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1. Personal data

Ewa Przeździecka

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

2. Education and degrees

2001-2008	Institute of Physics, Polish Academy of Sciences Ph.D in Physics Dissertation entitled: <i>„Electrical and optical properties of p-type ZnO obtained by oxidation of ZnTe”</i> .
1999-2001	University of Warsaw, Faculty of Physics, M. Sc.in Physics Thesis entitled: <i>„The influence of light on the conductivity of structures containing quantum dots”</i> .
1997-1999	University of Warsaw, Faculty of Physics, bachelor degree in Physics Thesis entitled: <i>„Research of planar doped heterostructures GaAs / InGaAs / AlGaAs by captitive methods”</i>

3. Information on current employment

01.08.2008 till today	Polish Academy of Sciences Position: Assistant Professor
01.01.2007-31.07.2008	Polish Academy of Sciences Position: physicist - photoluminescence measurements of ZnO samples made by thermal oxidation and ALD

01.07.2001-30.09.2001	Institute of Electron Technology Position: Engineer - Work with growth of semiconductor layers using MBE
01.04.2001-30.06.2001	Institute of Electron Technology Position: Trainee

Additional information about longer break at work:

In the period from 01.01.2011 to 08.01.2013 work as an assistant professor in part-time 0.5 and 0.6 time.

In the period from 30.12.2009 to 09.07.2010 sick leave (duration of 7 months).

In the period from 10.07.2010 to 10.12.2010 maternity leave.

4. Scientific achievement being the basis for the habilitation procedure in accordance with the art. 16 paragraph 2 of the Act of March 14th 2003 .

4.1 Title of the publication series and the list of publications which constitute this series.

The scientific achievements being the basis for the habilitation procedure consists of a series of ten publications in international journals entitled:

„ Research of dopant states and UV detection in ZnO-based layers and heterostructures”

The series constitute the following publications:

- [H1]** The chemical states of As 3d in highly doped ZnO grown by Molecular Beam Epitaxy and annealed in different atmospheres
E. Przeździecka, M. Stachowicz, W. Lisowski, E. Guziewicz, J.W. Sobczak, R. Jakiela, A. Jablonski, D. Jarosz, A. Kozanecki *Thin Solid Films* 605, 283-288 (2016).
- [H2]** XPS study of arsenic doped ZnO grown by Atomic Layer Deposition
D. Snigurenko, R. Jakiela, E. Guziewicz, **E. Przeździecka**, M. Stachowicz, K. Kopalko, A. Barcz, W. Lisowski, J.W. Sobczak, M. Krawczyk, A. Jablonski *Journal of Alloys and Compounds*, 582, 594–597 (2014).

- [H3] Arsenic chemical state in MBE epitaxial grown ZnO layers - Doped with As, N and Sb
E. Przeździecka, W. Lisowski, R. Jakiela, J.W. Sobczak, A. Jabłoński, M.A. Pietrzyk, A. Kozanecki *Journal of Alloys and Compounds*, 687, 937–942 (2016).
- [H4] Characteristics of ZnO:As/GaN heterojunction diodes obtained by PA-MBE
E. Przeździecka, A. Wierzbicka, A. Reszka, K. Gościński, A. Droba, R. Jakiela, D. Dobosz, T. A. Krajewski, K. Kopalko, J. M. Sajkowski, M. Stachowicz, M. A. Pietrzyk, A. Kozanecki *J. Phys. D: Appl. Phys.* 46 035101 (2013).
- [H5] Spectrum selective UV detectors from an *p*-ZnO:As/*n*-GaN diodes grown by Molecular Beam Epitaxy
E. Przeździecka, K. Gościński, M. Stachowicz, D. Dobosz, E. Zielony, J.M. Sajkowski, M.A. Pietrzyk, E. Płaczek-Popko, A. Kozanecki *Sensors and Actuators A: Physical*, 195, 27 (2013).
- [H6] Dual-acceptor doped *p*-ZnO:(As,Sb)/*n*-GaN heterojunctions grown by PA-MBE as a spectrum selective ultraviolet photodetector
E. Przeździecka, A. Wierzbicka, P. Dłużewski, M. Stachowicz, R. Jakiela, K. Gościński, M. A. Pietrzyk, K. Kopalko and A. Kozanecki *Physica Status Solidi A-Applications and Materials Science* 211, 2072-2077 (2014).
- [H7] Electron beam induced current profiling of the *p*-ZnO:N/*n*-GaN heterojunction
E. Przeździecka, M. Stachowicz, S. Chusnutdinow, R. Jakiela, A. Kozanecki *Appl. Phys. Lett.* 106, 062106 (2015).
- [H8] *n*-ZnO/*p*-4H-SiC diode: Structural, electrical, and photoresponse characteristics
M. Guziewicz, R. Schifano, **E. Przeździecka**, J. Z. Domagala, W. Jung, T. A. Krajewski, and E. Guziewicz *Appl. Phys. Lett.* 107, 101105 (2015).
- [H9] The *p*-ZnO:N/*i*-Al₂O₃/*n*-GaN heterostructure-electron beam induced profiling, electrical properties and UV detectivity
E. Przeździecka, S. Chusnutdinow, E. Guziewicz, D. Snigurenko, M. Stachowicz, K. Kopalko, A. Reszka, A. Kozanecki, *J. Phys. D: Appl. Phys.* 48, 325105 (2015).

4.2 Bibliometric data

My scientific activity resulted in **41** publications in total, according to the Journal of Citation Reports basis (as a Przeździecka and as a maiden name Ilczuk). The total impact factor of all publications amounts to **50.464**, whereas the total number of citations is **484** and **416** without auto-citations. H-index of my publications amounts to **12**.

The publications, in which I'm coauthor, appeared in many different journals, such as: Physical Review B, Journal of Applied Physics, Semiconductors Science and Technology, Microelectronic Engineering, Sensors and Actuators A, Journal of Crystal Growth, Physica Status Solidi B, Physica Status Solidi A – one publication in each of these journals; Thin Solid Films, Solid State Communication, Journal of Physics D, Applied Physics Letters – two publications; Physica Status Solidi C- three publications; Journal Alloys and Compounds – four publications, Acta Physica Polonica A- five publications.

The above data is in accordance with Web of Science (May 23rd 2017).

4.3 Introduction–scientific background

Zinc oxide (ZnO) is a wide band gap semiconductor which began its career in everyday life as powders and ceramics in dentistry, cosmetology and chemistry. This material is widely available, bio-compatible, safe for living organisms and non-toxic [1]. Thin ZnO layers and structures can be obtained, inter alia, by a variety of methods such as MOCVD¹, MBE², ALD³, sputtering method and hydrothermal method. This material can be deposited on various substrates including flexible films, tissue paper and paper. It is present in the form of layers, nanoparticles, nanowires, nanocolumns, and many others. The wide, straight band gap of ~ 3.37 eV at room temperature and the 60 meV exciton binding energy [2] make ZnO exceptionally attractive for applications in the structures for efficient light sources and detectors operating in the ultraviolet range (UV).

Due to the possibility of increasing the energy gap by magnesium doping, it is possible to use Zn_{1-x}Mg_xO alloys to obtain so-called "solar blind" [3] ultraviolet detectors, that are not only blind to visible light but also operate below 280. They are useful, for example, when working in the outer space, in the conditions of ionizing radiation. The high hardness of the material to high energy radiation, characteristic of ZnO, is in this case a desired feature [4]. It provides better durability of structures working in the outer space. Changing the energy gap also allows the growth of quantum structures, including quantum wells, with Zn_{1-x}Mg_xO layers acting as barriers for ZnO wells. This increases the efficiency of light structures, which is important from the point of view of applications in efficient light sources. Zinc oxide seems to be a very promising material, easy to obtain. It is important to note that the Zn content in the earth's crust is 70 ppm (0.007%) while the Ga or In content, used for production of GaN and InN layers and structures, is 19 ppm and 0.25 ppm, respectively.

To fully exploit the application potential of ZnO based layers in optoelectronic and micro-electronics, it is necessary to obtain a material with a controlled type of conductivity (both n- and p- type). Obtaining p- type conductivity is a major challenge because of the

¹ MOCVD *Metal Organic Chemical Vapor Deposition* is a chemical vapour deposition method used to produce single or polycrystalline thin films

² MBE *Molecular Beam Epitaxy* is an epitaxy method for thin-film deposition of single crystals.

³ ALD *Atomic Layer Deposition* is a thin film deposition technique that is based on the sequential use of a gas phase chemical process.

existence of n-type native defects, like oxygen vacancies [5] and interstitial zinc [6], as well as unintentional doping, eg., with hydrogen and carbon [7, 8]. Native defects and unintentional impurities are, i. a., responsible for the strong n-type conductivity in undoped ZnO layers, which is one of the reasons for the difficulties to obtain the p-type.

Despite the difficulty of p- type doping, many papers have reported obtaining p-type ZnO. Since the appearance of the first do p-type doping results in literature, there has been widespread discussion which has resulted in a number of theoretical models concerning the way in which acceptor dopants are incorporated into ZnO [9–13]. Among the acceptor dopants, group V elements are extremely important. Their mode of incorporation into the crystal structure of ZnO is still an open and controversial subject. Therefore, basic research aimed at understanding the nature of acceptor defects is thus extremely relevant and important. The use of multiple research techniques helps in better understanding of the nature of acceptor defects, allowing a broader view of this issue. Another extremely important element of the challenging puzzle, which is p-type doping of ZnO, is the matter of annealing the doped samples after growth. Many research reports show that annealing is often the essential element in achieving satisfactory results in doping, for example, with group V elements.

