_{n+1}+I_n}, \qquad (9)$$

$$\gamma\left(\frac{V_k+V_{k+1}}{2}\right)=\frac{V_{k+1}+V_k}{V_{k+1}-V_k}\times\frac{\alpha_{k+1}-\alpha_k}{\alpha_{k+1}+\alpha_k}, \qquad (10)$$

where $V_k=\dfrac{V_{n+1}+V_n}{2}$.

Further, for the fact that both: α and γ stand for the exponents in the expressions of $I(V)\propto V^{\alpha}$ and $I(V)\propto \exp\left(V^{\gamma}\right)$, while inspecting the junction *I-V* dependence, one can find therein the areas, in which one of the parameters, either α (V) or γ (V) remains constant. In such areas the *I-V* characteristics can be fairly well approximated with a power or exponential law, respectively. With the use of above procedure the following generation/recombination mechanisms, responsible for carrier transport in the junction can be defined (based on: [Lampert CIS70, Baron SSM70, Ciach SEM03, Zyuganov JCTE87, VolodinSC98]):

- **Ohm's law. Injection limited current** (**ILC**). The I-V characteristics becomes linear when the carrier concentration in semiconductor reaches the concentration in electrical contact (electrode). In such a case $\alpha = \mathbf{1}$;
- **Weak injection** of carriers through the contact ($\mathbf{1} < \alpha < \mathbf{1.5}$);
- **Double injection in semiconductor; bimolecular recombination** of carriers with efficiency given by $R = \gamma_r np$, where γ_r stands for the recombination coefficient, whereas n and p denote electron and hole concentration, respectively. For $n \approx p$ one obtains $R = \gamma_r n^2 = \gamma_r p^2$. In case of this mechanism $\alpha = \mathbf{1.5}$;
- **Monopolar injection in semiconductor** or dielectric with or without traps. Transport limited by **effective trapping**. In this regime the recombination rate is given by either $R = \tau_n / n$ or $R = \tau_p / p$, where τ_n and τ_p stand for the lifetimes of electrons and holes, respectively. For the case of this regime $\alpha = \mathbf{2}$;
- Transport limited by **trapping** (for **injection of one type of carriers**) or **recombination** (for **injection of their both types**). This regime imposes the condition of $\alpha > \mathbf{2}$;
- Super-high **double injection** regime with $\alpha = \mathbf{4}$.

From the presented list of transport mechanisms it can be seen that the differential approach applied to the theoretical analysis of current-voltage characteristics of rectifying structures equipped with the dielectric interlayer, as considered in the paper [**H6**] from the habilitation cycle, should allow drawing consistent conclusions concerning the physical phenomena influencing the transport processes in so-modified structures. This remark pertains to both: the Schottky junctions described in [**H6**] and previously discussed ZnO-based homojunctions ([**H3**], [**H4**]).

Concerning the short characterization of vertical ZnO/HfO$_2$/Ag structures, it should be stressed that their room temperature parameters were estimated through the fitting of experimental I-V data with the Shockley formula (4) transformed into (11):

$$V(I) = \frac{\eta k T}{q} \ln\left(\frac{I}{I_0} + 1\right) + I R_S . \tag{11}$$

Such transformation yields the explicit expression for the current I, thus, making the earlier-mentioned simplifications dispensable. This is for the fact that fitting the curve of the general form:

$$y(x) = A \ln(Bx + 1) + Cx , \tag{12}$$

to the experimentally obtained I-V dependences enables finding the η, I_0, R_S as well as the Schottky barrier height φ_B values directly. For the examined set of diodes they are gathered in Table 2. (after the paper [**H6**]).

Having a look at Table 2., the Reader can notice that vertical ZnO/HfO$_2$/Ag Schottky junctions reveal φ_B at the level of 0.6 – 0.7 eV, thus very similar to the planar ones. As can be deduced from the papers by Ip *et al.* ([Ip JCG06]) as well as Schifano *et al.* ([Schifano APL09]) such values are typical for the ZnO-based Schottky diodes owing to the influence of surface

HfO_2 thickness (nm)	Schottky barrier φ_B (eV)	Series resistance R_S (Ω)	Saturation current I_0 (A)	Ideality factor η	Rectification ratio I_{ON}/I_{OFF}
0	0.56	14.51 ± 0.94	$(8.67 \pm 1.49) \times 10^{-6}$	5.10 ± 0.19	9.87×10^{1} (±1.5V)
1.25	0.59	52.67 ± 6.50	$(2.06 \pm 0.36) \times 10^{-6}$	6.51 ± 0.25	2.26×10^{3} (±2.5V)
2.50	0.69	2.77 ± 1.04	$(5.83 \pm 3.00) \times 10^{-8}$	5.30 ± 0.38	1.73×10^{5} (±2.5V)
5.00	0.63	5.95 ± 0.66	$(4.64 \pm 1.77) \times 10^{-7}$	5.27 ± 0.30	3.12×10^{3} (±2.5V)
7.50	0.60	165.61 ± 6.17	$(1.67 \pm 0.09) \times 10^{-7}$	9.79 ± 0.14	7.44×10^{3} (±2.5V)

Table 2. Set of the basic parameters of $ZnO/HfO_2/Ag$ junctions constructed according to the vertical architecture. The appropriate theoretical modeling was made using the Shockley equation (4) in the form of (11) – see the related description in the text.

states in this material[25]. Noteworthy, for the vertical Schottky diodes the best parameters were also observed after capping the ZnO surface with the HfO_2 film of about 2.5 nm thick, right before the silver electrode evaporation. However, in this case the thing of particular importance is the obtained remarkable decrease (2 orders of magnitude when compared to the diode deprived of HfO_2 cover) in saturation current combined with very small series resistance (below 3 Ω) and substantially enhanced rectification ratio, reaching 1.7×10^5 for ± 2.5 V of polarizing voltage (see Fig. 12.). The increased value of η indicates, in turn, the necessity of taking into account several different mechanisms governing the electrical transport processes in the examined structure [*Schifano APL09, Tung MSE01*].

The analysis of α and γ parameters' behavior, performed hereafter for both directions of $ZnO/HfO_2/Ag$ diode polarization (see Figs. 13a. – k. and 14a. – f.) allowed to have a closer insight into the role of HfO_2 interlayer (0 – 7.5 nm) in the charge transfer processes. As can be noticed in Figs. 13b. and 14b., presenting the changes of α value in the junctions deprived of interlayer, in their case this parameter locates in the range of $\alpha > 1$ for the whole range of applied bias in both directions. Additionally (see Fig. 13c.), the value of $\gamma \approx 0.65$ is observed for low forward bias, being an evidence of nearly exponential shape of this part of *I-V* characteristics. However, not clearly exponential due to $\gamma < 1$. Moreover, as a result of extrapolation of the linear variability of α parameter towards V = 0V in the range of low voltages, a cut-off voltage of $V_{cut\text{-}forward} = 0.1$ V as well as $V_{cut\text{-}reverse} = -0.26$ V (for the forward and reverse polarization, respectively – see Figs. 13b. and 14b.) can be seen proving the coexistence of several competitive carrier transport mechanisms. The given facts are a kind of indication that facilitates explaining quite small (i.e. about 20, see Fig. 12.) rectification ratio of a described diode, when polarized with a voltage below ± 1 V. Another interesting feature in this context is the value of $\alpha = 4$ (see Fig. 13b) revealed for higher polarization voltages and finding its reflection in the saturation of the I_{ON}/I_{OFF} ratio. Such behavior is a proper one for the super-high double injection regime [*Ciach SEM03, Zyuganov JCTE87, Volodin SC98*].

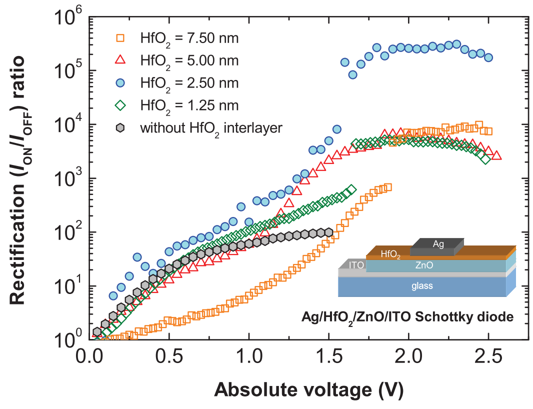

Fig. 12. Variability of the rectification ratio of examined $ITO/ZnO/HfO_2/Ag$ junctions constructed in the vertical architecture, dependently on the thickness of dielectric material and polarization voltage. Figure reprinted from the paper [**H6**].

---

[25] See also the *Introduction* section (§ III.1.)

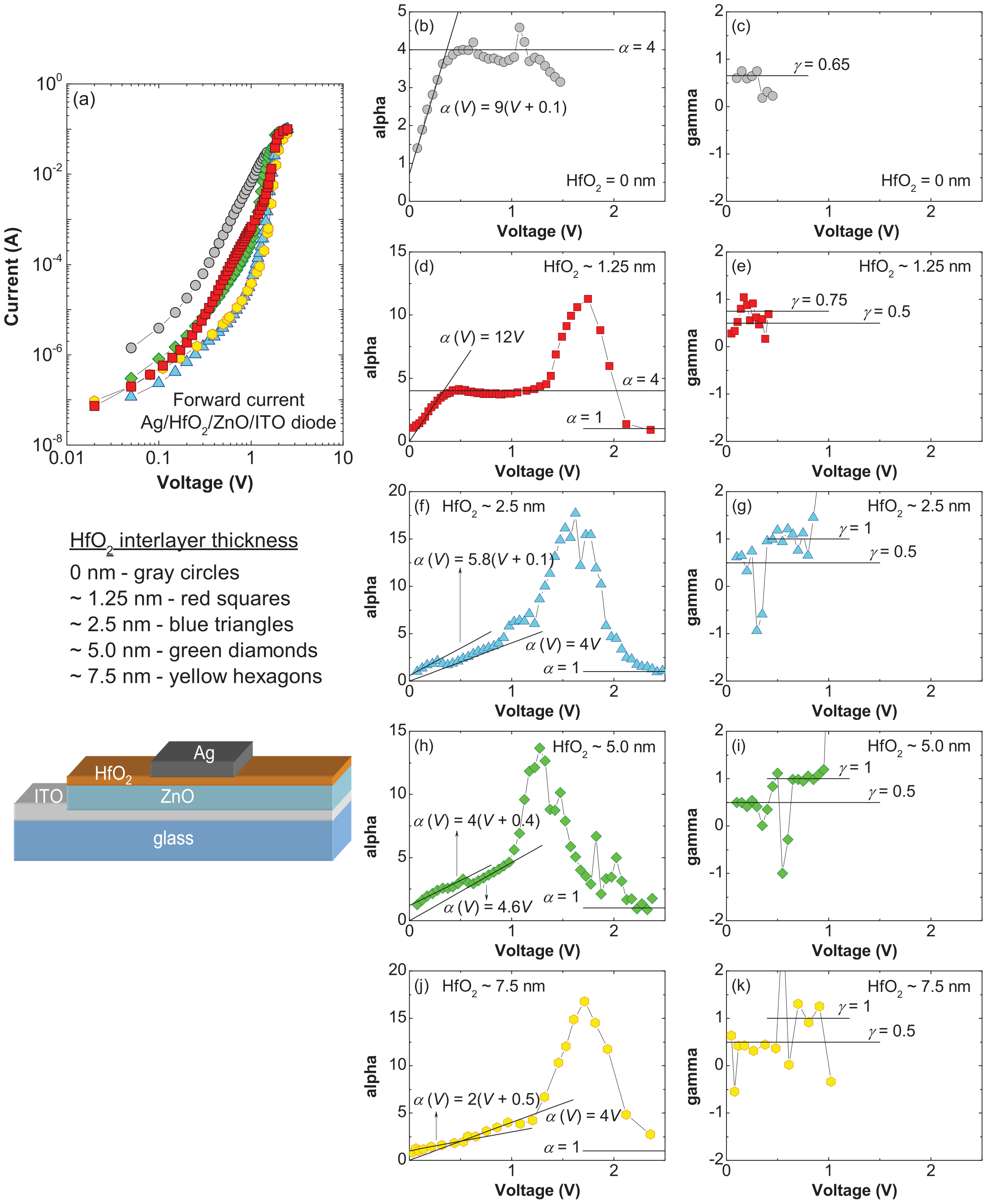

Fig. 13. The first (α) and second (γ) order dimensionless derivatives of room temperature forward current-voltage characteristics of ITO/ZnO/HfO_2/Ag junctions (see the scheme) for various (as indicated) thicknesses of HfO_2 interlayer separating the ZnO film from metallic (Ag) electrode. In panel (a) the forward parts of *I-V* characteristics of examined junctions are presented. Figure reprinted from the paper [**H6**].

The application of 1.25 nm thick HfO_2 interlayer to the ZnO/HfO_2/Ag diode does not change its *I-V* characteristics fundamentally. The relevant improvement of rectifying properties is still not observed ($0.5 < \gamma < 0.75$); in the forward direction the transport under super-high injection conditions takes place (see Figs. 13d., e.). On the other hand, while analyzing the reverse current flow, in the range of low voltages (up to -1 V), the range of $\alpha_{const} = 1.5$ was found (Fig. 14c), revealing the influence of efficient bipolar recombination that occurs for similar concentration of majority and minority carriers. Such behavior contributes

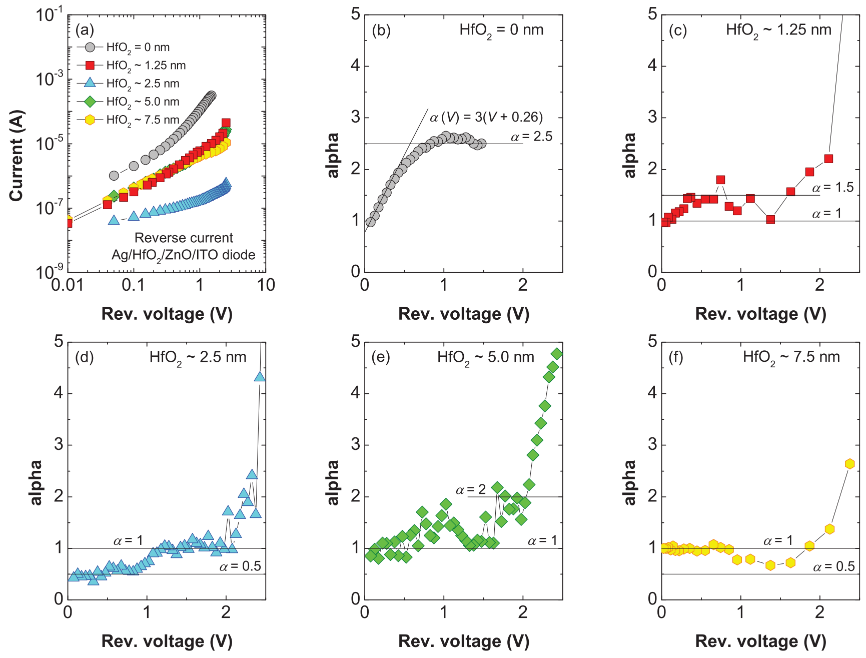

Fig. 14. The first order dimensionless derivative (α) of room temperature reverse current-voltage characteristics of ITO/ZnO/HfO_2/Ag junctions for various (as indicated) thicknesses of HfO_2 interlayer separating the ZnO film from metallic (Ag) electrode. In panel (a) the reverse parts of *I-V* characteristics of examined junctions are presented. Figure reprinted from the paper [**H6**].

to the quicker operation of the diode due to the absence of a counter field of space charge [*Lampert CIS70, Baron SSM70*].

The noticeable difference in *I-V* characteristics appears, however, as a result of insertion of about 2.5 nm of HfO_2 film. As seen in Figs. 13f., g. as well as 14d., the linearity of α parameter in low forward bias can be well approximated by the dependence of $\alpha(V) = 4V$. Besides, here also $\gamma = 1$ occurs, proving the clearly exponential run of *I-V* characteristics in this area. Considering the behavior of α in the reverse direction, a wide range of bias with $\alpha_{const} = 0.5$ can be noticed (Fig. 14d.). These together result in the rectification ratio of the order of 10^5 (see Fig. 12.). Such a case of nearly ideal behavior of diode parameters ensures the stable carrier injection and, thus, good rectifying properties.

The further augmentation of HfO_2 interlayer thickness up to about 5 nm results in the increase in carrier injection, particularly at low reverse bias ($0 < V < -1$V) and decay/saturation of rectification ratio in this range (as then $\alpha \rightarrow 1$ occurs – see Fig. 14e). However, the increase in polarizing bias up to about 1 V enforces the linear behavior of α parameter in the forward direction that can be approximated with the equation of $\alpha(V) = 4.6V$ with simultaneous $\gamma = 1$ (Figs. 13h., i.). Besides, in this range (for the reverse polarization) $\alpha = 2$ can be seen, indicating the necessity of taking into account the role of trap states existing in the HfO_2 interlayer, while describing the electrical transport [*Ciach SEM03, Łuka OE15*]. Phenomenon of the carrier trapping in HfO_2 material affects beneficially the junction's rectification ratio in the mentioned range of applied polarizing voltages, increasing it to the order of 10^3 (see Fig. 12.).

In case of the last tested thickness of dielectric interlayer (7.5 nm) the junction behavior close to the one described above (for HfO_2 = 5 nm) has been noticed, i.e. $\gamma = 1$ for the forward bias exceeding $V = 1$ V, accompanied by $\alpha = 0.5$ for the same range in reverse direction (see Figs. 13j., k. and 14f., respectively). This resulted in the increase in rectification ratio of the examined junction to the values of the order of $10^2 - 10^3$ for the polarizing bias higher than ± 1 V.

The carried out differential analysis of the behavior of vertically-constructed ITO/ZnO/HfO_2/Ag diode has evidently proven the justness of HfO_2 use as an interlayer leading to the substantial improvement of its parameters. Nevertheless, such an approach is impossible unless the optimization of a dielectric material growth process is carefully made, combined with a selection of its appropriate thickness. Comparing the results obtained for

Schottky junctions with the ones gathered for the experimental *I-V* data of ZnO-based homojunctions discussed in the papers [**H3**] and [**H4**] provides, in turn, the equally interesting research material, from which the respective conclusions will be shortly presented below.

As it has already been mentioned in §3.2., the Al_2O_3 interlayer separating ZnO homojunction parts plays a double role: in case of ZnO:N/ZnO diode containing the doped layer at the bottom of the structure it protects from the possible nitrogen diffusion to its top (intentionally undoped) part, whereas in the ZnO:(N, Al)/ZnO diode, apart from the above, may beneficially affect the carrier concentration in *n*-ZnO layer by increasing its electron conductivity due to the presence of aluminum.

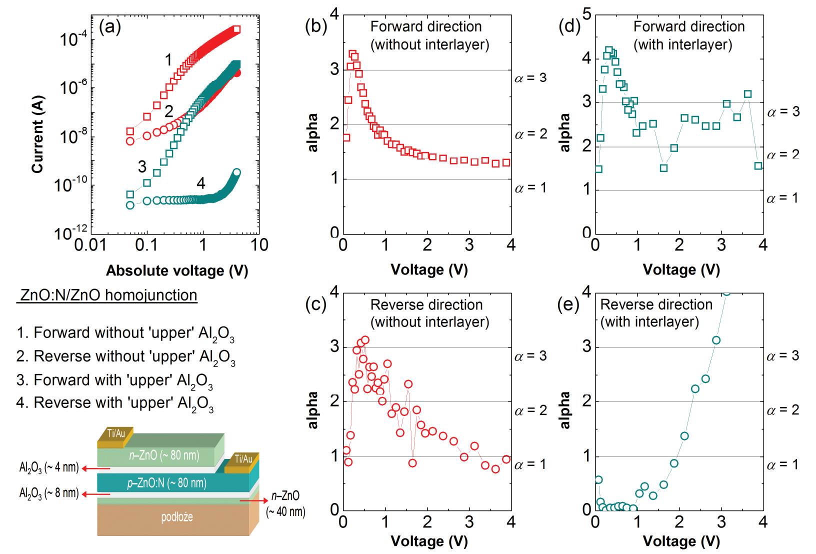

Fig. 15. Theoretical analysis of the *I*–*V* characteristics (see panel (a)) of ZnO:N/Al_2O_3/ZnO homojunction (depicted in the scheme) according to the *differential approach*. As presented, the insertion of dielectric interlayer between the structure parts enables the increase in its rectification ratio reaching 2 – 3 orders of magnitude, owing to the effective charge trapping in the dielectric film and monopolar injection of carriers (manifested by $\alpha \geq 2$ in panels (d) and (e) of the illustration). In case of lack of the interlayer, the junction works in the weak injection regime with its characteristics exhibiting nearly ohmic behavior ($\alpha \rightarrow 1 - 1.5$ for both polarization directions – see panels (b) and (c)). Figure reprinted from the paper [**H6**].

The analysis of *I-V* characteristics of the two kinds of homodiodes (deprived of dielectric interlayer as well as involving 4nm thick Al_2O_3 film) with the differential approach (see Figs. 15a. – e.) shows that applying the forward bias of $V > 1$ V to the junction without dielectric leads to the stabilization of α parameter at the level of $1 < \alpha < 1.5$ (as depicted in Fig. 15b.), indicating the junction working in the weak injection regime [*Ciach SEM03*]. This, in turn might explain its relatively small rectification, of the order of 10^2. The further increase in applied bias, substantially above ± 1 V causes the convergence of α to the limit of $\alpha \rightarrow 1$, corresponding to the decay of I_{ON}/I_{OFF} ratio, thus linear *I-V* characteristics (as noticeable for both polarization directions – see Fig. 15b, c.). According to the suggestions given in the related literature, the reason for such behavior can be the high recombination barrier which forms by local states in the forbidden gap. The existing approaches towards overcoming this issue are the following: (*i*) enhancement the injection of charge carriers from both contacts, (*ii*) decreasing the concentration of local trapping states through the better control of semiconductor structural quality and (*iii*) increasing the polarization voltage. However, it is worth-stressing that the low-voltage conditions of the examined junctions' performance (stemming from their low breakdown limit, which is around 4 V – see Fig. 15a.) make the latter option a slightly debatable one. Nevertheless, the issues of possible influencing the structural quality of used ZnO films as well as appropriate selection and preparation method of contact metallization are left open for discussion.

The situation is utterly different after separating the homojunction parts with 4 nm thick Al_2O_3 layer. As can be seen in Figs. 15d. and 15e., in such a case applying the forward bias exceeding 1 V stabilizes the value of α in the vicinity of $2 < \alpha < 3$ (Fig. 15d.), being an evidence for the occurring efficient monopolar injection, very likely assisted by a partial tunneling of the carriers through the Al_2O_3 layer containing the traps. In such a case the appearance of electrical transport governed by the *space-charge limited current (SCLC)* regime may be expected, enabling the description of diode *I-V* characteristics by the power law dependence, i.e. $I \propto V^{\alpha}$ with $\alpha = 2$ [*Ciach SEM03, Łuka OE15, Yang AM12*].

In parallel, the reverse structure polarization with a bias from -1 V to -3 V implies the α values in the vicinity of α = 1 or below (see Fig. 15e.), giving the reason for the observed remarkably high ($4–5\times10^5$ achieved for $V = \pm 2$V) I_{ON}/I_{OFF} ratio. Moreover, the noticed behavior of α parameter allows the assumption that the space charge formed at the local states in dielectric restricts the injection of minority carriers into the Al_2O_3 layer, contributing this way to the stabilization of junction performance. Furthermore, it should be mentioned that due to the application of dielectric interlayer in both: ZnO-based homojunctions as well as the earlier discussed *m-s* diodes, the substantially low saturation current ($I_0 \approx 50$ nA) was achievable, additionally making these structures promising ones for electronic applications.

In conclusion to this part of the summary it may be affirmed that the theoretical analysis of current-voltage characteristics of Schottky diodes and ZnO homojunctions carried out with taking an advantage of differential approach proved that the insertion of thin dielectric interlayers (either HfO_2 or Al_2O_3) can be the solution affecting beneficially their electrical parameters. However, for this purpose a precondition of precise optimization of complex growth process, aimed mainly at ensuring good interface quality between the coated semiconductor and metallic electrode (Schottky junctions) as well as effective and controllable doping (ZnO homodiodes) has to be fulfilled.

Other very interesting alternative allowing the advantageous use of charge trapping phenomenon in dielectric materials is applying them to the construction of *charge trapping memory (CTM)* elements. The concise characterization of such type of devices will be included in the last part of scientific accomplishment description. These issues have also been wider discussed in the paper [**H7**].

3.4. Charge trapping as a fundamental phenomenon for the performance of *CTM* memory elements ([H7])

As mentioned in the *Introduction* section, a very important feature of the class of materials known as high-*k* oxides (such as e.g. HfO_2 or Al_2O_3) is the presence of numerous states that are able to trap the charge carriers. This fact can be used while constructing the *charge trapping memory (CTM)* elements, gathering the increasing interest in the modern electronics. The motivation for including the related problems into the habilitation cycle was based on the intention to verify the possibility of an efficient external control of trapping mechanism which, in turn, would allow obtaining a relatively full view on the role of dielectric interlayers in previously analyzed rectifying junctions (see §§3.2. and 3.3.).

The experimental studies of CTM devices (which broader context is demonstrated in the paper [**H7**]) have been carried out during the research stays of the Applicant at the Institute of Solid State Physics of the Bulgarian Academy of Sciences (ISSP-BAS) in Sofia, realized from 2015 to 2017. Here, it ought to be stressed that the fruitful bilateral cooperation between the related group from ISSP-BAS and ON4.2 team of IP PAS is nowadays continued.

The growth of HfO_2/Al_2O_3 structures on Si:B (*p*-type) substrates exhibiting the resistivity of about 6 Ω.cm ($p \approx 2.2\times10^{15}$ cm^{-3}) were preformed by the ALD method at 135°C, according to the reactions given by the Eq. (2) and (3). Their growth parameters and qualitative sketch are gathered in Table 3. and depicted in the top panel of Fig. 16., respectively.

Sample number	ALD cycles		HfO_2/Al_2O_3 repetition	Sublayer thickness (nm)		Total stack thickness	HfO_2/Al_2O_3 ratio	Sample designation according to the stack buildup
	HfO_2	Al_2O_3	(*n*)	HfO_2	Al_2O_3	(nm)		
S2167 (1)	30	10	5	4.2	1	26	4.2	5×(30:10)
S2168 (2)	20	10	5	2.8	1	19	2.8	5×(20:10)
S2169 (3)	20	5	5	2.8	0.5	16.5	5.6	5×(20:5)
S2170 (4)	20	5	10	2.8	0.5	33	5.6	10×(20:5)
S2171 (5)	20	2	5	2.8	0.2	15	14	5×(20:2)

Table 3. Growth parameters of the five examined HfO_2/Al_2O_3 CTM structures – see also the scheme from Fig. 16. The thickness of sublayers contributing to the given structure remained unchanged. For the further details – see the respective parts of the text. Table reprinted from the paper [**H7**].

After obtaining the structures according to Table 3., part of them was subjected to the RTP annealing, respectively, in the oxygen- and nitrogen-rich atmospheres (1 min. at 800°C) as well as – for comparison – to the 20 minutes long furnace annealing in air at 600°C. The electrical metallization (Al) was made with the use of vacuum evaporation technique. Additionally, the top Al electrodes (gates) were patterned by photolithography to the square shape with an area of 10^{-4} cm^2.

The charge trapping properties of HfO_2/Al_2O_3 nanolaminated stacks were examined by acquiring their dark capacitance-voltage *(C-V)* characteristics with the used of 1 MHz probing voltage signal. Directly before the *C-V* acquisition, the square positive ($+V_p$) and negative ($-V_p$) voltage pulses of one second-long and different amplitudes were applied to the top Al electrode of the structures (see the scheme presented in the top panel of Fig. 16.). In parallel, the backside aluminum electrode was left grounded. The *C-V* measurement was carried out after each voltage pulse and the shift of the *C-V* curve (the applied gate voltage *V*, at which the capacitance equals to 20pF) was determined as the so-called *memory window* Δ*V* (see the sketch given in Fig. 16a.). The examples of real memory window measurements performed on the stack described as 5×30:10 – see Table 3., subjected to the RTP annealing in oxygen atmosphere are presented in Fig. 16b. During the characterization the pulses with the amplitude of ±5V, ±10V and ±15V were used, limiting the maximal value to ± 20 V with regard to the possible breakdown of the device.