The presence of defects both in acceptor doped layers and in layers with electron type of conductivity is extremely important from the point of view of applications. Defects in the volume and at the interfacial affect both the electrical and optical properties of the obtained structures and influence thus the final characteristics of the ZnO-based devices.

The purpose of my research is:

- Growth of high quality zinc oxide layers and intentional doping of these layers with group V atoms with the aim to obtain p-type conductivity.
- Performing a series of dedicated studies of these layers in order to understand better the way of incorporation of group V elements into the crystal structure of ZnO.
- Examining the influence of annealing and co-doping on the states of group V dopants and, consequently, a better understanding of their nature.
- Determining the best doping and annealing parameters of the doped ZnO layers; applying these layers to obtain high quality semiconductor junctions.
- Application of junctions containing zinc oxide for selective detection of UV radiation.
- Examining the influence of interface modifications, by adding isolating spacers, on the parameters of the structures.

I begin the introduction to the subject of my research with the problem of UV detection (4.3.1). Then I present the problem of doping ZnO layers, with particular reference to doping with group V elements, and the general issue of defects in ZnO affecting the final properties of devices based on ZnO (4.3.2).

4.3.1 Zinc oxide as material for the UV detectors

To the simplest semiconductor electronic devices belong semiconductor junctions. They are used in many applications, including structures operating as photodetectors. The fact that humans see well in the wavelength range from red to blue, whereas many animals, mostly insects, birds, but also some mammals, eg., reindeer, see clearly in the UV range, is one of the most important reasons for the need to make detectors for the UV range. Sunlight is a critical factor in the life on earth. Its wide spectral range contains also ultraviolet. A medically proven advantageous effect of UVB (290-320 nm) radiation on the skin is to enable the synthesis of vitamin D₃, which plays a fundamental role in the metabolism of calcium, increasing its intestinal absorption and stimulating thus the formation and mineralization of bone tissue. Moreover, D₃ plays important regulatory functions modulating cell growth in many organs and tissues. UV rays acting on the skin receptors improve vascularization and skin nourishment.

Beside the beneficial influence on living organisms, UV radiation has many adverse effects. Due to scientific development, in the last decades the awareness of this fact is commonly increasing. The generally recognized adverse effects of solar radiation are: sunburn, risk of developing skin cancer, immunosuppression, premature aging of the skin. In their generation the vital role is played by ultraviolet radiation, including UVA (320-400 nm) and UVB (290-320 nm). UVA rays are present all year round, even on cloudy days, and represent 95% of the ultraviolet radiation that reaches the earth's surface. These rays penetrate through clouds, glass, and cuticle. In contrast to UVB they do not cause pain. They can penetrate deeply into the skin, and reach the cells of the dermis. The UVC radiation (100-280 nm) has the lowest penetration range and because of the ozone layer should not reach the earth's surface. However, due to thinning of the ozone layer, even brief contact with UVC radiation can cause sunburn. In order to protect against the invisible to human eye UV radiation, it is important to be able to detect it. This is particularly important in view of the phenomenon known as the ozone hole, which makes us far more exposed to the adverse effects of UV radiation.

Radiation detectors accompany humans in many fields of science. The most widely used and established ultraviolet photodetectors are based on a Si active layer. UV detectors are useful for the detection of atmospheric pollutants and smoke. They can be applied to transfer information in space and are used in defense. They are also used during water sterilization, and in environmental protection, for example, in water reservoirs they detect the presence of oil compounds. Such devices are often used for leak detection in refueling systems on aircraft carriers and in ports. Ultraviolet detection is widely used also in many industrial applications to monitor the dose and spectrum of the ultraviolet radiation used. These can include disinfection and purification facilities, forensic analysis tools and photolithography steppers. Moreover, innovative idea of extreme ultraviolet lithography which is a next-generation lithography technology using an extreme ultraviolet (EUV) wavelength (currently expected to be 13.5 nm) needs also a new type of detectors, which could replace those working based on silicon [14]. It is preferable that the new type of detectors should be resistant to high energy radiation, so it is contemplated that they will be based on wide band gap materials. Ultraviolet detectors are widely used in combustion systems for controlling the flame and sparks. Many

of these applications require devices with a high signal-to-noise ratio and high speed response [15, 16]. Current solar atmospheric studies show that the need for improved UV observations is very important. BOLD (Blind to the Optical Light Detectors) is an international initiative dedicated to the development of novel, visible blind and with high radiation hardness, detectors for UV solar observations. Practically, the observational data can be obtained by emphasizing apparently independent detectors attributes: temporal, spectral, spatial resolutions, signal-to-noise ratio, field of view, etc. For scientific investigations, regarding the observation of the UV range, all of these aspects are beneficial. However, they are coupled by the physical processes to be observed and for example, smaller phenomena usually have less brightness, and evolve faster. This implies that the detectors parameters like high resolution and sensitivity are fundamentally indivisible, and the goal would be to maximize all of them simultaneously. Additionally, Li-Fi (Light-Fidelity) is high speed and innovative wireless communications through light emitting diodes (LEDs). This concept uses optical components such as off-the-shelf LEDs and photodetectors. In this aspect, very fast light detectors are wanted.

High-quality UV detectors should meet the following requirements: they should be very sensitive, have a high signal to noise ratio, have high spectral selectivity, be fast and stable. Detectors based on wide band gap materials (ZnO, GaN, and SiC) are often insensitive to the visible range and do not require additional filters, as it is the case, for example, in detectors based on silicon. This is because detectors based on wide band gap materials generally respond to radiation energy exceeding the energy gap of the material from which they are made. In the case of ZnO and GaN – they respond to radiation from the UV range. For silicon-based detectors used for work in space, cooling must be implemented to reduce the dark current and to prevent degradation from ionizing radiation. This is a challenging and costly concern in space missions. Other types of UV detectors like the CCDs, is inherently less sensitive to cosmic rays, and needs no cooling. But microchannel plates have major additional drawbacks like need high voltage for amplification. Both GaN and ZnO are much more resistant to ionizing radiation. The use of p-n junction in radiation detection enables detection without applying an external voltage [17]. The additional advantage of photodiodes⁴ over other types of detectors is that their response time to the incident radiation is typically much shorter than it is the case, for example, in photoconductors⁵.

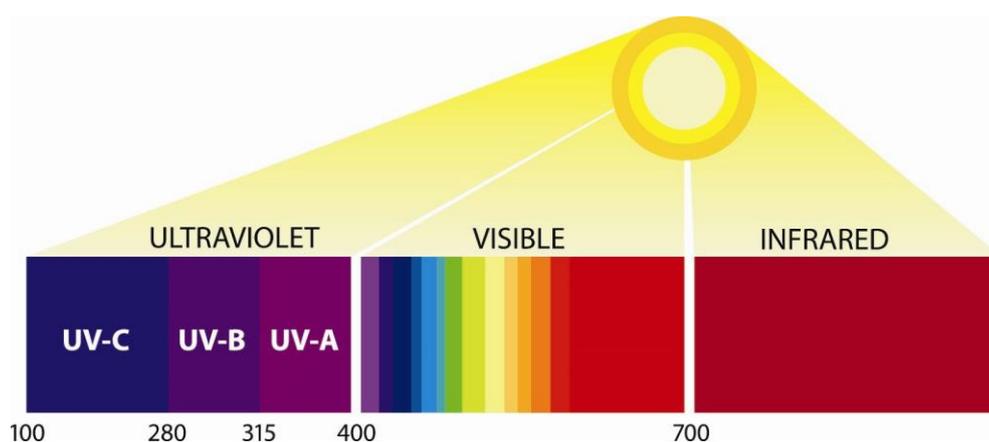


Fig. 1. A schematic diagram of the spectral range of sunlight divided into ranges: infrared, visible and ultraviolet.

⁴ Photodiode- is a semiconductor device that converts light into electrical current.

⁵ Photoconductor- a material, or a device, that exhibits or utilizes photoconductivity.

Defects occurring in the individual layers of the structures potentially used as light sources or effective light detectors may constitute a significant drawback in achieving high performance. Defects occurring within layers forming as well barriers as quantum well regions, limit the possibility of using these structures on a wider scale. Growth of films on different substrates can significantly change the type of defects present in them. In addition, the quality of interfaces between the individual layers, in particular nonradiative recombination centers occurring at the interface, constitute a basic problem which limits the intensity of light emitted by these structures. In order to obtain high-quality junctions, both for light sources and for detectors, it is important to control the quality of interfaces and defects. In the case of radiation detectors, one of the important parameters is the spectral selectivity. One of the methods to achieve highly selective detectors may be the use of two different semiconductors in a junction (heterojunction).

For many years, the combination of ZnO with GaN has been the subject of intensive research. Matching lattice parameters and structures of both materials makes ZnO growth on GaN suitable to obtain a good quality epitaxial layers. Due to the difficulty in obtaining p-type conduction in ZnO, n-ZnO/p-GaN junctions were widely studied. Very often the subject of these studies was electroluminescence of such structures. When I began my research, a few papers on radiation detection using n-ZnO/p-GaN junctions appeared. Selective radiation detection by ZnO nanowires/p-GaN junction was reported, however the ratio between the dark current (in the absence of light) and the light current (under illumination) was in this case only fifteen [18]. The reported n-ZnO/i-ZnO/p-GaN junction, on the other hand, had a relatively wide UV detection range [19].