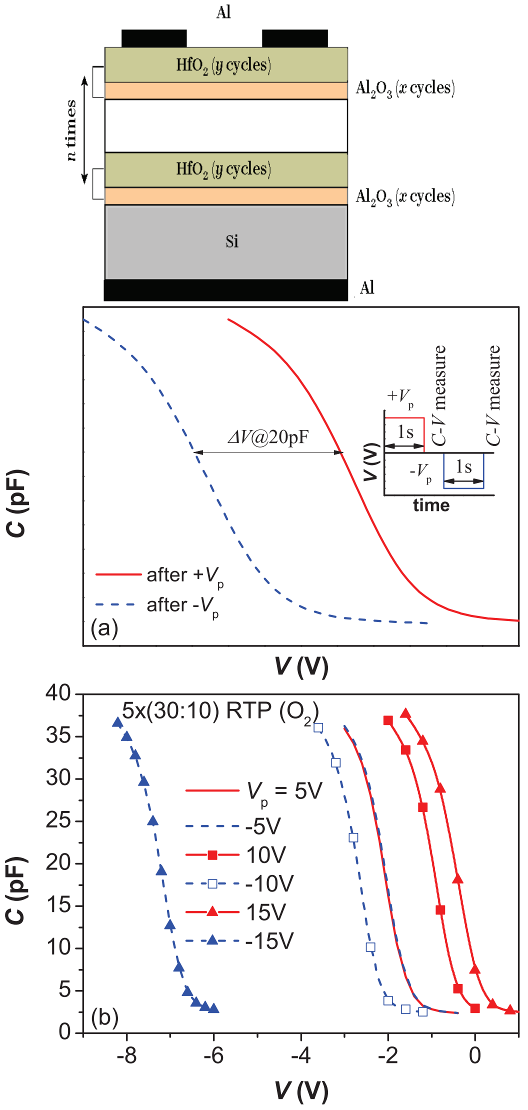

Fig. 16. Scheme of the examined HfO_2/Al_2O_3 (CTM) stacks together with the illustration of memory window measurement (a) and example of the real *C-V* data for 5×(30:10) stack, after its RTP annealing in oxygen (b). Figure reprinted from the paper [**H7**].

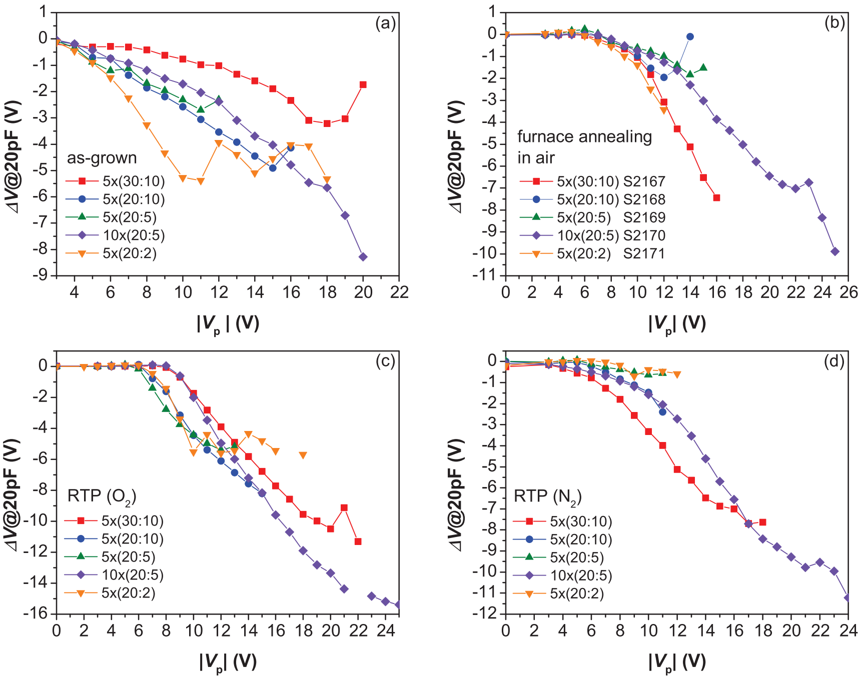

Fig. 17. Memory windows (ΔV) of the multilayered HfO_2/Al_2O_3 stacks (without the thermal treatment (a) and subjected to different temperature processing (b) – (d)) as a function of absolute value of the applied voltage pulse magnitude. The width of memory window is given for the reference capacitance of 20pF. The structures are marked according to the Table 3. Figure reprinted from the paper [**H7**].

As can be noticed from Fig. 17., presenting the width changes of memory windows in the analyzed multilayers dependently on the voltage pulse amplitude, ΔV is mainly influenced by the two most relevant factors, i.e.: Al_2O_3-to-HfO_2 thickness ratio (thus, the total stack thickness) as well as the annealing method and its ambient. Regarding this, the initial observations can be formed as follows:

- ✧ Structures not subjected to the RTP treatment exhibit definitely different electrical behavior than the annealed ones;
- ✧ The widest memory window can be obtained applying the thermal treatment in oxygen-rich atmosphere. In the stacks containing thinner Al_2O_3 films a saturation of ΔV occurs, suggesting the direct influence of this material on the charge trapping phenomenon;
- ✧ In case of annealing in the nitrogen ambient the structures reveal very small memory effect, observable for the absolute values of pulse amplitude below 14V.

The noticed hysteresis of *C-V* curves (see also Fig. 16b.) stems from the following physical processes: (*i*) injection and trapping of electrons/holes in the existent traps under positive/negative voltage pulse and (*ii*) charge generation as a result of stress attributed to the additional, high electric field, being a consequence of the pulse application. Here, it should be mentioned that first of these two phenomena, as a reversible process may be used for the program/erase operation of the CTM device, whereas the second one (as a permanent and irreversible degradation) with the lapse of time leads ultimately to the deterioration of CTM performance and, consequently, to its breakdown.

To shed some light on the contribution of these processes to the width of stacks' memory windows, a shift in their *C-V* characteristics induced by the applied voltage pulse V_p with an appropriate sign has been analyzed. This was done with regard to the initial position of the *C-V* curve, V_0, recorded in the absence of external pulse before the measurement. The

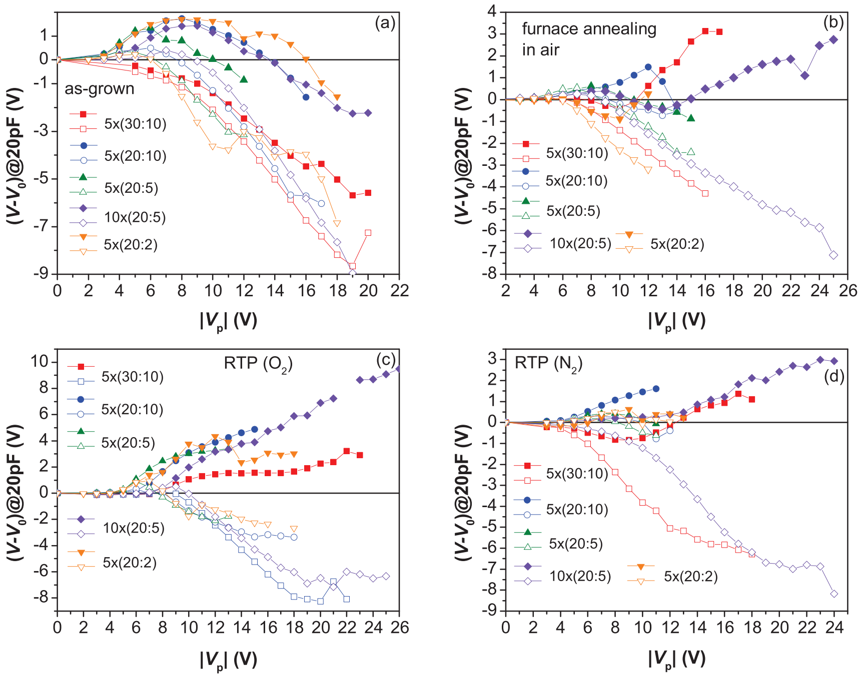

Fig. 18. Evolution of the V-V_0 shift of the C-V characteristics of HfO_2/Al_2O_3 CTM devices with respect to their initial position V_0.. Figure depicts the shift versus the absolute value of applied voltage pulse magnitude V_p as obtained for the reference capacitance of 20pF. In panel (a) the results gathered for the as grown structures are shown, whereas in panels (b)-(d) – for the samples subjected to the indicated thermal treatment. The stacks are designated according to Table 3. The full symbols refer to $+V_p$, pulse , whereas the empty (hollow) ones – to $-V_p$ pulse. Figure reprinted from the paper [**H7**].

respective results, as a dependence of V-V_0 difference versus the absolute voltage pulse magnitude are gathered in Fig. 18. The experiment has been carried out both: on the as grown structures as well as on the ones that have been pre-annealed in the above-mentioned conditions.

As can be concluded from Fig. 18a., in the **as grown** stacks the $+V_p$ pulse from the range of 5 – 14V causes electron trapping, visible as the C-V curve shift (V-V_0) with regard to the initial state reaching approximately +2V for V_p = 10V. Interestingly, this remark does not pertain to the structure containing 30 ALD cycles of HfO_2 (i.e., S2167 (1)), which does not reveal such an effect. The reason for this behavior is likely related to the competing (present next to the electron trapping) process of positive charge generation, induced by the stress caused by the $+V_p$ pulse. This phenomenon is efficient enough to "obscure" the electron trapping under higher $+V_p$ amplitudes. This, in turn, results in the positive net charge in the stack, despite the electron injection, in fact. Moreover, the increasing positive charge with increasing amplitude of V_p (for its both signs) allows the assertion that at least a part of trapped carriers is related to the presence of positively charged defects, resulting from the existing stress. The latter fact leads to progressive degradation of the described structure. On this basis, it can be concluded that the as grown stacks are more vulnerable to the stress-induced damages.

For the case of multilayers **annealed in oxygen- and nitrogen-rich atmospheres**, it was remarked that (see, Figs. 18c., d.) the biggest C-V curve shift, caused by the $-V_p$ pulse (thus, denoting the most effective holes' trapping) concerns the structures containing the thickest HfO_2 layers (involving 30 and 20 ALD cycles, i.e., S2167 (1) and S2170 (4)). Further, as it seems based on the obtained results, the efficiency of hole trapping process is not strictly dependent on the Al_2O_3 film thickness (the remaining stacks that contain 20 ALD cycles thick HfO_2 material exhibit similar behavior, irrespectively to the number of Al_2O_3 cycles). Concluding, it may be stated that hole trapping phenomenon appears dominantly in the HfO_2 material.

Furthermore, Fig. 18c. indicates that **annealing** the stacks in **oxygen-rich conditions** results in the **intense electron trapping** – a stable electron traps' generation, contributing substantially to the memory window widening begins already for small amplitudes of the $+V_p$ pulse. Simultaneously, the hole trapping, practically does not occur for the $-V_p$ not exceeding V_p = -(9 – 10V). As a result of oxygen annealing, the electron trapping efficiency outweighs hole trapping in all examined structures but the ones containing the thickest HfO_2 films (of 30 growth cycles). Moreover, the positive charge (hole) trapping process tends to saturate in all oxygen-annealed stacks, with increasing the amplitude of $-V_p$ pulse, suggesting this way more significant role of the already existing traps when compared to the similar states related to the stress induced by the applied voltage pulse.

The data presented in Fig. 18d., concerning the efficiency of carrier trapping after the **RTP annealing in nitrogen** demonstrate that the capture almost does not appear for the applied pulse amplitudes lower than ±12 – ±14V, if referring to the structures with the thinner HfO_2 and Al_2O_3 films. However, the increased tendency to trap the positive charge (holes) can be noticed for increasing thickness of both dielectrics in the stack as well as the bigger voltage pulse amplitude.

The results obtained after the **furnace annealing** of the examined samples **in air** (see Fig. 18b.), show that in this case the trapping process of both types of carriers can be initiated with the voltage pulse higher than about ±6V. Noteworthy, when compared to the as grown stacks, the furnace treatment slightly favors the electron trapping phenomenon, being more distinct for increasing V_p amplitude in the structures containing thicker dielectric films.

Hence, the above observations give a reasonable argument confirming the justness of dielectric interlayers' application in the junction considered in frames of the papers [H3] – [H6] **from the habilitation cycle, explaining simultaneously the physical mechanism of their performance. This, in turn allows understanding the noticeable improvement of the diodes' rectifying properties. However, the precondition that has to be fulfilled is a proper adjustment of growth process parameters as well as dielectric material thickness. The carried out investigations demonstrate also another reason, for which RTP annealing in oxygen is claimed to be one of the most effective approaches enabling the long-term stabilization of the electrical parameters of earlier-discussed ZnO:N/ZnO homojunctions with dielectric interlayer.**

The issue of charge trapping persistence in the examined capacitor-like structures has been analyzed separately, scrutinizing their retention and endurance characteristics (the details of respective measurements the Reader can find in the paper [**H7**]).

Judging from the long-term approximation of retention characteristics projected for the period of ten years from the sample fabrication it can be concluded that the release of negative charge is slightly faster than the positive one, however after a decade the stacks still retain (or – to be more exact – should retain) about 50 % of the initial memory window ΔV. As it has also been noticed, the time dependence of detrapping of both types of carriers cannot be described using a simple exponential decay, as in case of positive charge the kinetics behavior reveal rather the logarithmic character. Searching for the physical source of such situation, the relevance of carrier tunneling process from the dielectric layers to the substrate may be considered [*McWhorter TNS90, Kamohara ApSS08*], however, the decisive answer to this question would require the profound analysis carried out in the wide range of temperatures.

The discussion of negative charge detrapping kinetics is more complicated. One of the concepts being nowadays considered is based on taking into account the Poole – Frenkel mechanism, however, as indicated in the work by J. J. Chen *et al.* [*Chen Wiley-NMT08*], distinguishing between the particular mechanisms of positive and negative charge detrapping can cause difficulties, regarding the different origin (character) of trapping states for electrons and holes. Moreover, considering the Poole – Frenkel mechanism as the one governing the detrapping effect in the analyzed HfO_2/Al_2O_3 stacks imposes the condition that the electron traps should be shallow enough (located in the upper part of the dielectric bandgap) to enable their emptying assisted by the electric field already at room temperature. This issue will anyhow be subjected to further investigations.

The slight instability of electron trapping noticed in the endurance characteristics of the multilayers, particularly for the smaller number of "verifying" cycles of voltage pulses[26], indicates, in turn, that prior to the proper characterization the stacks should undergo a certain "training" aimed at achieving their electrical behavior stability. As shown in [**H7**], while increasing the number of $\pm V_p$ cycles, one can, however, remark that a slow but progressive decrease in the electron trapping ability occurs, observable as a diminishing width of the device memory window ΔV [*Grossi Springer16*]. This can be an evidence of the gradual decrease in the CTM performance quality (thus, limited number of program/erase operations), constituting a complement for the conclusions drawn from the behavior of retention characteristics.

4. Summary of the cycle of publications [H1]–[H7]. The most significant research achievements

Quest for the possibly full description of the electrical properties of junction structures involving thin zinc oxide films obtained by the ALD technique were started from the optical (photoluminescent) as well as electrical studies of the defect structure of ZnO itself. This is for the fact that the respective literature data are, despite their abundance, in many aspects still discrepant, making their clear interpretation a puzzling problem.

On the other hand, without understanding the specificity of native defects and their contribution to the electrical conductivity of ZnO thin films it is almost impossible to discuss the charge transport mechanisms in more advanced structures, what constituted, actually, a goal of the presented construction of habilitation cycle. Hence, basing on the optical and electrical investigations carried out at room temperature on a series of thin ALD-ZnO films deposited between 100°C and 200°C, the *n*-ZnO/*p*-GaN heterojunction has been constructed, used subsequently for the measurements involving the methods relying on the observation of capacitance relaxation kinetics of such diode. This allowed, in turn, an insight into the defect structure of ZnO in the range of temperatures from 77 K to 330 K.