Also, the growth of ZnO on silicon carbide (SiC) layers/substrates has for many years attracted much interest [20, 21]. In the case of ZnO/SiC heterojunctions the SiC polytype used is of importance. Radiation detection was examined in n-ZnO/p-SiC(6H) structures [22], whereas electroluminescence was detected in n-ZnO/p-SiC(4H) structures [23].

For applications in UV detectors also ZnO/Si heterojunctions were tested, but in this case detection both in the UV and in the visible range was often observed [24–27]. In order to improve the selectivity of ZnO/Si junctions, additional interlayers of suitable thickness, e.g., SiO₂, were added on ZnO/Si interfaces [28].

Heterostructures composed of ZnO doped with group V elements and GaN have not been extensively studied before I started my research. Ultraviolet detectors based on ZnO [17], GaN [29, 30], or SiC [31, 32] were known, but for the most part these detectors were not highly selective (typically, detection was observed in a wide spectral range in the ultraviolet region). As mentioned earlier, the search for structures that can detect radiation in a narrow spectral range with fast reaction time and big difference between dark and bright current is one of the challenges of modern physics. Fundamental research of the layers that make up such a structure, understanding the nature of doping and the defects therein is an important and necessary step in their potential application.

4.3.2 Doping of ZnO with group V elements and defects control in ZnO.

Doping is a method that can significantly change the parameters of semiconductors. Literature about ZnO layers doped with group V elements in order to obtain p-type conductivity, is very rich. Acceptors were introduced into ZnO in many ways, successfully or not in obtaining p-type conductivity. The difficulty of doping a wide-gap semiconductor such as ZnO is often related to either low dopant solubility or a high defect ionization energy, so that the defect is not ionized at normal operating temperature. Although the low solubility of

the dopants can sometimes be overcome by using nonequilibrium growth techniques, such as molecular beam epitaxy (MBE), decreasing the ionization energy of the acceptor has been a challenging issue, especially for oxides and nitrides [33]. In the case of doping with arsenic (As), antimony (Sb), and phosphorus (P) it has been found that these dopants have low solubility when replacing oxygen in ZnO, due to the large ionic radii mismatch: P^{3+} (2,12 Å), As^{3+} (2,22 Å), and Sb^{3+} (2,45 Å) as compared to O^{2+} (1,38 Å) [34]. This fact is also supported by theoretical calculations, which suggest that these elements should become more stable when localized on zinc sites. In addition, energy levels of P, As, Sb replacing oxygen (As_O , Sb_O , P_O) are located deep within the band gap of ZnO. In the case of As_O , Sb_O the ionization energy would be greater than 1 eV [9], while in the case of the nitrogen acceptor, N_O , the ionization energy would be 0.4 eV [9]. In 2004 a new doping model of As and Sb in ZnO was proposed, in which the dopant occupies a Zn site (donor) and forms a complex with two zinc vacancies (acceptors). This gives as a result shallow complexes made of one donor plus two acceptors [10]. In some sense, this model resembles codoping, this means doping acceptors together with donors in proportion 2:1. Moreover, in 2012 a new concept of doping appeared, which demonstrated that stable complexes of group V dopants in ZnO may consist of a substitutional dopant surrounded by three zinc vacancies ($D_{Zn}-3V_{Zn}$ where $D=P$, As, or Sb) [11]. However, in both cases, i.e., in the case of defects of the form of ($D_{Zn}-3V_{Zn}$) and ($D_{Zn}-2V_{Zn}$) where $D=P$, As, or Sb, these were theoretical models. The study of a ZnO bulk crystal implanted with arsenic partially confirmed the theoretical calculations and demonstrated that this element does not substitute oxygen but rather zinc [35].

The acceptor wave-functions, especially those of a shallow acceptor, have similar character to those forming the valence band maximum (VBM), which consists mostly of anion p , cation p , and cation d states. Therefore, to achieve a shallow acceptor level, the dopant should be as electronegative as possible; that is, it should have low p orbital energy. Among substitutional, group V dopants in II-VI semiconductors, nitrogen seems to be the most promising. It is related to the fact that the atomic, p -orbital, energy level of N is the lowest (the most electronegative) of all group V elements. Therefore, N_x ($x=O, S, Se, Te$) has been the preferred acceptor dopant for II-VI semiconductors [33].

However, the simple N_O acceptor (nitrogen replacing oxygen) appears to be relatively deep (~0.4 eV) [9]. In recent years, therefore, new theories concerning the problem of nitrogen incorporation into ZnO appeared. In 2011 Lautenschlaeger and co-authors proposed a complex consisting of a pair of nitrogen atoms stabilized by hydrogen, N_O-H-N_O . In 2012 Liu and co-authors proposed a complex in the form $N_{Zn}-V_O$ [12]. In 2013 Boonchun et al. showed that the N_2 molecule at the Zn site may be a shallow acceptor, whereas N_2 in place of O is a donor, and a single N atom in the place of O acts as a deep acceptor [36]. In the same year Reynolds et al. suggested that a complex of the form $V_{Zn}-N_O-H^+$, with 130 meV ionization energy, is responsible for p-type conductivity of nitrogen doped ZnO [13]. In 2015 a paper suggesting that $(NH_4)_{Zn}$ also may be a shallow acceptor in ZnO was published [37]. As can be seen, the problem of nitrogen incorporation into the ZnO lattice is still open. It is known that the efficiency of nitrogen doping is very often quite low, this means that a large number of nitrogen atoms introduced into the oxide layer usually yields a low concentration of electrically active dopants. This effect is probably associated with the formation of N-N complexes [38]. Accordingly, it is desirable to use a more active source of nitrogen, such as NO gas or nitrogen plasma.

Furthermore, codoping (donors plus acceptors) and dual acceptor doping was used in order to increase the doping efficiency. The codoping method has been proposed to reduce the

ionization energy of the acceptor level [39] and dual doping has been successfully used in the case of simultaneous introduction of group I and V atoms into ZnO [40–42].

Beside defects intentionally introduced into the material there are also native defects [43, 44], the presence of which also affects significantly the final properties of ZnO-based devices. Native defects and unintentional impurities present in ZnO depend on the process/method and the conditions under which the ZnO layer was formed. Their presence also affects the incorporation of the intentional dopants. It seems thus reasonable to expect that doping ZnO layers grown by different methods with the same element may result in a different outcome in the sense of final parameters of the obtained layers and devices.

Another important issue in designing the construction of junctions for useful applications, e.g., UV detectors, is the control of interfaces. This is particularly important for heterojunctions, wherein two different materials are combined. Defects present on junction interfaces have a significant impact on their final electrical parameters.

The impurity states in the crystal can be studied with use of many research techniques, such as: photoluminescence, deep level transient spectroscopy (DLTS), photocurrent, microscopy techniques, and X-ray photoemission spectroscopy (XPS). As previously mentioned, the acceptor doping of ZnO is not a simple matter, and to understand how impurities build into the structure of the matrix is not an easy task.

Changes of photoluminescence (PL) in ZnO layers due to doping with group V elements were shown in many publications [45–47], which in most cases discussed additional peaks in the luminescence spectra attributed to acceptor transitions. In this case the high sample quality and the accuracy of PL measurements allowed observation of more optical transitions and a thus their deeper interpretation - in this respect also my earlier publications (before starting work on habilitation) constitute an important contribution [48, 49]. However, the proposed interpretation of the PL lines in ZnO doped with group V elements was not always consistent. It should be emphasized that a single luminescence measurement does not give us a clear identification of the doping induced defect. However, in combination with other experimental techniques it is an important contribution to the knowledge of impurities in ZnO. Among others, PL measurements as a function of temperature allow determination of the thermal (de)activation energy of the respective transitions and thus estimation of the energy level position in the matrix band gap.

XPS analysis allows determination of the chemical surrounding of the atom and its position in the crystal lattice, e.g., the arsenic atom in ZnO. Such preliminary studies on acceptor doped ZnO were conducted before the start of our research [47, 50–53]. In XPS studies of zinc oxide doped with arsenic a broad peak associated with As was observed. Lack of high resolution XPS data impeded interpretation. XPS investigations of ZnO:Sb have shown that Sb is located rather at zinc than at oxygen sites [54–58]. It should be mentioned that in case of broad XPS peaks changes in the chemical state of the dopants related to annealing or additional doping are difficult to observe. Both of these methods (annealing and additional doping) are often used to obtain p-type conductivity.

As it can be seen, carrying out dedicated studies on the state of acceptor dopants in ZnO is highly justified as well as interface quality studies. Such studies must be carefully planned and the crystals examined should be selected to represent a series of samples that are the basis of selected and advanced studies.

4.4 Examination of dopant states and UV detection in ZnO-based layers and heterostructures - description of the publication series H1-H9

At the beginning of the presentation of the series of papers constituting the habilitation, I will outline [H1-H3] the research results on the impact of annealing, doping, and additional doping on the states of group V elements in ZnO layers, with special emphasis on arsenic. Next, I will present [H4-H9] the results concerning the use of ZnO layers, in particular layers doped with atoms of group V, in semiconductor heterojunctions. In addition, the impact of doping, defects, and modifications of the interface on the parameters of the obtained UV detector diodes will be discussed.