Results of the above experiments have appeared to be extremely significant for constructing the ZnO:N/ZnO and ZnO:(N, Al)/ZnO homojunctions as well as the ZnO/Ag Schottky diodes. While making an effort towards the optimization of their electrical parameters, mainly focused on obtaining the highest possible rectification ratio with the simultaneously protected low ideality factor, a number of technological modifications were tested. These involved such solutions as: ZnO films codoping or their RTP annealing in the appropriately adjusted conditions (homojunctions), changes in the junctions' architecture from vertical to planar one (ZnO/Ag diodes) or the insertion of thin dielectric film passivating the ZnO surface under the metallic electrode (HfO_2 in Schottky rectifiers) or constituting the buffer layer separating the structure parts (Al_2O_3 in ZnO-based homojunctions).

---

[26] The acquisition of endurance characteristics of HfO_2/Al_2O_3 multilayers was based on the alternate (cyclic) application of one second-long $+V_p$ and $-V_p$ pulses followed by the observation of *C*-*V* curve shift stability for the reference capacitance of 20pF.

In course of investigations it has been noticed that dielectric interlayer is the element playing a particularly beneficial role in terms of the rectifying junctions' performance. Considering its influence on the carrier transport processes in the investigated structures, a thorough theoretical analysis of their *I-V* characteristics has been made, based e.g. on the differential approach. Additionally, the series of CTM stacks involving the multilayer consisting of the alternately deposited HfO_2 and Al_2O_3 dielectrics has been constructed to demonstrate the ability of effective control of existing transport mechanisms through steering the charge trapping processes in such structures. The latter was achievable due to the thermal treatment of CTM elements in appropriately adjusted temperature and ambient conditions.

According to the opinion of Applicant, the above-discussed cycle of seven scientific publications broadens the existing polemic focused on the analysis of various mechanisms responsible for the electrical transport in wide-band-gap materials-based structures. The most significant accomplishments of the cycle may be formed as follows:

✧ **Identification of the main types of native defects in intentionally undoped ALD-ZnO thin films deposited between 100°C and 200°C. This has been made with the use of room temperature photoluminescent measurements as well as electrical investigations in the temperature range of 77 – 330K – papers** [**H1**], [**H2**]

Paper [**H1**] demonstrates that the change of electrical parameters of the ALD-ZnO films obtained as a result of their RTP annealing (i.e. the substantial decrease in carrier concentration reaching three orders of magnitude when compared to the as grown material) is combined with the substantial modification of deep level emission (DLE) band intensity of the related room temperature PL spectra. The new (latest) results, achieved after the Ph.D. degree conferment, have shown that the RTP treatment of ZnO layers in nitrogen-rich conditions reveals the enhanced contribution to the DLE band peaked in the vicinity of 2.23 – 2.38 eV (~520 – 560nm), attributed in the literature to the presence of native defects in oxygen sublattice of ZnO (mainly V_O). Contrarily to the above, annealing of ZnO films in oxygen ambient yields the quenched luminescence in the mentioned area of visible green light (what might be ascribed to the diminished influence of oxygen vacancies – now partially filled), shifting its maximum towards lower energies (1.7 – 1.9 eV, i.e. ~650 – 730 nm), where the dominant contribution stems from the defects existing in the zinc sublattice (involving V_{Zn}). This has been proven by the performed detailed analysis of the RT PL spectra of examined layers deconvoluted into the Gaussian components within the energy range of $1.53 \leq E \leq 2.75$ eV, supported by the existing literature data.

The above remarks were subsequently used for the *n*-ZnO/*p*-GaN heterojunction (with the ZnO layer grown at 100°C) examination with the methods involving the profound study of its capacitance behavior, i.e. its relaxation kinetics as well as some elements of the admittance spectroscopy (see [**H2**]). Respective studies have confirmed the presence of defect level located about 0.54 – 0.60eV below the ZnO conduction band (assigned to the existent V_O defect therein). Moreover, these investigations allowed the detection of E_C–0.24eV level as well, frequently attributed to the interstitial zinc in ZnO.

Undoubtedly, the significant achievement of the papers [H1] **and** [H2] **is therefore a proof** (**due to the independent but complementary measurements, performed using two different techniques**) **that such native defects as V_O and V_{Zn} can remarkably affect the electrical properties of thin ALD-ZnO films. The**

importance of this contribution to the related scientific discussion has also been appreciated by the Editorial Board of *Journal of Applied Physics* in 2013 with a personal gratulatory letter handled to every Co-Author of the [H2] publication.

However, here it should be undoubtedly stressed that the studies presented in the current summary definitely do not exhaust the subject of ZnO defect structure analysis, which, taking into account the degree of its complexity, still remains the source of numerous interesting scientific reports.

✧ **Identification (basing on the conclusions from the papers [H1] and [H2]) of the factors giving the main contribution to the rectification effect observed on the ZnO-based homojunctions – publications [H3], [H4]**

Relying on the conclusions from the paper [**H1**] and [**H2**], in publications [**H3**] and [**H4**] it has been proven that constructing the ZnO:N/ZnO junction according to the appropriate architecture (i.e. with the ZnO:N layer as a bottom partner) and applying the adjusted thermal treatment conditions, the rectification ratio of about 2×10^2 for the polarizing voltage of ±2V can be achieved. **Further increase in the I_{ON}/I_{OFF} parameter was gained due to the insertion of thin dielectric film (4nm Al_2O_3), separating the homojunction parts, which resulted in the remarkable improvement of rectifying properties ($I_{ON}/I_{OFF} = 4\times10^4$ for ±2V). This is for the fact that such a solution prevented the whole device from the uncontrolled diffusion of nitrogen to the top ZnO layer in the lapse of time.**

Alternatively, a very similar effect can be obtained in the analogous structure containing the bottom ZnO layer codoped with nitrogen and aluminum (ZnO:(N, Al) – ANZO). **Owing the application of ANZO film in combination with Al_2O_3 interlayer, the necessity of post-growth RTP annealing of the codoped layer could be excluded, additionally simplifying the technological process. Importantly, the dielectric interlayer, because of the presence of Al affects beneficially (stabilizes) the demanded electron concentration in the top (*n*-ZnO) part of the homojunction.**

It should be mentioned that according to the existing literature data the results described in the habilitation achievement are currently among the best ones within the topic.

✧ **Description of the charge transport mechanisms in the rectifying structures by the theoretical modeling of their *I-V* characteristics according to the differential approach. Explanation of the influence of thermal treatment and construction modifications on the rectifying properties of ZnO/Ag Schottky diodes as well as ZnO-based homojunctions – papers [H5] and [H6]**

Assessing the beneficial influence of Al_2O_3 dielectric interlayer on the rectifying properties of ZnO-based homojunctions, in papers [**H5**] and [**H6**] its comparison was made with the effectiveness of HfO_2 material used for similar purposes in the ZnO/HfO_2/Ag diodes built in the planar and vertical configurations. **As demonstrated by the performed theoretical modeling of room temperature *I-V* characteristics of both types of structures according to the differential approach (see, paper [H6]), the monopolar injection assisted by the effective tunneling/trapping of charge carriers in a dielectric material (of 2.5 – 5nm thick) as well as the SCLC mechanism are mainly responsible for the desired modification of their transport properties.**

- ✧ **Demonstration of the relevant role of charge carriers' trapping in the transport processes existing in the junctions equipped with the dielectric layer passivating the semiconductor surface** (HfO_2 **in ZnO/Ag diodes) or separating** (Al_2O_3) **the homojunction parts. Proving, based on the analysis of electrical behavior of CTM memory elements, the possibility of effective steering of the charge trapping processes in these structures through the appropriate selection of their thermal treatment and electrical measurement conditions – papers** [**H5**] – [**H7**]

  Deeper insight into the problems described in publications [**H5**] and [**H6**] was possible owing to the analysis presented in the paper [**H7**] devoted to the discussion of electrical transport phenomena present in the CTM memory elements based on the HfO_2/Al_2O_3 multilayers. As shown therein, the post-growth annealing of such stacks in oxygen-rich conditions at adjusted temperatures leads to the particularly effective electron trapping in dielectric material, provided the voltage pulse of an appropriate amplitude is applied to the structure. **This is manifested through the widening of a memory window** ΔV **and the persistence of memory effect. Noteworthy, this observation is also of fundamental importance regarding the sought explanation of the positive role of dielectric interlayers in the earlier-described rectifying structures.**

According to the Applicant, the presented description of the scientific aim of the publications constituting the habilitation cycle entitled *"Junction structures involving thin zinc oxide films obtained by the Atomic Layer Deposition (ALD) technique"*, proves that the discussed issues (judging only from the progressively increasing number of related publications available in different databases) still do not lose their scientific attractiveness.

For this reason, the excerpt from the Applicant research activity presented in the current summary, with the results published so far in the journals listed in **Attachment 3** constitutes an individual contribution to the wider spectrum of available data. The above-mentioned problems are still the subject of live scientific discussion motivated by the perspective of use of analyzed materials in many branches of contemporary electronics.

The end of this part of the summary gives a short description of the Applicant personal contribution to each of the publications included in the habilitation cycle:

- ✧ **Publication** [**H1**]: Realization of all electrical and photoluminescent measurements on the examined films, analysis of the experimental results and redaction of the article text except from §§3.2.1 and 3.2.2. Contribution to setting the plan of experiments. Leading of the NCN project (UMO-2013/09/D/ST5/03879) that assured financial support of the research;
- ✧ **Publication** [**H2**]: Active contribution to planning the experiment (in cooperation with the second Co-Author – P. S.) and to making the electrical measurements of *n*-ZnO/*p*-GaN heterojunction as well as to the analysis of the obtained results. Besides, preparation of the article text;
- ✧ **Publication** [**H3**]: Performing the electrical studies of ZnO-based homojunction. Supervision (as a co-supervisor of Ph.D. thesis of M.Sc. D. Snigurenko) over the electrical measurements of thin ALD-ZnO films. Besides, participation in the analysis and interpretation of the obtained results and partial redaction of the article text, particularly its §3.3 concerning the electrical behavior of the examined homojunction. This also includes preparing a part of article figures, including Fig. 4. as a whole;

- ✧ **Publication** [**H4**]: Performing the electrical studies of ZnO-based homojunction. Supervision (as a co-supervisor of Ph.D. thesis of M.Sc. D. Snigurenko) over the electrical measurements of thin ALD-ZnO films. Making substantive comments and amendments to the article text, particularly concerning its part devoted to the electrical behavior of the examined homojunction. This also includes a participation in preparing a part of article figures as well as Fig. 5. as a whole. Moreover, leading of one of the NCN projects (UMO-2013/09/D/ST5/03879) that assured the financial support of the research;

- ✧ **Publication** [**H5**]: Contribution to planning (in cooperation with the paper first Author – A. J. Z.) the whole experiment. Performing all the electrical measurements of the described rectifying junctions. Partial redaction of the article text (i.e., fragments pertaining to the results of experimental studies – this also includes preparation of Fig. 1. as a whole). Active contribution to the discussion of theoretical fits performed by the first Author. Besides, leading of one of the NCN projects (UMO-2013/09/D/ST5/03879) that assured the financial support of the research;

- ✧ **Publication** [**H6**]: Planning the whole experiment, performing and interpretation of all electrical measurements of the investigated junctions. Discussion with the respective Co-Authors over the results of other characterization measurements carried out by Them on the ALD-ZnO layers used subsequently for the junctions' construction. In cooperation with the second Co-Author (P. S. S.) – active contribution to the theoretical modeling of the obtained rectifying structures and discussion of its results. Besides, redaction of the publication text and leading the NCN project (UMO-2013/09/D/ST5/03879) that assured the financial support of the research;

- ✧ **Publication** [**H7**]: Contribution to setting the plan of experimental work, performing on the obtained structures the measurements, which results were analyzed and depicted in Figs. 2 – 5. Contribution to the discussion and to the redaction of publication text. The respective experiments were carried out by the Applicant during his research stays in Sofia, described in details in paragraph III. L) of the **Attachment 3**.

IV. Discussion of the remaining scientific achievements of Applicant[27]

1. Achievements unrelated to the topic of habilitation cycle

First experimental works at the Institute of Physics PAS in Warsaw were started by the Applicant during his master course in physics at the Department of Mathematics and Natural Sciences, College of Science, Cardinal Stefan Wyszyński University, while preparing the master thesis under the supervision of Dr Elżbieta Guziewicz, in the ON4.2 group of IP PAS. The thesis entitled *„Badania elektryczne cienkich warstw tlenku cynku otrzymanych w niskotemperaturowym procesie ALD”* (English translation: *“Electrical investigations of zinc oxide films obtained in low temperature ALD process”*) and defended in June, 2007, concerned the analysis of basic dependences between the structural, optical and electrical properties of ALD-ZnO films. Here, it ought to be remarked that the research performed by the Applicant in frames of the master thesis preparation were the first studies of electrical properties of the semiconducting layers grown by the ALD method in the laboratory of ON4.2 group at IP PAS.

These issues were continued in frames of the Applicant's participation in the International Ph.D. studies at IP PAS between 2007 and 2012, when the research focused on finding the reason for the dominant *n*-type conductivity observed in thin ZnO films deposited in the wide range of growth temperatures have been carried out. In the Ph.D. thesis entitled *„Właściwości elektryczne cienkich warstw tlenku cynku otrzymywanych w procesie osadzania warstw atomowych (ALD)”* (English translation: *“Electrical properties of thin ZnO films obtained in the Atomic Layer Deposition (ALD) process”*), redacted by the Applicant under the supervision of Prof. Dr Elżbieta Guziewicz and defended at IP PAS on October 10, 2012, it was proven, basing on the highly crystalline ALD-ZnO films that one of the donor-type native defects influencing their electrical properties is the interstitial zinc. In parallel, the attempt was taken towards describing the main scattering mechanisms, limiting the Hall mobility in these layers in the temperature range of 4 K – 450 K. Moreover, the first results of ZnO-based Schottky junctions serving as gas and organic liquids sensors were successfully demonstrated. Critical review of the above-mentioned experiments as well as their development made also partially after the Ph.D thesis defense resulted in the publications marked as [N1]–[N3] in the shortened list below.

What is crucial for the current summary, the Ph.D. thesis did not discuss explicitly the broad context of influence of defects present in the ALD-ZnO films on the charge transport mechanisms occurring in the rectifying junctions involving such layers. This is for the fact that the diversity of factors possibly affecting the electrical transport processes in such structures (e.g. annealing or technological modifications) undoubtedly creates from the related issues a separate and definitely worth-studying scientific problem which, as such, has become a base for the present habilitation achievement.

The research activity of Applicant, unrelated to the topic of habilitation cycle [**H1**]–[**H7**] includes also the common works with Dr Ewa Przeździecka from IP PAS, Dr Marek Guziewicz from the Institute of Electron Technology as well as Dr Rafał Pietruszka from IP PAS. In the first two cases of cooperation, the investigations pertained to the measurements and analysis of rectifying properties of the ZnO:As/GaN heterojunction obtained by the *Plasma Assisted MBE* method [N4] as well as to the verification of the possibility of using the *n*-ZnO/*p*-4H-SiC structure as a double-sided, high-quality UV detector [N5]. The remarkable success of these

---

[27] The complete list of Applicant's scientific achievements is included in **Attachment 3**. In the current section of the summary only its shortened version is given to avoid repeating the same information.

investigations has resulted in a patent application for the detector construction, accepted and registered by the Patent Office of the Republic of Poland under the number PL-227759.

The cooperative investigations with Dr Pietruszka constituted, in turn, the additional accomplishment of the Applicants' research project, financed by the National Science Centre of Poland (NCN) between 2014 – 2017 (under the contract UMO-2013/09/D/ST5/03879). These studies concerned the construction of photovoltaic cell, based on the n-Zn$_{(1-x)}$Mg$_x$O/p-Si junction, involving the polycrystalline ZnO films doped with Mg within the range of 0 – 4 at.%. As it has been shown, owing to the appropriate growth conditions and doping level, in the optimally working cell the overall efficiency of 7.1 % may be achieved [N6]. Dr Pietruszka was one of the investigators in the mentioned NCN project.

Finally, a part of the Applicant's activity unrelated to the habilitation cycle was also devoted to the analysis of electrical properties of the ZnO thin films implanted with selected rare earth (RE) ions, e.g. Yb [N7], carried out in IP PAS as well as the ZnO:Al layers deposited on porous substrates, performed in frames of the bilateral cooperation with the Institute of Solid State Physics of Bulgarian Academy of Sciences in Sofia [N8] – see the list below.

[N1] E. Guziewicz, M. Godlewski, Ł. Wachnicki, *T. A. Krajewski*, G. Łuka, S. Gierałtowska, R. Jakieła, A. Stonert, W. Lisowski, M. Krawczyk, J. W. Sobczak, A. Jabłoński
„ALD grown zinc oxide with controllable electrical properties"
Semiconductor Science and Technology **27**, 074011 (2012).

[N2] *T. A. Krajewski*, K. Dybko, G. Łuka, E. Guziewicz, P. Nowakowski, B. S. Witkowski, R. Jakieła, Ł. Wachnicki, A. Kamińska, A. Suchocki, M. Godlewski
„Dominant shallow donors in zinc oxide layers obtained by the low temperature Atomic Layer Deposition: Electrical and optical investigations"
Acta Materialia **65**, pp. 69 – 75 (2014).

[N3] *T. A. Krajewski*, K. Dybko, G. Łuka, Ł. Wachnicki, K. Kopalko, W. Paszkowicz, M. Godlewski, E. Guziewicz
„Analysis of scattering mechanisms in zinc oxide films grown by the atomic layer deposition technique"
Journal of Applied Physics **118**, 035706 (2015).

[N4] E. Przeździecka, A. Wierzbicka, A. Reszka, K. Gościński, A. Droba, R. Jakieła, D. Dobosz, *T. A. Krajewski*, K. Kopalko, J. M. Sajkowski, M. Stachowicz, M. A. Pietrzyk, A. Kozanecki
„Characteristics of ZnO:As/GaN heterojunction diodes obtained by PA-MBE"
Journal of Physics D: Applied Physics **46**, 035101 (2013).

[N5] M. Guziewicz, R. Schifano, E. Przeździecka, J. Z. Domagała, W. Jung, *T. A. Krajewski*, E. Guziewicz
„n-ZnO/p-4H-SiC diode: Structural, electrical, and photoresponse characteristics"
Applied Physics Letters **107**, 101105 (2015).

[N6] R. Pietruszka, R. Schifano, *T. A. Krajewski*, B. S. Witkowski, K. Kopalko, Ł. Wachnicki, E. Zielony, K. Gwóźdź, P. Biegański, E. Płaczek-Popko, M. Godlewski
„Improved efficiency of n-ZnO/p-Si based photovoltaic cells by band offset engineering"
Solar Energy Materials and Solar Cells **147**, pp. 164 – 170 (2016).

[N7] E. Guziewicz, R. Ratajczak, M. Stachowicz, D. Snigurenko, *T. A. Krajewski*, C. Mieszczyński, K. Mazur, B. S. Witkowski, P. Dłużewski, K. Morawiec, A. Turos
„Atomic layer deposited ZnO films implanted with Yb: The influence of Yb location on optical and electrical properties"
Thin Solid Films **643**, pp. 7 – 15 (2017).

[N8] B. S. Blagoev, E. Vlakhov, V. Videkov, B. Tzaneva, G. Łuka, B. S. Witkowski, P. Terziyska, J. Leclercq, *T. A. Krajewski*, E. Guziewicz, D. Z. Dimitrov, V. B. Mehandzhiev, P. Sveshtarov
„Atomic layer deposition of ZnO:Al on PAA substrates"
Journal of Physics Conf. Series **764**, 012004 (2016).

2. Invited lectures, conference oral presentations and seminars (also discussing the results of realized research projects) given personally by the Applicant

As a part of the hitherto scientific activity, the Applicant has personally delivered the following invited lectures and oral presentations on the domestic and international conferences:

Invited lectures (with 3 of them given after the Ph.D. degree conferment, related to the habilitation cycle):

[I1] *T. A. Krajewski*, G. Łuka, S. Gierałtowska, A. J. Zakrzewski, P. S. Smertenko, Ł. Wachnicki, B. S. Witkowski, M. Godlewski, E. Guziewicz
„Schottky junctions based on the ALD-ZnO thin films for electronic applications"
E-MRS Fall Meeting, September 19 – 23, 2011, Warsaw, Poland

[I2] *T. A. Krajewski*, P. Stallinga, E. Zielony, R. Schifano, K. Gościński, G. Łuka, D. Snigurenko, T. Aschenbrenner, D. Hommel, M. Godlewski, E. Guziewicz
„The influence of defect states on electrical properties of rectifying junctions based on ZnO"
Energy Materials and Nanotechnology (EMN) Qingdao Meeting, June 14 – 17, 2015, Qingdao, P. R. China

[I3] *T. A. Krajewski,* P. S. Smertenko, G. Łuka, D. Snigurenko, K. Kopalko, E. Łusakowska, R. Jakieła, E. Guziewicz
„The influence of dielectric interlayer on the electrical behavior of ZnO–based rectifying junctions – modeling and experimental studies"
Energy Materials Nanotechnology (EMN) Prague Meeting, June 21 – 24, 2016r, Prague, Czech Republic

[I4] *T. A. Krajewski*, P. S. Smertenko, P. Stallinga, G. Łuka, R. Schifano, D. Snigurenko, K. Kopalko, E. Łusakowska, R. Jakieła, E. Guziewicz
„ZnO–based rectifying structures – modeling and experimental studies"
E-MRS Fall Meeting, September 19 – 22, 2016, Warsaw, Poland

Conference oral presentations (6 of them given after the Ph.D. degree conferment):

[O1] *T. A. Krajewski,* G. Łuka, Ł. Wachnicki, M. I. Łukasiewicz, A. J. Zakrzewski, B. S. Witkowski, R. Jakieła, E. Łusakowska, K. Kopalko, B. J. Kowalski, M. Godlewski, E. Guziewicz
„Schottky junctions with silver based on zinc oxide grown by Atomic Layer Deposition"
8th International Conference on Electronic Processes in Organic and Inorganic Materials (ICEPOM-8) May, 17 – 22, 2010, Residence Synyogora, Huta, Ivano-Frankivsk Region, Ukraine

[O2] *T. A. Krajewski,* G. Łuka, K. Dybko, Ł. Wachnicki, B. S. Witkowski, P. Nowakowski, A. Suchocki, R. Jakieła, E. Łusakowska, M. Godlewski, E. Guziewicz
„Origin of the n-type conductivity in low temperature ZnO thin films"
15th International Conference on II-VI Compounds (II-VI 2011), August 21 – 26, 2011, Cancún, Mexico

[O3] *T. A. Krajewski,* G. Łuka, K. Dybko, A. J. Zakrzewski, R. Jakieła, Ł. Wachnicki, B. S. Witkowski, M. I. Łukasiewicz, M. Godlewski, E. Guziewicz
„Schottky junctions based on zinc oxide thin films grown by low temperature Atomic Layer Deposition"
Coupled WOCSDICE/EXMATEC 2012 Conference, May 28 – June 1, 2012r, L'Île de Porquerolles, Toulon-Hyères, France

[O4] *T. A. Krajewski*, K. Dybko, P. Nowakowski, G. Łuka, D. Snigurenko, R. Jakieła, B. S. Witkowski, Ł. Wachnicki, A. Kamińska, A. Suchocki, E. Guziewicz, M. Godlewski
„Optical and transport properties of zinc oxide layers grown by the low temperature Atomic Layer Deposition (ALD) process"
International Conference for Young Scientists "Low Temperature Physics 2013" (ICYS-LTP-2013), June 3 –7, 2013, Kharkiv, Ukraine

[O5] *T. A. Krajewski*, K. Dybko, G. Łuka, Ł. Wachnicki, B. S. Witkowski, P. Nowakowski, A. Suchocki, E. Guziewicz, M. Godlewski
„Scattering processes and the influence of defects on the electrical properties of ZnO thin films grown by the low temperature Atomic Layer Deposition"
8th International Workshop on Zinc Oxide and Related Materials (IWZnO-2014), September 7 – 11, 2014, Niagara Falls, Ontario, Canada

[O6] *T. A. Krajewski*
„The chosen applications of ZnO-based rectifying junctions"
EAgLE Workshop – „Towards effective cooperation with industry", April 15 – 16, 2015, Jachranka, Poland

[O7] *T. A. Krajewski*, P. S. Smertenko, G. Łuka, D. Snigurenko, A. J. Zakrzewski, K. Gościński, K. Kopalko, E. Guziewicz
„Comparison of electrical properties of the rectifying junctions based on zinc oxide – tuning the rectification ratio by using thin dielectric interlayer"
7th Polish Conference on Nanotechnology (7-KKN), 25 – 27. 06. 2015r., Poznań, Poland

[O8] *T. A. Krajewski*, P. S. Smertenko, G. Łuka, D. Snigurenko, A. J. Zakrzewski, K. Gościński, K. Kopalko, E. Guziewicz
„Rectifying structures based on zinc oxide grown by ALD – comparative studies of Schottky diodes and homojunctions"
Light in Nanoscience and Nanotechnology (LNN-2015) Conference, October 19 – 22, 2015r, Hissar, Bulgaria

[O9] *T. A. Krajewski*, P. Terziyska, G. Łuka, E. Łusakowska, R. Jakieła, E. S. Vlakhov, E. Guziewicz
„Influence of thermal treatment on the contribution of native defects to the n-type conductivity of ZnO films obtained by the Atomic Layer Deposition"
10th International Workshop on Zinc Oxide and Other Oxide Semiconductors (IWZnO-2018), September 11 – 14, 2018, Warsaw, Poland

The Applicant has also given the following research seminars:

[S1] *T. A. Krajewski*
"Electrical investigations of thin ZnO films obtained in the low temperature ALD process"
(„Badania elektryczne cienkich warstw ZnO otrzymanych w niskotemperaturowym procesie ALD")
The ON4 Division Seminar, IP PAS, November 27, 2007

[S2] *T. A. Krajewski*
"Optimization of the electrical parameters of thin ZnO films obtained by the low temperature ALD growth"
(„Optymalizacja parametrów elektrycznych cienkich warstw ZnO otrzymanych w niskotemperaturowym wzroście metodą Atomic Layer Deposition")
The ON4 Division Seminar, IP PAS, October 14, 2008

[S3] *T. A. Krajewski*, G. Łuka, Ł. Wachnicki, B. Witkowski, B. J. Kowalski, R. Jakieła, N. Huby, G. Tallarida, E. Guziewicz, M. Godlewski
"Optical and electrical characterization of point defects in thin zinc oxide films obtained by the Atomic Layer Deposition technique"
(„Optyczna i elektryczna charakteryzacja defektów punktowych w cienkich warstwach tlenku cynku otrzymywanych techniką Osadzania Warstw Atomowych (ALD)")
The ON4 Division Seminar, IP PAS, June 9, 2009

[S4] *T. A. Krajewski*, Ł. Wachnicki, G. Łuka, K. Kopalko, E. Guziewicz, M. Godlewski
"Electrical properties of the ALD-ZnO films and metal/ZnO Schottky junction"
(„Właściwości elektryczne warstw ALD-ZnO i złącza Schottky'ego metal/ZnO")
Seminar given in frames of the special session concerning the research tasks realized within the Key Project NANOBIOM entitled *"Quantum semiconductor nanostructures for applications in biology and medicine – development and commercialisation of new generation devices for molecular diagnostics on the basis of new Polish semiconductor devices"* , IP PAS, October 15, 2009

[S5] *T. A. Krajewski*, G. Łuka, Ł. Wachnicki, S. Gierałtowska, A. J. Zakrzewski, K. Kopalko, E. Guziewicz, M. Godlewski
"Optimization of the electrical properties of thin ALD-ZnO films – applications in metal/ZnO Schottky junctions"
(„Optymalizacja właściwości elektrycznych cienkich warstw ALD-ZnO – zastosowania w złączach Schottky'ego metal/ZnO")
Seminar given in frames of the special session concerning the research tasks realized within the Key Project NANOBIOM entitled *"Quantum semiconductor nanostructures for applications in biology and medicine – development and commercialisation of new generation devices for molecular diagnostics on the basis of new Polish semiconductor devices"*, IP PAS, April 13, 2010

[S6] *T. A. Krajewski,* G. Łuka, Ł. Wachnicki, K. Dybko, S. Gierałtowska, A. J. Zakrzewski, K. Kopalko, M. Godlewski, E. Guziewicz
"Investigations of electrical properties of thin ALD-ZnO films. Applications in metal/ZnO Schottky junctions"
(„Badania właściwości elektrycznych cienkich warstw ALD-ZnO. Zastosowania w złączach Schottky'ego metal/ZnO")
Seminar given in frames of the 2nd Ph.D. Symposium "*Jadwisin 2010*", May 7 – 8, 2010, Jadwisin, Poland

[S7] *T. A. Krajewski,* G. Łuka, Ł. Wachnicki, K. Dybko, S. Gierałtowska, A. J. Zakrzewski, K. Kopalko, M. Godlewski, E. Guziewicz
"Investigations of electrical properties of thin ALD-ZnO films. Applications in metal/ZnO Schottky junctions"
(„Badania właściwości elektrycznych cienkich warstw ALD-ZnO. Zastosowania w złączach Schottky'ego metal/ZnO")
Seminar on Condensed Matter Physics, IP PAS, May 11, 2010