4.4.1 Change of acceptor dopant state due to annealing [H1]

One of the most commonly used methods to change the properties of ZnO layers doped with elements that may be the source of acceptors is their annealing. Annealing can affect the number of native defects and the concentration and type of unintentional impurities. As it has already been mentioned, native defects and unintentional impurities significantly affect the properties of the material. The high temperature during annealing may reduce the concentration of possible contamination of ZnO layers, e.g., by hydrogen [59]. It is known that hydrogen, present in a number of growth techniques, is a shallow donor in ZnO [60]. This element may be responsible for the high n-type concentration in undoped layers of ZnO.

With a suitable selection of the parameters and the method of annealing of intentionally doped ZnO layers we can also influence the solubility and the chemical state/position in the crystal lattice of the intentional dopants. Therefore, annealing can influence both the native defects as well as unintentional and intentional impurities. The suitable procedure to change the state of the dopant (for example in order to obtain p-type conductivity), encompassing the annealing type and parameters, is often called dopant activation [61, 62].

The first work in the series, [H1], concerns the after growth annealing of ZnO:As layers obtained by plasma assisted molecular beam epitaxy (PA-MBE). It shows the influence of the annealing atmosphere on the arsenic properties and on the general properties of ZnO layers. The combination of two experimental methods, i.e., XPS and PL, gives a wider picture of the effect of annealing on the defects resulting from the presence of As. The samples tested contained, intentionally, the same amounts of arsenic and were annealed after growth at the same temperatures, but in various atmospheres (oxygen, nitrogen, argon) by RTP⁶.

The application of the high resolution XPS method, proper planning and preparation of samples and measurement parameters gave us a unique opportunity for careful observation of dopants. The analysis of the As3d peak obtained with high resolution XPS revealed three As-related contributions (Fig. 2). There are two main contributions, present both in the "as grown" as well as in the annealed samples, represented by the As3d doublet peaks at binding energies (BE) of 44.0 and 45.5 eV, respectively. Contributions of As3d located between 44.3 eV and 45 eV may be attributed to arsenic at the zinc site, As_{Zn}, and two zinc vacancies V_{Zn} as next nearest neighbors. The formation of this type of defect (As_{Zn}-2V_{Zn}) has been proposed previously [10] in order to explain p-type conductivity in As doped ZnO. According to this model, such complexes are formed in the energetically favorable reaction between As_{Zn} and zinc vacancy and lead to the creation of stable As_{Zn}-2V_{Zn} shallow acceptor state, located 0,15 eV above the valence band maximum. As already mentioned, theoretical calculations have

⁶ RTP- *Rapid Thermal Processing*

shown that arsenic may replace Zn (then it acts as a donor) creating in its vicinity two zinc vacancies (acting as acceptors). The $As_{Zn}-2V_{Zn}$ complex has the nature of an acceptor. Additionally, it was suggested that arsenic may also form a complex with three zinc vacancies, $As_{Zn}-3V_{Zn}$ [11], however, this model has not yet been confirmed experimentally. In fact, the coexistence of p-type conductivity and As3d electron states between 44.5 and 45 eV has been observed in several XPS studies of As doped ZnO [63, 64]. Taking into account the optical studies and XPS data, shown in [H1], we can attribute XPS state at BE 45,5 eV to As_{Zn} (in ZnO) [63–65] and the XPS peak at BE 44,5 eV probably to the $As_{Zn}-2V_{Zn}$ complex. The third, smallest contribution to the signal, represented by the As3d doublet peaks at BE of 40.9 and 41.6 eV, can be attributed to As–Zn bonding (arsenic at oxygen site As_O) [63, 64, 66]. This confirms the assumption that the arsenic (group V atom) does not simply occupy the oxygen site (group VI atom) what we would expect with a simple substitution model. In addition, the observed intensity of the $As_{Zn}-2V_{Zn}$ complex observed in [H1] suggests that in the epitaxial ZnO: As layers we should expect a large number of acceptor states associated with the As. In all tested samples, strong emission attributed to free electron recombination with acceptor holes as well as to donor-acceptor pair are observed, which also confirms the existence of a large number of acceptor states in the studied layers.

In [H1] it has been shown that in the case of ZnO:As layers obtained by MBE some of the dopant atoms are substitutionally incorporated (both in Zn as well as O sites), while others form complexes, revealing the complicated problem of arsenic doping. Moreover, the relative intensities of the contributions to the As3d peak depend on the annealing atmosphere of samples. Thus, the number of arsenic atoms replacing Zn and O, or entering the Zn site surrounded by vacancies, changes. The luminescence from samples annealed at different atmospheres changes as well, confirming the change of the layer properties. It should be mentioned that in all experiments parts of the same sample obtained in one growth process were used. All samples directly after growth and immediately after annealing were vacuum-packed in order to avoid prolonged contact of the surface with the atmosphere.

It has been shown that two properties change simultaneously as a result of annealing: the intensity of the individual contributions to the As3d peak and the luminescence of the samples (Fig 3 (a-c) from [H1]). Therefore, the annealing atmosphere influences the state of the arsenic dopant in MBE grown ZnO:As layers. The high resolution XPS investigations revealed that the relative intensity of three XPS contributions depends on the annealing atmosphere, but in all the cases none of them clearly dominates, which is a fingerprint of the complicated nature of the arsenic states in ZnO. This result is important in the wide discussion concerning acceptor doping of ZnO.

The observed changes of the dopant state due to the annealing of ZnO layers after growth shown in [H1] explains the need of annealing in order to "activate" the dopant. It also demonstrates that in the process of "activation" of dopant an important role play not only the temperature but also the atmosphere in which we annealed the layers.

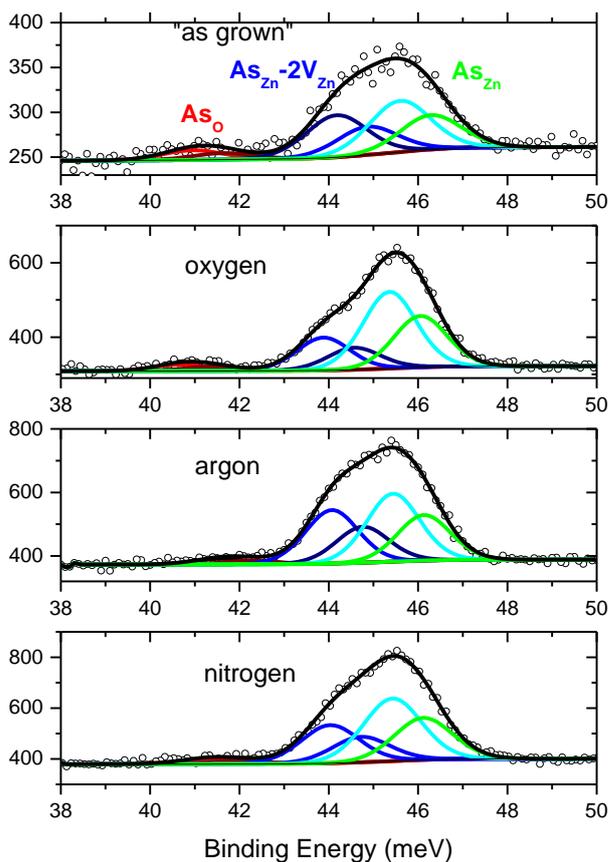


Fig. 2 High-resolution XPS spectra of the As3d for ZnO-MBE films as grown and annealed in different atmospheres (oxygen, argon, nitrogen) at 700 °C. As 3d XPS spectra, were deconvoluted into three components, represented by the three As3d_{5/2}–As3d_{3/2} doublets. The deconvolution of As 3d XPS spectra was performed using CasaXPS software

4.4.2 The state of dopant in the ZnO layers made of different growth conditions [H1, H2]

Zinc oxide is a semiconductor which can be obtained using various growth methods such as molecular beam epitaxy (MBE), atomic layer deposition (ALD), hydrothermal method, sputtering and others. The variety of method allows growing this material at very different temperatures from room temperature to very high temperatures. So the question arises, if the material obtained by various methods has the same properties and if it is possible to have general conclusions regarding doping when ZnO is doped by the same impurity but in different growth conditions e.g growth temperatures and in zinc or oxygen rich conditions. In the case of ZnO, the type of native defects depends on the growth conditions of the layers [67] and thus it has a significant effect on the incorporation of the dopant atoms into the structure and on effective doping, including the formation of the p-type of conductivity.

A separate problem is the way in which the dopant is introduced. Arsenic may be introduced into ZnO by variety of methods in-situ or ex-situ, using various sources, e.g.: Zn₃As₂ [46, 68], annealing in an atmosphere of arsenic [69]; diffusion from GaAs substrates [70], solid state effusion cell with pure arsenic [45].

The existing literature on the chemical state of As impurities in the ZnO is inconsistent [50, 71, 72]. The results presented in the literature, concern the ZnO samples obtained by

different methods. In the case of ZnO layers on a GaAs substrate made by MOCVD [71] photoemission spectrum of the As3d state shows two peaks at BE 45.2 eV and at BE 43.9 eV are observed. Higher binding energy peak is attributed to As-O bonding in As_2O_3 . Arsenic state at 43.9 eV is correlated with the complex $\text{As}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ and contributions of As_{Zn} and As_{O} are not observed. It should be emphasized that, in case of the broad peak is not easy to separate the contributions of various states of the dopant.

In the case of ZnO layers obtained by a pulsed laser ablation from a $\text{ZnO}/\text{As}_2\text{O}_3$ target, the authors presented one wide As3d peak localized at BE $\sim 45\text{eV}$ which is attributed to the arsenic in zinc site [50]. Next, in case of ZnO obtained by magnetron sputtering the single As3d peak at BE $\sim 45\text{eV}$ is ascribed to $\text{As}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ [72] (Rys. 2). A similar situation is observed in case of samples obtained by MOCVD on GaAs substrates [70].