[S8] *T. A. Krajewski*, G. Łuka, Ł. Wachnicki, S. Gierałtowska, M. I. Łukasiewicz, A. J. Zakrzewski, S. Yatsunenko, R. Jakieła, K. Kopalko, M. Godlewski, E. Guziewicz
"Construction of the metal/ZnO Schottky junctions and optimization of their parameters. Schottky diode with high (10^5) rectification ratio"
(„Wykonanie złącz Schottky'ego ZnO/metal i optymalizacja ich parametrów. Dioda Schottky'ego o wysokim (10^5) współczynniku prostowania")
Seminar given in frames of the special session concerning the research tasks realized within the Key Project NANOBIOM entitled *"Quantum semiconductor nanostructures for applications in biology and medicine – development and commercialisation of new generation devices for molecular diagnostics on the basis of new Polish semiconductor devices"*, IP PAS, October 21, 2010

[S9] *T. A. Krajewski*, B. S. Witkowski, G. Łuka, Ł. Wachnicki, M. I. Łukasiewicz, S. Gierałtowska, R. Jakieła, E. Łusakowska, K. Kopalko, B. J. Kowalski, M. Godlewski, E. Guziewicz
„Zinc oxide thin films grown by Atomic Layer Deposition method"
Seminar given in frames of the research stay at the *Facultés Universitaires Notre-Dame de la Paix* in Namur, December 12 – 18, 2010, Namur, Belgium

[S10] *T. A. Krajewski,* G. Łuka, Ł. Wachnicki, S. Gierałtowska, M. I. Łukasiewicz, A. J. Zakrzewski, S. Yatsunenko, R. Jakieła, K. Kopalko, M. Godlewski, E. Guziewicz
"Technology of the thin ZnO films and optimization of electrical parameters of these films for Schottky junctions. Construction of the metal/ZnO Schottky junctions and optimization of their parameters"
(„Opracowanie technologii cienkich warstw ZnO i optymalizacja parametrów elektrycznych tych warstw do złącz Schottky'ego. Wykonanie złącz Schottky'ego ZnO/metal i optymalizacja ich parametrów")

Seminar given in frames of the special session concerning the research tasks realized within the Key Project NANOBIOM entitled *"Quantum semiconductor nanostructures for applications in biology and medicine – development and commercialisation of new generation devices for molecular diagnostics on the basis of new Polish semiconductor devices"*, IP PAS, April 20 – 21, 2011

[S11] *T. A. Krajewski*, G. Łuka, Ł. Wachnicki, S. Gierałtowska, A. J. Zakrzewski, M. I. Łukasiewicz, R. Jakieła, K. Kopalko, M. Godlewski, E. Guziewicz
"Growth of the highly-resistive thin ZnO films. Construction of the ZnO/metal Schottky junctions and optimization of their parameters"
(„Wytworzenie wysokooporowych cienkich warstw ZnO. Wykonanie złącz Schottky'ego ZnO/metal i optymalizacja ich parametrów")
Seminar given in frames of the Experts' Panel concerning the research tasks realized within the Key Project NANOBIOM entitled *"Quantum semiconductor nanostructures for applications in biology and medicine – development and commercialisation of new generation devices for molecular diagnostics on the basis of new Polish semiconductor devices"*, IP PAS, December 1 – 2, 2011

[S12] *T. A. Krajewski*, G. Łuka, K. Dybko, S. Gierałtowska, A. J. Zakrzewski, Ł. Wachnicki, B. S. Witkowski, R. Jakieła, M. Godlewski, E. Guziewicz
"Possible reasons for the n-type conductivity of thin ALD-ZnO films. ZnO-based Schottky diodes"
(„Możliwe przyczyny przewodnictwa typu n w cienkich warstwach ALD-ZnO. Diody Schottky'ego na bazie ZnO")
The ON4 Division Seminar, IP PAS, March 27, 2012

[S13] *T. A. Krajewski*, K. Dybko, G. Łuka, Ł. Wachnicki, B. S. Witkowski, E. Guziewicz, M. Godlewski
"Scattering mechanisms in zinc oxide – theory and experiment (thin ALD-ZnO films)"
(„Mechanizmy rozpraszania w tlenku cynku – teoria i eksperyment (cienkie warstwy ALD-ZnO)")
The ON4 Division Seminar, IP PAS, October 15, 2013

[S14] *T. A. Krajewski*, P. Stallinga, E. Zielony, K. Gościński, P. Kruszewski, Ł. Wachnicki, T. Aschenbrenner, D. Hommel, E. Guziewicz, M. Godlewski
"Analysis of defect levels in the p-GaN/n-ZnO heterojunction"
(„Analiza poziomów defektowych w heterozłączu p-GaN/n-ZnO")
The ON4 Division Seminar, IP PAS, March 24, 2015

[S15] *T. A. Krajewski*
"ZnO-based Schottky and homojunctions – transport properties and the methods of improving electrical parameters"
(„Złącza Schottky'ego i homozłącza na bazie ZnO – właściwości transportowe i metody poprawy parametrów elektrycznych")
The ON4 Division Seminar, IP PAS, November 29, 2016

[S16] *T. A. Krajewski*, P. Terziyska, G. Łuka, E. Łusakowska, R. Jakieła, E. S. Vlakhov, E. Guziewicz
"Influence of thermal treatment on the contribution of native defects to the n-type conductivity of ZnO films obtained by the Atomic Layer Deposition"
(„Wpływ wygrzewania na wkład defektów rodzimych do przewodnictwa typu n w cienkich warstwach ALD-ZnO")
The ON4 Division Seminar, IP PAS, December 11, 2018

Apart from the above, between 2007 and 2018 the Applicant was a Co-Author of 27 conference invited talks, 26 conference oral presentations and an Author or Co-Author of 97 conference poster presentations. The detailed list of these achievements is included in **Attachment 3**.

3. Leading and participation of the Applicant in Polish and international research projects (in chronological order)

Between 2007 and 2018 the Applicant led and/or participated in the following research projects (the list including projects' titles, their running periods as well as the Applicant's role therein is arranged in the chronological order):

[P1] Participation in the international research project entitled: *„Vertically stacked memory cells based on heterojunctions made of hybrid organic/inorganic materials"*, Specific Targeted Research Projects (STREP) IST-026714 VERSATILE, STMicroelectronics/Intel Italy, realized between **January 2, 2006 – July 31, 2009** in frames of the EU 6th Framework Programme: FP6-IST – Information Society Technologies: thematic priority under the specific programme „Integrating and strengthening the European research area" (2002 – 2006).
Role of the Applicant in the project: **investigator**
Project coordinator: MDM National Laboratory – Consiglio Nazionale delle Ricerche (CNR-INFM), Milan, Italy

[P2] Participation in the research project entitled: *"Quantum semiconductor nanostructures for applications in biology and medicine – development and commercialisation of new generation devices for molecular diagnostics on the basis of new Polish semiconductor devices"*, realized between **2007 – 2013** in the framework of the Operational Programme Innovative Economy 2007 – 2013 (POIG.01.01.02-00-008/08 (NANOBIOM)).
Role of the Applicant in the project: **investigator**. Results obtained by the Applicant within the project have been repeatedly presented (by Him, personally, or by the Co-Authors) on the domestic as well as international conferences.
Project coordinator: Institute of Physics, PAS

[P3] Participation in the research project entitled: *„Modern Materials and Innovative Methods for Processing an Monitoring the Energy (MIME)"*, realized between **2009 – 2014** in the framework of the Operational Programme Innovative Economy (POIG 01.01.02-00-108/09).
Role of the Applicant in the project: **investigator**
Project coordinator: Institute of Physics, PAS

[P4] Participation in the research project entitled: *"Electrical properties of thin zinc oxide films obtained in the Atomic Layer Deposition (ALD) process" (Polish title: „Właściwości elektryczne cienkich warstw tlenku cynku otrzymywanych w procesie osadzania warstw atomowych (ALD)")*, financed by the National Science Centre of Poland (NCN), realized between **April 11, 2011 – October 10, 2012**, under the contract number 1669/B/H03/2011/40.
Role of the Applicant in the project: **sole** (**individual**) **investigator**
Project leader: Prof. Dr Elżbieta Guziewicz (Applicant's Ph.D. thesis supervisor)
Project coordinator: Institute of Physics, PAS

[P5] Participation in the research project SONATA entitled: *"Influence of the growth conditions, doping and thermal processing on the defect structure of zinc oxide thin films obtained by the epitaxial methods" (Polish title: „Wpływ warunków wzrostu, domieszkowania i obróbki termicznej na strukturę defektową cienkich warstw tlenku cynku otrzymanych metodami epitaksjalnymi")*, financed by the National Science Centre of Poland (NCN), realized between **February 18, 2014 – February 17, 2017**, under the contract number UMO-2013/09/D/ST5/03879.
Role of the Applicant in the project: **project leader**
Project coordinator: Institute of Physics, PAS

[P6] Participation in the research project entitled: *"Light-emitting photonic structures based on ZnO implanted with the rare-earth elements (ZnOLUM)" (Polish title: „Świecące struktury fotoniczne na bazie ZnO implantowanego pierwiastkami ziem rzadkich (ZnOLUM)")*, financed by The National Centre for Research and Development (NCBiR), realized between **October 1, 2013** – **September 30, 2017**, under the contract number PBS2/A5/34/2013
Role of the Applicant in the project: **investigator**
Project leader: Prof. Dr Elżbieta Guziewicz
Project coordinator: Institute of Physics, PAS

4. Patent applications and patents obtained by the Applicant. Construction of the unique scientific equipment

In frames of the hitherto scientific activity, the Applicant has been an Author and/or Co-Author of the following three technological solutions registered and patented in the Polish Patent Office (the table below includes also the list of Co-Authors and the Exclusive Right Number ascribed to the given solution/invention):

N°	Excl. Right N°	Year	Patent title (in English)	Authors	Country
1.	PL-220462	2015	"Rectifying junction Ag/ZnO and method for manufacturing this junction"	*T. A. Krajewski*, G. Łuka, E. Guziewicz, M. Godlewski, K. Kopalko	Poland
2.	PL-223727	2016	"*p-n* homo-connection structure based on ZnO and the method for producing the *p-n* homo-connection structure based on ZnO"	D. Snigurenko, *T. Krajewski*, E. Guziewicz	Poland
3.	PL-227759	2018	"Structure of a transparent ultraviolet detector and method for producing the structure of the transparent ultraviolet detector"	M. Guziewicz, W. Jung, E. Guziewicz, E. Przeździecka, R. Schifano, *T. Krajewski*	Poland

Unique scientific equipment. Improvement of the equipment base of the electrical laboratory of ON4.2 group in IP PAS made by the Applicant

One of the aims of research project led by the Applicant (UMO-2013/09/D/ST5/03879 [P5]) was an improvement of the equipment base of the electrical laboratory of ON4.2 group in IP PAS. According to the plans, this should allow the profound measurements of electrical parameters of obtained junctions as well as the analysis of defect levels in such structures also using the low frequency probing voltage signal (apart from the most frequently available one with $f = 1$ MHz). This is particularly important in case of examining the ZnO-based rectifying junctions. Regarding to the above, taking an advantage of the financial support guaranteed by the project, the universal impedance (LCR) meter was purchased and launched in the laboratory.

Additionally, part of the project financial support was also dedicated to the purchase of an option broadening the range of available measurement frequencies of the *Zurich Instruments* lock-in (which basic version was obtained in frames of the project of Dr Ewa Przeździecka). In order to achieve the further expansion of measurement possibilities, an additional option of *"MI-IA"* was subsequently applied to the equipment, allowing the substantial increase in measuring the absolute impedance value due to the program algorithms, compensating the shortcomings of measurement system. The Applicant has participated both: in the purchase and launching processes of the described equipment.

5. Supervising, teaching and popularizing activity of the Applicant. Supervision of the scientific trainees

The Applicant is currently an Auxiliary Supervisor (Co-Supervisor) of the Ph.D. thesis of M.Sc. D. Snigurenko, entitled: *"Correlation between the (low) growth temperature, structural properties and doping effectiveness of the ZnO films"* (Polish title: *„Korelacja pomiędzy (niską) temperaturą wzrostu, a właściwościami strukturalnymi i efektywnością domieszkowania warstw ZnO")*. The Supervisor in doctorial conferment procedure of M.Sc. D. Snigurenko is Prof. Dr Elżbieta Guziewicz. (According to the protocol of the Scientific Council Meeting of Institute of Physics, PAS, dated January 23, 2014). M.Sc. D. Snigurenko currently participates in the International Ph.D. studies at the Institute of Physics, PAS.

* * *

Within the hitherto scientific work, the Applicant is active in teaching and popularizing fields as well. This kind of the Applicant activity includes:

[D1] Providing (starting from the academic year of 2008/2009, with a break in 2011) the one-semester laboratory exercises for the fourth-year students of Physics at the Department of Mathematics and Natural Sciences, College of Science, Cardinal Stefan Wyszyński University in frames of the *Physics Laboratory II* subject. At the beginning the task was a part of the wider exercise entitled *"Atomic Layer Deposition"*, whereas nowadays (starting from 2013/2014) it is an independently provided and coordinated experiment entitled *"Semiconductor junctions"*;

[D2] Providing (starting from the academic year of 2012/2013) the semester exercises in the laboratory of Atomic Layer Deposition (belonging to the ON4.2 group in IP PAS), organized for the students of the *Nanostructure Engineering* specialization (in Polish: *Inżynieria Nanostruktur*) of the Department of Physics of the University of Warsaw. Initially, these exercises were given in the winter term of the third year of studies, whereas nowadays, the subject *Laboratory of Technology and Designing of New Materials* (in Polish: *Laboratorium „Technologie i Projektowanie Nowych Materiałów"*) is included in the schedule of summer term of the second year. Title of the co-supervised laboratory task: *"The ALD technology of oxide compounds"* (in Polish: *„Technologia ALD związków tlenkowych")*;

[D3] In frames of the popularizing activity, the Applicant within one month (November 5 – December 2, 2012) supervised the research stay in IP PAS of the Turkish secondary school student, who was one of the laureates of the international *First Step to Nobel Prize in Physics* competition. The Laureate while his stay in IP PAS under the supervision of the Applicant has gained a basic knowledge in the subject of ALD technology through the active participation in the optical and electrical characterization of thin ALD-ZnO films. In parallel, he took the opportunity of visiting the laboratories of different (selected) research groups in IP PAS;

[D4] The second aspect of the Applicant's popularizing activity was the didactic supervision over the three participants of the cyclic Workshop organized at IP PAS and coordinated by the State Children Fund (Polish name: Krajowy Fundusz na Rzecz Dzieci). In frames of the Workshop the Applicant was responsible for the task entitled *"The mysteries of semiconductor junctions"* (Polish title: *„Tajemnice złącz półprzewodnikowych"*). The Workshop was organized between January 13 – 18, 2013 (40 hours in total). Apart from being the experiment leader, the Applicant has also prepared and evaluated the correctness of the related qualifying task solution. Final assessment of the participants' fluency and commitment during the Workshop task, prepared by the Applicant, has been subsequently transferred to the Fund Office. Thus, at the stage of preparation and leading the Workshop, the Applicant remained a member of the wider team of experts;

[D5] Additionally: Demonstration of the laboratories belonging to the ON4 Division of IP PAS to the visiting group of students from the Faculty of Science (*Faculteit der Natuurwetenschappen, Wiskunde en Informatica*) of the Radboud University in Nijmegen (The Netherlands), October 29, 2012.