The presence of only one broad peak between binding energy 42 eV and 48 eV significantly hinders or even prevents its correct interpretation. In order to better understand how As builds up into the ZnO matrix high resolution XPS studies on high quality samples have been performed [works H1, H2, H3]. In addition, there is no work in the literature, that compares dedicated series of samples, where we change, for example, only one parameter of growth or annealing, measured on the same measurement system with a given resolution.

In order to compare the state of arsenic impurities in ZnO layers made by different growth methods, in publication [H2], we are looking on arsenic in ALD samples made in temperature of 280°C , which is much lower than for MBE layers whose growth temperature is around 500°C . In this samples arsenic was introduced by annealing in arsenic atmosphere. Concentration of As atoms in this samples was 1%. In the ALD-doped samples the high resolution XPS studies revealed, the presence of three contributions of As3d, the origin of which we associate to the presence of As in oxygen or zinc site and to arsenic complex. Mutual intensity of the XPS contributions is similar (Fig. 3 from H2) e.g. in sample annealed at 850°C , but different from the results obtained in case of MBE samples (Fig. 3) in which the contribution from As located in the oxygen site is very low – only a few percent (Fig. 1). Thus, comparing ZnO:As samples obtained by MBE and ALD method, we see that in these samples As incorporated differently. Primarily a significant difference is between the amount of arsenic in the oxygen site (Fig. 3).

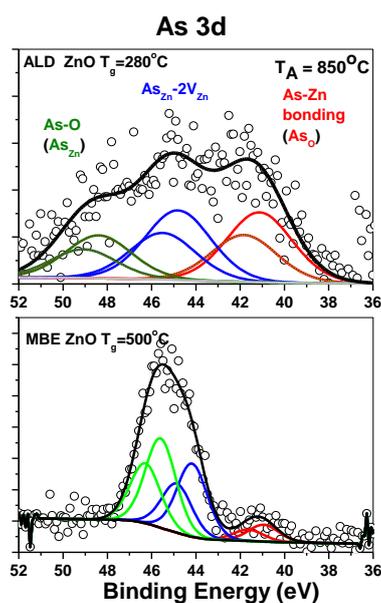


Fig. 3. Comparison of chemical state of As3d in ZnO layers made by ALD at 280°C and by MBE method at a temperature of 500°C . In the case of ALD layers arsenic is introduced as a result of annealing in the ampule under an atmosphere of arsenic, in the case of the MBE growth layer by the use of a As Knudsen cell. Top figure taken from work [H2] and bottom figure from work [H1].

Additionally, in [H2], we observed that a change in annealing temperature from 850° C to 950° C results in a change in the As3d chemical state. Mutual relation between contributions interpreted as arsenic at zinc site As_{Zn} , arsenic in oxygen site As_O and arsenic in the complex $As_{Zn}-2V_{Zn}$ is changed. Wherein the input from $As_{Zn}-2V_{Zn}$ is greater in the case of annealing at a higher temperature. Moreover, for higher annealing temperature arises a new peak at the energy 3.355 eV in the low temperature luminescence, interpreted as an exciton bound to neutral acceptor A^0X . The presence of this peak in the PL spectrum demonstrates the additional acceptor states in the sample (Fig. 2 from [H2]). In contrast to samples described in the work [H1], ALD ZnO:As samples show higher contributions of arsenic in oxygen site. Information presented above give an evidence that the chemical state of arsenic impurities in ZnO layers, and as a consequence effective acceptor doping, depends on the growth method, doping and annealing.

It must be emphasized that chemical state of As depends on the type of annealing and growth conditions of ZnO layers. This is the very important result. Considering how the dopant is incorporated into the matrix of ZnO, we must also think about the conditions of layer growth.

4.4.3 Changes of acceptor states on the effect of the additional doping [H3]

One of the proposed methods of obtaining p-type doped ZnO is „dual acceptor doping” [73], involving the simultaneous introduction of two acceptor impurity. Theoretical calculations and experiments show that ZnO can be effectively doped by, for example: dual doping by silver and nitrogen (Ag+N) [42] or phosphor plus nitrogen (P+N) [74], or by lithium plus nitrogen (Li+N) [40, 41]. In literature, we cannot find comprehensive information how such a double doping affects the state of a single dopant, or environment around this dopant in the ZnO matrix or if a new type of complex is formed? To meet these difficult issues, we made and characterized ZnO MBE samples doped only by arsenic, doubly by arsenic and nitrogen and triple by arsenic, nitrogen and antimony. The presence of dopants was confirmed by secondary ion mass spectrometry (SIMS) (Fig. 1 from H3).

The high resolution XPS analysis was made on as grown and on RTA annealed samples in oxygen or in argon atmosphere. The emphasis was on dopant states. Quantity of arsenic atoms on the oxygen site was small in all as grown samples (5-10 %) and moreover, this contribution was relatively lower in the sample individually doped with arsenic. The main contribution of arsenic in as grown ZnO:As samples comes from a peak assigned to arsenic in a zinc side As_{Zn} . While, in double and triple doped samples the peak is assigned to $As_{Zn}-2V_{Zn}$ dominated.

As I mentioned earlier, annealing of samples in oxygen and argon atmospheres results in changes of the As 3d spectral features. In all samples annealed in oxygen the As at the Zn site As_{Zn} dominates and the contribution of this state decreases when samples were additionally doped with Sb and/or N, whereas simultaneously the contribution assigned to $As_{Zn}-2V_{Zn}$ increases. The peak related to the As_o state is significantly lower than in “as-grown” samples.

In samples annealed in argon situation is different. The high intensity doublet of the As 3d_{5/2} peak at BE of 44.2 eV was detected, which we assign to the arsenic complex involving two zinc vacancies $As_{Zn}-2V_{Zn}$. These peaks coexist with smaller intensity peaks due to arsenic at zinc sites As_{Zn} .

The high resolution XPS analysis of the arsenic As 3d states for As doped ZnO MBE samples shows that additional acceptor doping affects the position of arsenic within the ZnO matrix. Moreover, arsenic position in ZnO crystal is strongly related to post growth annealing.

Therefore, the additional doping can modify the acceptor dopant state, and observation of these changes allow for a better understanding of the issue of double acceptor doping.

For a deeper understanding of why the dopant atoms change their location / environment in the crystal matrix as a result of dual doping we should also consider how the atoms of additional additives (in this case, Sb and N) build into this matrix. In the case of ZnO:AsNSb sample photoemission spectra show the peak Sb3d3 at the binding energy of 539.5 eV [H3]. As reported in a previous study the Sb ions in Sb-doped ZnO occupy Zn sites rather than O sites, owing to the similarity between the ionic radii of Sb^{3+} (0.76 Å) and Zn^{2+} (0.74 Å). The change of oxidation state of Sb between 3+ and 5+ was revealed previously using XPS and XANES⁷ studies [75].

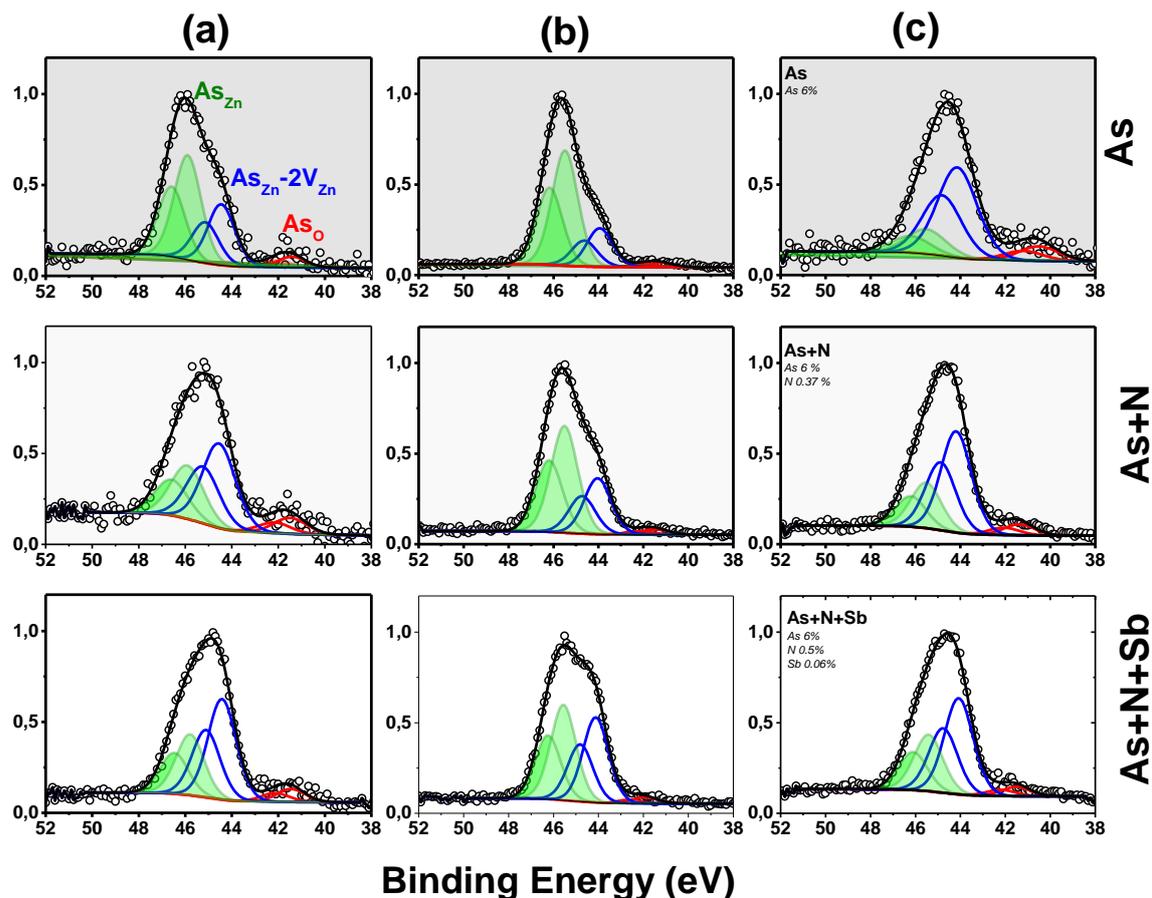


Fig. 4. Normalized high-resolution XPS spectra of the As3d for ZnO-MBE films single, double or triple doped by As, N and Sb, “as grown” (a) and annealed: in oxygen (b), or argon atmospheres (c) at 700 °C.