* * *

The list scientific trainees supervised and/or co-supervised by the Applicant in frames of their research activity in IP PAS includes:

[Pr 1] Supervision over the students of the *Nanostructure Engineering* specialization (in Polish: *Inżynieria Nanostruktur*) of the Department of Physics of the University of Warsaw (student trainees – 2 people between September 2 – 27, 2013). Within the training period the students were involved in the ALD growth processes as well as electrical characterization of the thin film-based structures in the laboratories belonging to the ON4.2 group in IP PAS;

[Pr 2] Supervision over the second year students of the Department of Physics of the University of Warsaw (specialization: *Nanostructure Engineering*). The students (3 people) within their training period (July – August, 2014) were involved in the ALD growth processes as well as electrical and optical characterization of the thin film-based structures in the laboratories belonging to the ON4.2 group in IP PAS;

[Pr 3] Supervision over the third year students of the Department of Physics of the University of Warsaw (specialization: *Nanostructure Engineering*). The students (2 people) within their training period (September 1 – 30, 2015) were involved in the ALD growth and electrical characterization of thin ZnO films as well as the electrical measurements of Schottky and *p-n* rectifying junctions, carried out in the laboratories of the ON4.2 group in IP PAS;

[Pr 4] Co-supervision in frames of the ON4.2 group in IP PAS over the two students: one of the Department of Physics of the University of Warsaw (specialization: *Nanostructure Engineering* – second year) and one of the Faculty of Applied Physics and Mathematics of the Gdańsk University of Technology (third year). The students within their training period (i.e. July 12 – August 10, 2018) were involved in the ALD growth and electrical characterization of the ZnO-based rectifying structures (Schottky junctions).

6. Organization of the scientific conferences and charing the conference sessions. Reviewing and editorial activity of the Applicant

The Applicant acted as **the Scientific Committee Secretary** of the *10th International Workshop on Zinc Oxide and Other Oxide Semiconductors (IWZnO-2018)* organized in Warsaw between September 11 – 14, 2018. The Workshop was chaired by Prof. Dr Elżbieta Guziewicz and coordinated by the Institute of Physics, PAS.

Short characteristics of the Conference:

Organized according to the biennial cycle in different locations all over the world (including the United States of America, Japan, Germany, P. R. China, France, Canada or Taiwan), the IWZnO workshop has been initiated in 1999 by Prof. David Look and Prof. Yicheng Lu from U.S.A. It is regarded to be the world biggest scientific conference focused on the zinc oxide-related topics that every time gathers a large group of international scientists, being the remarkable experts in the area of properties and applications of wide band-gap materials (this particularly concerns ZnO). The 10th jubilee edition of this highly recognizable meeting, organized in 2018 (for the first time in Poland) gathered around 100 participants from different countries of the world. Further details pertaining to the IWZnO-2018 workshop are available at: *iwzno-2018.org*.

* * *

Apart from the above, the Applicant acted also as a chairman of the two sessions during the *Energy Materials and Nanotechnology (EMN) Meeting* in Qingdao (P. R. China) and Prague (Czech Republic):

[C1] Energy Materials and Nanotechnology (EMN) Qingdao Meeting, June 14 – 17, 2015, Qingdao, P. R. China (session entitled *"Iron and Iridium based superconductivity VI"*);

[C2] Energy Materials and Nanotechnology (EMN) Prague Meeting, June 21 – 24, 2016, Prague, Czech Republic (session entitled *"Nanostructured Materials IV"*).

* * *

In frames of the hitherto scientific activity the Applicant has reviewed the total number of *28* scientific publications (excluding the review declinations) for both: international and Polish journals of various *impact factor*. The detailed list of journals includes:

1. *Acta Physica Polonica A* – **10 publications** (2012 – 1, 2013 – 1, 2014 – 1, 2015 – 2, 2016 – 1, 2017 – 2, 2018 – 1, 2019 - 1)
2. *Materials Science Poland* – **5 publications** (2014 – 1, 2015 – 1, 2016 – 1, 2017 – 1, 2019 – 1)
3. *Thin Solid Films* – **3 publications** (2014 – 1, 2015 – 1, 2018 – 1)
4. *IEEE Transactions on Electron Devices* – **2 publications** (2010 – 1, 2016 – 1)
5. *Semiconductor Science and Technology* – **2 publications** (2018 – 2)
6. *Journal of Physics D: Applied Physics* – **2 publications** (2017 – 1, 2018 – 1)
7. *Solid State Phenomena* – **2 publications** (2012 – 1, 2014 – 1)
8. *Materials Chemistry and Physics* – **1 publication** (2017)
9. *RSC Advances* – **1 publication** (2018)

V. References

[*Albrecht JAP99*] J. D. Albrecht, P. P. Ruden, S. Limpijumnong, W. R. L. Lambrecht, K. F. Brennan, *J. Appl. Phys.* **86** (12) (1999) 6864 – 6867.

[*Allen APL06*] M. W. Allen, M. M. Alkaisi, S. M. Durbin, *Appl. Phys. Lett.* **89** (2006) 103520.

[*Anantachaisilp JL15*] S. Anantachaisilp, S. M. Smith, C. Ton-That, S. Pornsuwan, A. R. Moon, C. Nenstiel, A. Hoffmann, M. R. Phillips, *J. Lumines.* **168** (2015) 20 – 25.

[*Auret APL01*] F. D. Auret, S. A. Goodman, M. Hayes, M. J. Legodi, H. A. van Laarhoven, D. C. Look, *Appl. Phys. Lett.* **79** (19) (2001) 3074 – 3076.

[*Auret APL02*] F. D. Auret, S. A. Goodman, M. J. Legodi, W. E. Meyer, D. C. Look, *Appl. Phys. Lett.* **80** (8) (2002) 1340 – 1342.

[*Baron SSM70*] R. Baron, J. W. Mayer, *Double injection in semiconductors*, In: *Semiconductors and Semimetals*, Academic Press, New York, 1970, vol. 6, pp. 201 – 313.

[*Bian APL04*] J. M. Bian, X. M. Li,C. Y. Zhang, L. D. Chen, Q. Yao, *Appl. Phys. Lett.* **84** (2004) 3783 – 3785.

[*Blatter PRB86*] G. Blatter, F. Greuter, *Phys. Rev. B* **33** (6) (1986) 3952 – 3966.

[*Calderon PSSb05*] C. Calderon, G. Gordillo, J. Olarte, *Phys. Status Solidi (b)* **242** (2005) 1915 – 1919.

[*Chao SCT13*] L.-C. Chao, J.-W. Chen, H.-C. Peng, C.-H. Ho, *Surf. Coat. Technol.* **231** (2013) 492 – 495.

[*Chasin APL12*] A. Chasin, S. Steudel, K. Myny, M. Nag, T.-H. Ke, S. Schols, J. Genoe, G. Gielen, P. Heremans, *Appl. Phys. Lett.* **101** (2012) 113505.

[*Chen Wiley-NMT08*] J. J. Chen, N. R. Mielke, C. C. Hu, *Nonvolatile memory technologies with emphasis on flash: A comprehensive guide to understanding and using NVM devices*, In: S. K. Tewksbury, J. E. Brewer (Eds.), Wiley-IEEE Press, New Jersey, 2008, p. 470.

[*Chou ApSS08*] S.-M. Chou, M.-H. Hon, I.-C. Leu, *Appl. Surf. Sci.* **255** (2008) 2958 – 2962.

[*Ciach SEM03*] R. Ciach, Yu. P. Dotsenko, V. V. Naumov, A. N. Shmyryeva, P. S. Smertenko, *Sol. Energy Mater. Sol. Cells* **76** (2003) 613 – 624.

[*Duan PRB09*] X. M. Duan, C. Stampfl, M. M. M. Bilek, D. R. McKenzie, *Phys. Rev. B* **79** (2009) 235208.

[*Dunlop APL08*] L. Dunlop, A. Kursumovic, J. L. MacManus-Driscoll, *Apel. Phys. Lett.* **93** (2008) 172111.

[*Dyba APPA09*] P. Dyba, E. Płaczek-Popko, E. Zielony, Z. Gumienny, J. Szatkowski, *Acta Phys. Pol. A* **116** (5) (2009) 944 – 946.

[*Ellmer TSF08*] K. Ellmer, R. Mientus, *Thin Solid Films* **516** (2008) 4620 – 4627.

[*Fernández-Hevia APL03*] D. Fernández-Hevia, J. de Frutos, A. C. Caballero,J. F. Fernández, *Appl. Phys. Lett.* **83** (13) (2003) 2692 – 2694.

[*Figge APL02*] S. Figge, R. Kröger, T. Böttcher, P. L. Ryder, D. Hommel, *Appl. Phys. Lett.* **81** (25) (2002) 4748 – 4750.

[*Frank APA07*] T. Frank, G. Pensl, R. Tena-Zaera, J. Zúñiga-Pérez, C. Martínez-Tomás, V. Muñoz-Sanjosé, T. Ohshima, H. Itoh, D. Hofmann, D. Pfisterer, J. Sann, B. Meyer, *Appl. Phys. A* **88** (2007) 141 – 145.

[*Gomi JJAP03*] M. Gomi, N. Oohira, K. Ozaki, M. Koyano, *Jpn. J. Appl. Phys.* **42** (2003) 481 – 485.

[*Grossi Springer16*] A. Grossi, C. Zambelli, P. Olivo, *3D Flash Memories*, In: R. Micheloni (Ed.), Springer Science & Business Media, Dordrecht, 2016, p. 29.

[*Gu APL07*] Q. L. Gu, C. C. Ling, X. D. Chen, C. K. Cheng, A. M. C. Ng, C. D. Beling, S. Fung,

A. B. Djurišić, L. W. Lu, G. Brauer, H. C. Ong, *Appl. Phys. Lett.* **90** (2007) 122101.

[*Guziewicz APL15*] M. Guziewicz, R. Schifano, E. Przeździecka, J. Z. Domagała, W. Jung, T. A. Krajewski, E. Guziewicz, *Appl. Phys. Lett.* **107** (2015) 101105.

[*Guziewicz SST12*] E. Guziewicz, M. Godlewski, Ł. Wachnicki, T. A. Krajewski, G. Łuka, S. Gierałtowska, R. Jakieła, A. Stonert, W. Lisowski, M. Krawczyk, J. W. Sobczak, A. Jabłoński, *Semicond. Sci. Technol.* **27** (2012) 074011.

[*Hamad TSF05*] O. Hamad, G. Braunstein, H. Patil, N. Dhere, *Thin Solid Films* **489** (2005) 303 – 309.

[*Han MChP02*] J. P. Han, A. M. R. Senos, P. Q. Mantas, *Mater. Chem. Phys.* **75** (2002) 117 – 120.

[*Hoffmann PRL02*] D. M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. B. Orlinskii, J. Schmidt, P. G. Baranov, *Phys. Rev. Lett.* **88** (2002) 045504.

[*http-semtod16*] Data taken from the following website: http://www.semiconductor-today.com/news_items/2016/jul/ieee_260716.shtml. Accessed: Oct. 3, 2018.

[*Ip JCG06*] K. Ip, G. T. Thaler, H. Yang, S. Y. Han, Y. Li, D. P. Norton, S. J. Pearton, S. Jang, F. Ren, *J. Cryst. Growth* **287** (2006) 149 – 156.

[*Janotti RPP09*] A. Janotti, C. G. Van de Walle, *Rep. Prog. Phys.* **72** (2009) 126501.

[*Jun ML08*] W. Jun, Y. Yintang, *Mater. Lett.* **62** (2008) 1899 – 1901.

[Kalyanaraman JPCS13] S. Kalyanaraman, R. Thangavel, R. Vettumperumal, *J. Phys. Chem. Solids* **74** (2013) 504 – 508.

[*Kamohara ApSS08*] S. Kamohara, T. Okumura, *Appl. Surf. Sci.* **254** (2008) 6174 – 6176.

[*Kanai JJAP90*] Y. Kanai, *Jpn. J. Appl. Phys.* **29** (8) (1990) 1426 – 1430.

[*Kashiwaba ApSS13*] Y. Kashiwaba, M. Sakuma, T. Abe, A. Nakagawa, I. Niikura, Y. Kashiwaba, M. Daibo, H. Osada, *Appl. Surf. Sci.* **286** (2013) 126 – 130.

[*Kennedy ApSS16*] J. Kennedy, P. P. Murmu, J. Leveneur, A. Markwitz, J. Futter, *Appl. Surf. Sci.* **367** (2016) 52 – 58.

[*Kennedy CAP14*] J. Kennedy, A. Markwitz, Z. Li, W. Gao, C. Kendrick, S. M. Durbin, R. Reeves, *Curr. Appl. Phys.* **6** (2006) 495 – 498.

[*Kennedy JAC14*] J. Kennedy, P. P. Murmu, E. Manikandan, S. Y. Lee, *J. Alloy. Compd.* **616** (2014) 614 – 617.

[*Kim SST12*] H. Kim, A. Sohn, D.-W. Kim, *Semicond. Sci. Technol.* **27** (2012) 035010.

[*Kim TEEM15*] H. Kim, *Trans. Electr. Electron. Mater.* **16** (5) (2015) 285 – 289.

[*Kolkovsky SST14*] V. Kolkovsky, D. Snigurenko, R. Jakieła, E. Guziewicz, *Semicond. Sci. Technol.* **29** (2014) 085006.

[*Kowalik JCG09*] I. A. Kowalik, E. Guziewicz, K. Kopalko, S. Yatsunenko, A. Wójcik-Głodowska, M. Godlewski, P. Dłuzewski, E. Łusakowska, W. Paszkowicz, *J. Cryst. Growth* **311** (2009) 1096 – 1101.

[*Krajewski AM14*] T. A. Krajewski, K. Dybko, G. Łuka, E. Guziewicz, P. Nowakowski, B. S. Witkowski, R. Jakieła, Ł. Wachnicki, A. Kamińska, A. Suchocki, M. Godlewski, *Acta Mater.* **65** (2014) 69 – 75.