Nitrogen dopant examinations by XPS are difficult because of the small photoionization cross section of this element. We performed these tests on ZnO:AsN and ZnO:N samples. With the long-term collections of the N1s spectrum we observed that the nitrogen peak is composed of several components, but the signal is still noisy making difficult to clear interpretation of results (unpublished data).

In addition, analysis of the states of native defects in a ZnO matrix is also important. Examining of the peak coming from oxygen, we can conclude also if oxygen atoms are surrounding by less numbers of oxygen atom than it is in the ideal ZnO structure. This

⁷ XANES- X-ray absorption near edge structure

contribution allows us to indirectly infer the amount of oxygen vacancies in the crystal. The amount of oxygen or zinc vacancies can significantly affect how impurities built-up. In the case of research of layers doped with single, double or triple by V group atoms, we looked at the oxygen component attributed to a deficiency of oxygen in the second coordination zone-at binding energy 531.4 eV [76, 77]. In our studies, we observed that the As_O peak is significantly lower in annealed samples than in the layers immediately after growth, while the peak associated with the oxygen deficiency increases (Fig. 5 from H3).

The paper H3 shown that the chemical environment of dopants in the crystal structure of ZnO depends also on the additional doping. It is important to note that additional doping with V atoms increases the concentration of As atoms embedded in the $As_{Zn}-2V_{Zn}$ arsenic complex both in as grown as well as in the heated samples. Such results have not been reported so far.

However, in existing literature we can find XPS examinations that show changes in nitrogen state related to additional donor doping: aluminum Al [78], gallium Ga [79] or indium In [80]. Changes in doping states in the case of double doping by I and V group element, was also reported e.g. change in lithium state Li on the effect of the additional doping with nitrogen [81] and change in silver state Ag on the effect of the additional doping with nitrogen [82, 83].

The presented papers present a comprehensive study of group V dopants, in particular arsenic, to zinc oxide. High resolution photoemission investigations allowed to observe changes in a chemical state of dopants in response to various type of annealing, dual doping as well as different methods of growth and ways of introduction of dopants. The research has been performed on a dedicated series of high-quality samples and annealing conditions have been carefully chosen. Such a systematic research, which provided unique knowledge on group V atoms location in the ZnO lattice, has not been performed before. Application of the high resolution XPS method allowed to disclosure details on dopants' atoms location and was able to elicit the complexity of chemical states of dopants in the zinc oxide lattice. The results presented here provided a substantial contribution to a wide spread discussion on the nature of p-type doping of zinc oxide.

It has been shown that annealing and introducing intentional dopants influence the type and amount of native defects and, on the other hand, the native defects existing in the material affect the way in which the dopant is incorporated and hence the properties of the layers. This result shows us the significant role of advanced basic research required for planning and obtaining layers and as a result structures with predefined and controlled physical parameters.

4.4.4 Control of the interfaces and defects in order to obtain a high-quality junctions [H4 - H8]

In order to obtain high quality junctions, control of the physical parameters of the individual layers in the structures is very important: that is a better understanding of the physical processes in the doped ZnO layers, including changes in the state of the impurities due to annealing or additional doping (described in papers H1-H3), is of fundamental importance, since it paves the way to their improvement as well as to their application. Doped and undoped ZnO layers were extensively characterized and used to produce the semiconductors junctions investigated in H4-H9. In particular, in H4-H7 and H9, the ZnO layers singly or doubly doped with V group elements and annealed after growth, were

examined. Analysis of the basic properties of the ZnO layers and of the dopants state in these layers as well as research on the preparation procedure of the junctions has allowed a better physical understanding and, as consequence, to achieve structures with higher quality.

In order to obtain, heterostructures with a good crystallographic quality GaN substrates represent a suitable choice, because, in this case, zinc oxide is grown on a substrate / layer with an hexagonal structure and a a-plane mismatch between the matrixes of 1.8%. Moreover, as was mentioned in the introduction, in order to activate V group dopants post growth annealing is usually needed and in case of a ZnO/GaN structure long distance diffusion of the dopant from ZnO into the GaN layer is not observed. At the same time the GaN substrate/layer, which plays the role also of n-type partner, is thermally stable in the temperature regimes here used, i.e. does not provide atomic species that could diffuse into the ZnO layers. Such dopant redistribution could take place e.g. in the case of ZnO based homojunctions and was previously observed in the case of ZnO layers grown on GaAs substrates, actually being one of the method for obtaining ZnO:As [48, 84, 85].

Control of the uniformity of the doped layer is important in case semiconductor junctions are realized. Uniformity and the doping profiles of the intentional dopants in MBE ZnO layers were examined by secondary ion mass spectrometry (SIMS) [H4, H5]. We experimentally find (Fig. 1 from H4; Fig. 1 from H7; Fig. 1 from H5), that by means of molecular beam epitaxy it is possible to uniformly introduce dopants (in our case: arsenic, nitrogen or antimony) throughout the whole thickness of the ZnO layers, and we do not observe the effect of long distance diffusion of these elements into the GaN substrate, i.e. we achieve heterojunctions with a sharp interface. Furthermore, since defects, traps and interlayers located at the interfaces can effectively reduce the application potential of the structures. The ZnO/GaN interface was carefully investigated by using microscopic techniques such as scanning electron and transmission microscopy, while testing some key parameters related to the GaN substrates chemical pretreatment and the growth initial conditions. Proper chemical pretreatment of GaN substrates before growth is very important. In the GaN substrates chemical pretreatment case, a two-step chemical etching procedure is used, based on a $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ (1:1) and a subsequent $\text{NH}_4\text{F}\cdot\text{HF}$ ⁸ dip. This treatment protect the surface against oxidation and from formation of an unintentional Ga_2O_3 oxide layer [86].

Equally important is the modality used to initiate the ZnO growth process on GaN. Preliminary experimental work was dedicated to develop an optimal procedure. This method is based on the deposition of a thin metallic layer of Zn on the substrate surface prior to exposure to oxygen and before switching on the oxygen plasma - source that provides the active oxygen. The procedure essential parameters are: *i*) the deposition temperature –that has to be chosen to achieve a proper adhesion of the Zn layer and *ii*) the appropriate thickness of the metallic layer. Additionally, the initial stage of growth was controlled “in situ” using reflection high-energy electron diffraction (RHEED) technique. Following the optimization of the above described procedure, published TEM studies (Fig. 3 from H6) confirmed the absence of an unintentional layer of Ga_2O_3 oxide at the ZnO/GaN interface, with the growth of the ZnO layer occurring directly on GaN. In addition, in this case cross section analysis by SEM and by cathodoluminescence, showed a smooth and defined ZnO/GaN interface. Furthermore, the X-ray diffraction studies revealed that the ZnO layer grown directly on GaN are completely relaxed and the layer growth takes place in the c-direction (Fig. 2 from H6).

⁸ $\text{NH}_4\text{F}\cdot\text{HF}$ -amonium fluoride plus hydrofluoric acid.

In H4-H7, H9, junctions containing ZnO layers doped by V group elements were examined. The results presented in those publications is based on an extensive study carried out simultaneously, on the annealing response of the ZnO layers [H1], and additional preliminary work to appropriately select the concentration of the dopant. This resulted in an accurate control of the interfaces, thus giving us the possibility to obtain junctions with good electrical properties.

In the case of ZnO:As/n-GaN junctions, described in papers H4 and H5, the diode ideality factor η was, $\eta = 1.4$. The maximum forward-to-reverse current ratio (the ratio of current flowing in the forward direction, I_F , to the current flowing in the reverse direction, I_R , was $I_F/I_R \sim 10^5$. The built in potential at 300 K was 0.6 V (Fig. 2 from H5). As mentioned in the introduction, prior to our study on ZnO based heterojunctions, examinations of electrically inverse n-ZnO/p-GaN were known and research on ZnO:As/n-GaN junctions was also reported [87]. However, in the cited publication the detailed electrical parameters of the junction were not given, and based on the presented results of current-voltage characteristics we can only estimate that the forward to reverse current ratio was several orders of magnitude smaller than that of our structures.