[*Krajewski JAC17-1*] T. A. Krajewski, P. Terziyska, G. Łuka, E. Łusakowska, R. Jakieła, E. S. Vlakhov, E. Guziewicz, *J. Alloy. Compd.* **727** (2017) 902 – 911.

[*Krajewski JAC17-2*] T. A. Krajewski, P. S. Smertenko, G. Łuka, D. Snigurenko, K. Kopalko, E. Łusakowska, R. Jakieła, E. Guziewicz, *J. Alloy. Compd.* **693** (2017) 1164 – 1173.

[*Krajewski JAP13*] T. A. Krajewski, P. Stallinga, E. Zielony, K. Gościński, P. Kruszewski, Ł. Wachnicki, T. Aschenbrenner, D. Hommel, E. Guziewicz, M. Godlewski, *J. Appl. Phys.* **113** (2013) 194504.

[Lajn JEM10]	A. Lajn, H. von Wenckstern, G. Bendorf, C. P. Dietrich, M. Brandt, G. Biehne, H. Hochmuth, M. Lorenz, M. Grundmann, *J. Electron. Mat.* **39** (5) (2010) 595 – 600.
[Lampert CIS70]	M. Lampert, P. Mark, *Current Injection in Solids*, Academic Press, New York, 1970.
[Lan JAP13]	X. Lan, X. Ou, Y. Cao, S. Tang, C. Gong, B. Xu, Y. Xia, J. Yin, A. Li, F. Yan, Z. Liu, *J. Appl. Phys.* **114** (2013) 044104.
[Li APL05]	X. Li, B. Keyes, S. Asher, S. B. Hang, S.-H. Wei, T. J. Coutts, *Appl. Phys. Lett.* **86** (2005) 122107.
[Lee AdvM11]	J. S. Lee, S. N. Cha, J. M. Kim, H. W. Nam, S. H. Lee, W. B. Ko, K. L. Wang, J. G. Park, J. P. Hong, *Adv. Mater.* **23** (2011) 4183 – 4187.
[Lee ML07]	C. Lee, S. Y. Park, J. Lim, H. W. Kim, *Mater. Lett.* **61** (2007) 2495 – 2498.
[Lima JIM01]	S. A. M. Lima, F. A. Sigoli, M. Jafelicci Jr, M. R. Davolos, *Int. J. Inorg. Mater.* **3** (2001) 749 – 754.
[Limpijumnong PRL04]	S. Limpijumnong, S. B. Zhang, S. H. Wei, C. H. Park, *Phys. Rev. Lett.* **92** (2004) 155504.
[Lin APL01]	B. Lin, Z. Fu, Y. Jia, *Appl. Phys. Lett.* **79** (2001) 943 – 945.
[Lin JAP09]	S. S. Lin, H. P. He, Y. F. Lu, Z. Z. Ye, *J. Appl. Phys.* **106** (2009) 093508.
[Lin SSC08]	S. S. Lin, J. G. Lu, Z. Z. Ye, H. P. He, X. Q. Gu, L. X. Chen, J. Y. Huang, B. H. Zhao, *Solid State Commun.* **148** (2008) 25 – 28.
[Liu APL12]	W. Z. Liu, H. Y. Xu, L. X. Hang, C. Zhang, J. G. Ma, J. N. Wang, Y. C. Liu, *Appl. Phys. Lett.* **101** (2012) 142101.
[Liu SCTS11]	J. Liu, J. L. He, J. Hu, W. C. Long, *Sci. China Tech. Sci.* **54** (2011) 375 – 378.
[Look JEM06]	D. C. Look, *J. Electron. Mat.* **35** (2006) 1299 – 1305.
[Look PRL05]	D. C. Look, G. C. Farlow, P. Reunchan, S. Limpijumnong, S. B. Zhang, K. Nordlund, *Phys. Rev. Lett.* **95** (2005) 225502.
[Łuka OE15]	G. Łuka, K. Kopalko, E. Łusakowska, L. Nittler, W. Lisowski, J. W. Sobczak, A. Jabłoński, P. S. Smertenko, *Org. Electron.* **25** (2015) 135 – 142.
[Malinkiewicz RSCA12]	O. Malinkiewicz, M. Lenes, H. Brine, H. J. Bolink, RSC Adv. **2** (2012) 3335 – 3339.
[McWhorter TNS90]	P. J. McWhorter, S. L. Miller, W. M. Miller, *IEEE Trans. Nucl. Sci.* **37** (1990) 1682 – 1689.
[Monakhov APL05]	E. V. Monakhov, J. S. Christensen, K. Maknys, B. G. Svensson, A. Yu. Kuznetsov, *Appl. Phys. Lett.* **87** (2005) 191910.
[Mtangi PhB09]	W. Mtangi, F. D. Auret, C. Nyamhere, P. J. Janse van Rensburg, M. Diale, A. Chawanda, *Phys. B* **404** (2009) 1092 – 1096.
[Murmu JAP11]	P. P. Murmu, R. J. Mendelsberg, J. Kennedy, D. A. Carder, B. J. Ruck, A. Markwitz, R. J. Reeves, P. Malar, T. Osipowicz, *J. Appl. Phys.* **110** (2011) 033534.
[Nakamura JAP11]	A. Nakamura, J. Temmyo, *J. Appl. Phys.* **109** (2011) 093517.
[Nikitenko ZnO05]	V. Nikitenko, *Optics and Spectroscopy of Point Defects in ZnO*, In: N. H. Nickel, E. Terukov (Eds.), *Zinc Oxide – A Material for Micro– and Optoelectronic Applications*, Springer: Dordrecht, The Netherlands, 2005, pp. 69 – 81.
[Oba JAP01]	F. Oba, S. R. Nishitani, S. Isotani, H. Adachi, I. Tanaka, *J. Appl. Phys.* **90** (2001) 824 – 828.
[Ortiz-Conde SSE00]	A. Ortiz-Conde, F. J. García Sánchez, J. Muci, *Solid State Electron.* **44** (2000) 1861 – 1864.

[*Ozawa SRL02*]	K. Ozawa, K. Edamoto, *Surf. Rev. Lett.* **9** (2002) 717 – 722.
[*Pakkala HDT10*]	K. Pakkala, M. Putkonen, In: *“Handbook of Deposition Technologies For Films and Coatings – Science, Applications and Technology”*, Chapter 8, Edited by P. M. Martin, Elsevier Inc. (2010).
[*Pearton S§M03*]	S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, T. Steiner, *Superlattices and Microstructures* **34** (2003) 3 – 32.
[*Perkins JAP05*]	C. L. Perkins, S.-H. Lee, X. Li, S. E. Asher, T. J. Coutts, *J. Appl. Phys.* **97** (2005) 034907.
[*Pra JCE08*]	M. Pra, G. Csaba, C. Erlen, P. Lugli, *J. Comput. Electron.* **7** (2008) 146 – 150.
[*Przeździecka PRB07*]	E. Przeździecka, E. Kamińska, I. Pasternak, A. Piotrowska, J. Kossut, *Phys. Rev.* B **76** (2007) 193303.
[*Przeździecka SActA13*]	E. Przeździecka, K. Gościński, M. Stachowicz, D. Dobosz, E. Zielony, J. M. Sajkowski, M. A. Pietrzyk, E. Płaczek-Popko, A. Kozanecki, *Sensor. Actuat. A-Phys.* **195** (2013) 27 – 31.
[*Roth PRB82*]	A. P. Roth, J. B. Webb, D. F. Williams, *Phys. Rev. B* **25** (1982) 7836 – 7839.
[*Schein APL13*]	F.-L. Schein, H. von Wenckstern, M. Grundmann, *Appl. Phys. Lett.* **102** (2013) 092109.
[*Schifano APL07*]	R. Schifano, E. V. Monakhov, U. Grossner, B. G. Svensson, *Appl. Phys. Lett.* **91** (2007) 193507.
[*Schifano APL09*]	R. Schifano, E. V. Monakhov, B. G. Svensson, S. Diplas, *Appl. Phys. Lett.* **94** (2009) 132101.
[*Schmidt-Mende MT07*]	L. Schmidt-Mende, J. L. MacManus-Driscoll, *Materials Today* **10** (2007) 40 – 48
[*Schuster ACSN14*]	F. Schuster, B. Laumer, R. R. Zamani, C. Magén, J. R. Morante, J. Arbiol, M. Stutzmann, *ACSNano* **8** (5) (2014) 4376 – 4384.
[*Sheng APL02*]	H. Sheng, S. Muthukumar, N. W. Emanetoglu, Y. Lu, *Appl. Phys. Lett.* **80** (2002) 2132 – 2134.
[*Shohata JJAP80*]	N. Shohata, T. Matsumura, T. Ohno, *Jpn. J. Appl. Phys.* **19** (9) (1980) 1793 – 1794.
[*Smertenko ACIS05*]	P. Smertenko, L. Fenenko, L. Brehmer, S. Schrader, *Adv. Colloid Interface Sci.* **116** (2005) 255 – 261.
[*Snigurenko MRX16*]	D. Snigurenko, E. Guziewicz, T. A. Krajewski, R. Jakieła, Y. Syryanyy, K. Kopalko, W. Paszkowicz, *Mater. Res. Express* **3** (2016) 125907.
[*Snigurenko SST15*]	D. Snigurenko, K. Kopalko, T. A. Krajewski, R. Jakieła, E. Guziewicz, *Semicond. Sci. Technol.* **30** (2015) 015001.
[*Spassov TSF18*]	D. Spassov, A. Paskaleva, T. A. Krajewski, E. Guziewicz, G. Łuka, T. Ivanov, *Thin Solid Films* (2018) 1700854.
[*Spiga APEX12*]	S. Spiga, F. Driussi, A. Lamperti, G. Congedo, O. Salicio, *Appl. Phys. Express* **5** (2012) 021102.
[*Stallinga OEM09*]	P. Stallinga, *“Electrical characterization of organic electronic materials and devices”*, John Wiley & Sons, 2009, Chapters 3 and 4, pp. 67 – 153.
[*Sun ACSAMI15*]	C.-E. Sun, C.-Y. Chen, K.-L. Chu, Y.-S. Shen, C.-C. Lin, Y.-H. Wu, *ACS Appl. Mater. Interfaces* **7** (2015) 6383 – 6390.
[*Suntola HCG94*]	T. Suntola, “*Handbook of Crystal Growth*”, Part 3b – Growth Mechanisms and Dynamics, D.T.J Hurle, Elsevier, Amsterdam, Lausanne, New York 1994, pp. 605 – 663.
[*Suntola USP-1*]	T. Suntola., J. Anton, US Patent No. 4058430 (1977).
[*Suntola USP-2*]	T. S. Suntola, A. P. Pakkala, US Patent No. 4389973 (1983).

[*Tam JPCB06*] K. H. Tam, C. K. Cheung, Y. H. Leung, A. B. Djurišić, C. C. Ling, C. D. Beling, S. Fung, W. M. Kwok, W. K. Chan, D. L. Phillips, L. Ding, W. K. Ge, *J. Phys. Chem. B* **110** (2006) 20865 – 20871.

[*Thomas JPCS57*] D. G. Thomas, *J. Phys. Chem. Solids* **3** (1957) 229 – 237.

[*Tsai JCG11*] S.-Y. Tsai, M.-H Hon., Y.-M. Lu, *J. Cryst. Growth* **326** (2011) 85 – 89.

[*Tung MSE01*] R. T. Tung, *Mater. Sci. Eng. R-Rep.* **35** (2001) 1 – 138.

[*VandeWalle PhB01*] C. G. van de Walle, *Phys. B* **308-310** (2001) 899 – 903.

[*VandeWalle PRL00*] C. G. van de Walle, *Phys. Rev. Lett.* **85** (2000) 1012 – 1015.

[*Vanheusden APL96*] K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, J. A. Voigt, *Appl. Phys. Lett.* **68** (1996) 403 – 405.

[*Vlasenko PRB05*] L. S. Vlasenko, G. D. Watkins, *Phys. Rev. B* **71** (2005) 125210.

[*Volodin SC98*] N. M. Volodin, A. V. Khanova, P. S. Smertenko, L. L. Fedorenko, *Semiconductors* **32** (12) (1998) 1318 – 1322.

[*Wang APL96*] Y.-P. Wang, W.-I. Lee, T.-Y. Tseng, *Appl. Phys. Lett.* **69** (12) (1996) 1807 – 1809.

[*Wang SM14*] Z. W. Wang, Y. Yue, Y. Cao, *Superlatt. Microstr.* **65** (2014) 7 – 13.

[*Wang TSF97*] P. W. Wang, S. Sui, W. Wang, W. Durrer, *Thin Solid Films* **295** (1997) 142 – 146.

[*Wu APL01*] X. L. Wu, G. G. Siu, C. L. Fu, H. C. Ong, *Appl. Phys. Lett.* **78** (2001) 2285 – 2287.

[*Xia ML12*] Q. X. Xia, K. S. Hui, K. N. Hui, D. H. Hwang, J. Singh, Y. R. Cho, S. K. Lee, W. Zhou, Z. P. Wan, C.-N. Ha Thuc, Y. G. Son, *Mater. Lett.* **78** (2012) 180 – 183.

[*Xu NIMB03*] P. S. Xu, Y. M. Sun, C. S. Shi, F. Q. Xu, H. B. Pan, *Nucl. Instrum. Methods B* **199** (2003) 286 – 290.

[*Yamamoto PhB01*] T. Yamamoto, H. Katayama-Yoshida, *Phys. B* **302-303** (2001) 155 – 162.

[*Yamamoto TSF02*] T. Yamamoto, *Thin Solid Films* **420-421** (2002) 100 – 106.

[*Yang AM12*] T.-H. Yang, J.-M. Wu, *Acta Mater.* **60** (2012) 3310 – 3320.

[*You APL10*] H.-W. You, W.-J. Cho, *Appl. Phys. Lett.* **96** (2010) 093506.

[*Young SST08*] S. J. Young, L-W. Ji, J. Chang, Y. P. Chen, S-M. Peng, *Semicond. Sci. Technol.* **23** (2008) 085016.

[*Yu NT10*] J. Yu, S. J. Ippolito, W. Wlodarski, M. Strano, K. Kalantar-zadeh, *Nanotechnology* **21** (2010) 265502.

[*Zakrzewski TED15*] A. J. Zakrzewski, T. A. Krajewski, G. Łuka, K. Gościński, E. Guziewicz, M. Godlewski, *IEEE T. Electron. Dev.* **62** (2) (2015) 630 – 633.

[*Zhu APL10*] C. Zhu, Z. Huo, Z. Xu, M. Zhang, Q. Wang, J. Liu, S. Long, M. Liu, *Appl. Phys. Lett.* **97** (2010) 253503.

[*Zyuganov JCTE87*] A. N. Zyuganov, N. N. Koren', P. S. Smertenko, *J. Commun. Technol. Electron.* **32** (3) (1987) 611 – 622.

Warsaw, March 11, 2019

dr Tomasz A. Krajewski