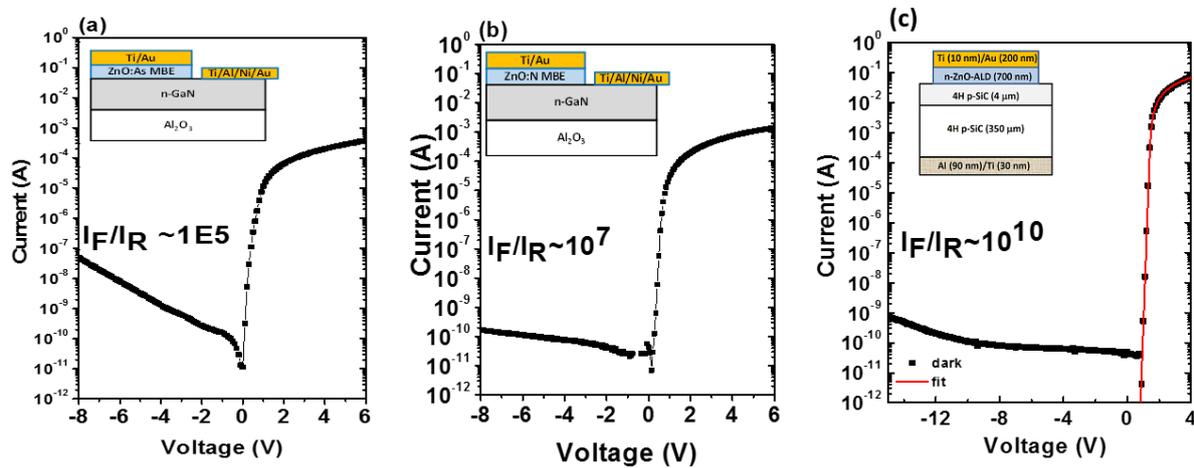


Fig. 5. Examples of current-voltage characteristics of heterojunctions: (a) ZnO:As/n-GaN (b) ZnO:N/n-GaN (c) ZnO/p-SiC. Figure based on results from H4, H7, H8.

The ZnO:AsSb/GaN structures were described in [H6]. We note, that annealing of the junctions can be used to effectively reduce the dark current as was shown in the case of junctions with double doped (by arsenic and antimony) ZnO layers (Fig. 5 from H6). In that case the dark current was at the level of 10^{-11} A. In the case of junctions based detectors one of the key parameters is the difference between the dark and light current in the reverse direction with a low dark current being favorable to light detection. In the case of the investigational diodes [H6], due to the low dark current, this difference was generally several orders of magnitude under ~ 1 mW incident illumination. Thus the structures realized resulted suitable for the detection of low power radiation.

To obtain the ZnO:N layers a nitrogen plasma was used provide a low-energy flows of atomic nitrogen that can be incorporated, as dopant, during the growth process. Nitrogen was introduced into ZnO at the level of 10^{20} at/cm³ as verified by SIMS. It is known that dopant introduction into the crystal can cause the appearance of point defects and complexes in the

bulk that might affect the final properties of the layers and structures. Luminescence was chosen as main technique to investigate the characteristics of the defects in the bulk as well as dopant intentionally introduced. As an example, the luminescence results as a function of temperature presented in the work H7 (Fig. 2 work H7) allowed to determine the activation energy of the nitrogen dopant that was found equal to 130 meV. The values of the nitrogen activation energy reported in the literature are not entirely consistent. In earlier works, published values of the activation energy for the nitrogen acceptor, obtained from the optical tests, varied in the 165 to 248 meV range [88–90], whereas lower activation energies (90 meV [91] and 100 meV [92]) have been extracted from temperature dependent Hall effect measurements. Among the elements of groups V, nitrogen is considered as the most promising p-type impurity. However, it is known that nitrogen acceptor can be compensated by defects such as oxygen vacancies or complexes like N_O-Zn_O , where N_O indicate an isolated nitrogen atom located at oxygen site. Additionally, N_O is a rather deep acceptor. Theoretical calculations also point to an acceptors compensation action of nitrogen molecules, N_2 , localized in the place of O anions as possible cause in the present difficulties in obtaining p-type conductivity. Therefore, the use of a more reactive form of nitrogen such as a nitrogen plasma, is preferred and has been chosen during the studies here presented.

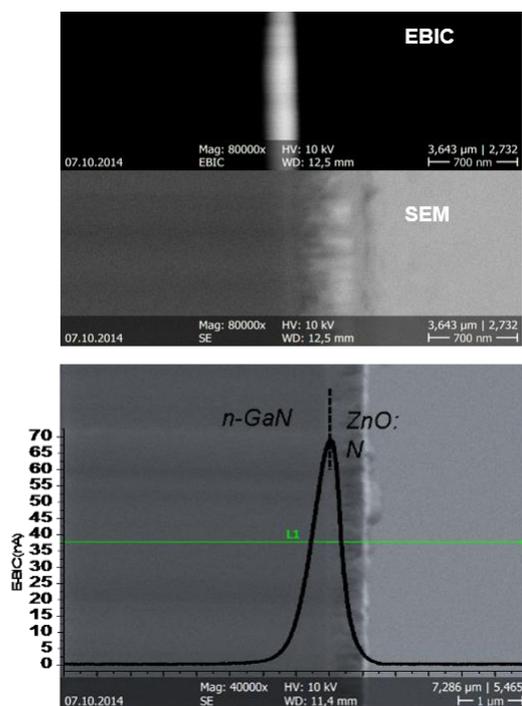


Fig. 6 Cross-sectional image of ZnO:N/GaN in secondary electrons (SE), E-BIC line scan is superimposed on the SE image.

The interface of the ZnO:N/GaN was studied by combining scanning electron microscopy (SEM) and electron beam induced current (E-BIC) measurements (Fig. 6). The E-BIC research has shown that the maximum current signal corresponds to the ZnO:N/n-GaN interface thus confirming that the junction is located exactly at the interface between the ZnO and GaN layers. This is a unique result, previously not reported, for this type of structures that confirms the presence and location of the depleted layer in the structure and is particularly important in the case of materials, like ZnO:N, for which reported electrical performance resulting from the introduction of nitrogen or other p-type dopant candidates are inconsistent.

In the annealed ZnO:N/GaN structures a high forward to reverse current ratio I_F/I_R 10^7 and very low dark current 10^{-10} A were obtained. The mentioned junctions have good

electrical parameters and they can be used for the detection of UV radiation. Furthermore, a difference between dark and light (UV 363.8 nm) current of 4 orders of magnitude was observed and reported in this case (Fig. 5 from H7).

As was mentioned earlier, one of the challenges of modern physics of semiconductor structures is the search for structures working as a selective and fast detectors of UV radiation. To accomplish this task, it is necessary to obtain structures with very good, controllable electrical parameters. Moreover, for implementing new and innovative ideas like "Blind to the Optical Light Detectors" or Li-Fi "Wireless data from every light", the realization of fast and selective light detectors is crucial.

The heterostructures described in the works H4-H7, in which the doped ZnO layer was grown by MBE, may be used for detecting the UV radiation. In addition, here it is important to note, that for the mentioned junctions we were able to get a high spectral selectivity. In detail, for the ZnO:As/GaN, ZnO:N/GaN, ZnO:AsSb/GaN structures the half width maximum of the photocurrent peaks were very small, at the level of 12-27 nm. Moreover, the detection was possible in front side (i.e. the ZnO side) and in back side (i.e. substrate side) illumination due to the use of wide bandgap materials on both sides. It is noteworthy and relatively rarely reported, that it is possible to observe the change in peak position when the structure is illuminating in front or in back side, due to very narrow detection peaks. Such peaks are located at 364 nm and 367 nm at 0V, respectively, for front and back side illuminations (Fig.6 from [H6]).

In order to find structures that can work as a selective UV detectors, n-ZnO/p-SiC junctions were also tested. In the case of such structures the n-type ZnO layer was grown at low temperature by ALD method. The SiC (4H-polytype) substrates were chemically prepared directly before the growth. In this case, the growth temperature was selected to achieve a proper concentration of native defects of donor type [93] and a good crystal quality of the layers (Fig. 1 from H8).

Heterojunctions with a very high forward to reverse current ratio $I_F/I_R \sim 10^{10}$ (Fig. 4) and with very good ideality factor $\eta=1.17$, were realized. In the mentioned diodes, the density of the dark current was 10^{-8} A/cm^2 and the presented results [H8] were among the best reported for ZnO/SiC (4H) structures so far.

Photoresponsivity of the n-ZnO/p-4H-SiC structures as a function of photon energy reveals 4 Gaussian contributions located at about 3.37 eV, 3.23 eV, 3.12 eV, and 2.75 eV. In this case, the structures were illuminated on the back side, i.e. from the side of the 4H silicon carbide substrate. In this configuration, photons with energies less than or near the band gap energy of 4H-SiC (3.23 eV) penetrate the entire thickness of the device and can interact with large optical cross section defects present in the active region of the device like other SiC polytype inclusions or zinc vacancies. As the photon energy increases above 3.23 eV, band to band indirect-transitions start to take place in 4H-SiC and photo-generated carriers are collected causing the appearance of the 3.23 eV peak. When the energy of the incident photons increases further, due to the fact that 4H-SiC has an indirect band gap and, therefore, absorption is small, the light with energy above ZnO band gap can still reach the SiC/ZnO interface, and there being absorbed. Hence, in this case, the strongest contribution to the photocurrent spectrum at energy 3.37 eV, is originating from the ZnO layer with the contributions in the visible region being significantly less than the peak detected in the UV range (the difference is approximately one order of magnitude if the peaks at 3.37 eV and 3 eV are compared). Finally, for the aforementioned ZnO/SiC (4H) structures the full width at half maximum of the main contribution to photocurrent was ~ 24 nm.

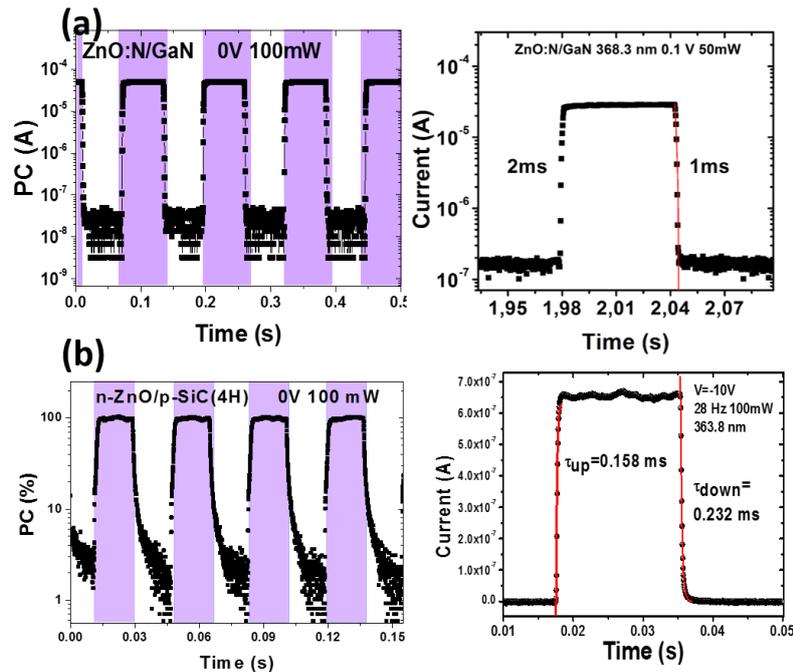


Fig. 7. Examples of detectors response times to UV light in case of a (a) ZnO:N/n-GaN (b) ZnO/p-SiC structure.

Our results according selective detection of UV from junction structures are at the forefront of global results obtained for detectors based on wide band gap materials such as GaN [94], ZnO and SiC. In the absence of additional filters we obtain visible blind structures that detect in a very narrow ultraviolet light spectral range. This paves the way to the realization of line or matrix of junctions working in slightly different spectral ranges that would allow not only to detect UV radiation, but also to identify precisely the spectral range of the incident radiation.

Furthermore, from the application point of view of such junctions as radiation detectors [15], very important device characteristics are: the speed of response to the incident light and the time necessary to return to the ground state, i.e. the recovery time. The response time of detector structures strongly depend on their type and quality [17], and on the presence of defects either native or introduced by doping. Amidst of the possible semiconductor structures that can be used as detectors, p-n junctions and a p-i-n diodes are the fastest. However, in the case of detector structures, based on ZnO, response time is very often a significant problem since zinc oxide surface is extremely gas-sensitive. The surface sensitivity while being useful for the realization of ZnO based gas sensors, represents a clear disadvantage, when this material is used for UV detection, since it can significantly affect the time response of the detectors structures. This effect is particularly pronounced in the case of solutions where the ZnO surface is exposed to the external atmosphere and at the same time its roughness is increased significantly to reduce reflection and increase the detector active area as in the case, among the others, of ZnO nanowires based solutions. In such devices, the atmosphere has a significant influence on the overall electric characteristics due to the absorption /desorption of oxygen or OH groups on the surface [95, 96].

As a consequence, response times of detector structures based on such concept vary typically in the 100s to 1s range and depend on the atmosphere in which the experiment was performed - therefore commercial applications must involve some additional technological step.

On the contrary, in the studied structures [H4-H8], the detection volume is located in the active region of the junction that is close to the interface between ZnO and other wide band gap material. Thus, it is spatially separated from the surface of the structure and the device responses are, as discussed in detail hereafter, strong enough even without any surface treatment to increase the surface roughness, thus being ready to use devices.

Furthermore, it was experimentally verified that the response times are the same both in vacuum and in air or in a nitrogen gas flow. Response time measurements were measured using a mechanical chopper for modulating the laser light. For the junctions described in the works H4-H8 response times are at about 1ms, and this time is limited by the experimental setup.

The stability of a sensor, another key characteristic of a device that is intended to be used as a UV detector, is evaluated by the change of sensing behavior after numerous times of switching between 'ON' state and 'OFF' state. The stability is good when the sensing performance shows little change after numerous cycles. In this sense, the structures we have obtained can be considered stable (Fig. 8).

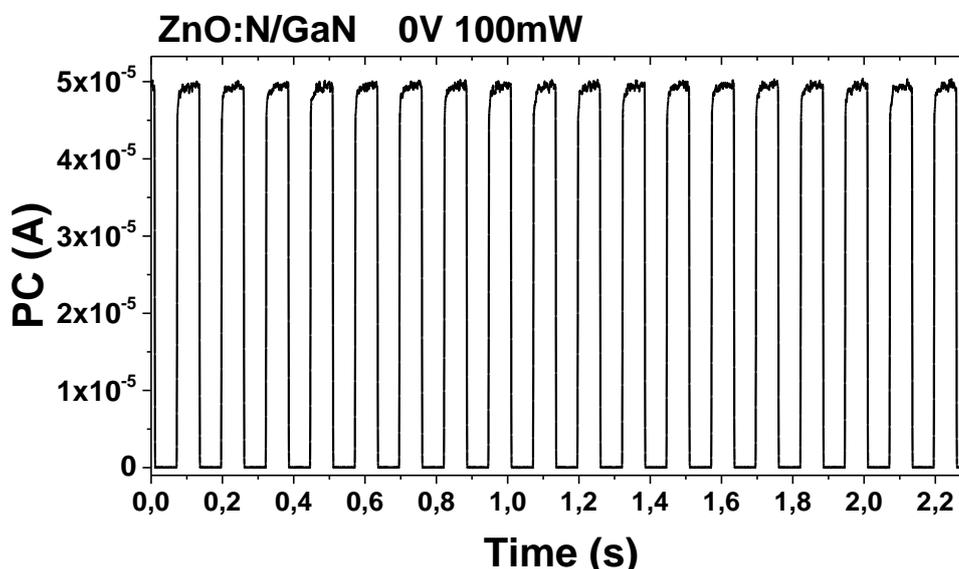


Fig. 8 Multiple response to the incident UV radiation of the detector structure, showing its 'ON' to 'OFF' stability.

Another advantage of the light detectors that have been realized is the ability to detect radiation without applying external voltage. Low power consumption increases uptime and lowers overall costs of final devices. Additionally, considering that the electron-irradiation damage for ZnO and the other semiconductors here used as heterojunction counterpart is less severe than that found in other common semiconductor materials, this suggests the possibility of using the ZnO based detectors obtained in space applications [97].

In addition, considering potential applications in the field of secure communications and space detection, selfpowered and zero power consumption type photodetectors are highly desirable properties. The vertical heterojunction structure photodiode can satisfy the above requirements.

In the case of light detection, another important aspect is the ability to detect light with low intensity. The quality of the structures and, in particular, the dark current value i.e. the current flowing through the structure in the reverse direction in the absence of illumination are in this case important. Dark current in the tested junctions was very low about 10^{-10} A.

Such low dark current allows the detection of radiation at the level of 0.6 μ W with still a difference between dark current and light current of about an order of magnitude.

Control of the growth process of the ZnO layers as well as their doping and the post-deposition annealing; proper preparation of the substrate surface and thus interface control are necessary to obtain high quality heterojunctions and have been achieved [H4-H8]. The high quality of the structures, in particular the low dark current and the high rectification ratio, enabled high quality detector structures. The high performances of the devices obtained have led to patent; Patent No.: PL 220515, title: *UV Detector Structure and UV Detector Structure*, and in the form of two consecutive patent applications in this field of study; and won two innovation prizes at the INTARG (Katowice) where they received silver medal and at the Brussels Innova (Brussels) where they were awarded a gold medal.

4.4.5 The interface modifications and its effect on the parameters of structures [H9]

One method for obtaining high-quality junctions consists in introducing an additional undoped layer between layers with n-type and p-type conductivity. Such a layer is typically added in order to reduce dark current and increase photocurrent, to change the detection range of the structure or to increase the efficiency of electroluminescence signal extracted from the structure.

In the case of ZnO/GaN, the reported conduction band misalignment ΔE_c , is ~ 0.73 eV [98]. Band mismatch reduction, beneficial for reduction of the recombination at the interface, as well as interfacial states passivation can be obtained by introduction of an intermediate layer. Various isolating spacers are used for this purpose, for example: magnesium oxide (MgO) [99–101], Al₂O₃ [102, 103] or isolating zinc oxide *i*-ZnO [104].

The addition of spacers can significantly improve the junction quality, but also may introduce defects at the interface, in the depleted region of the layer, and in the whole volume of the layer. Used spacers are not always matched to ZnO due to differences in lattice constants and in crystal structures. Moreover, if an amorphous material is used as insulating layer this inhibits the epitaxial growth of the oxide layer that is growing in polycrystalline form instead.

The effect of adding an insulator layer between ZnO and GaN, has been discussed in the work H9. Between the ZnO layer and the GaN layer – a thin amorphous Al₂O₃ layer has been added (with a thickness of about 10 nm - based on the number of ALD cycles). These layers were grown at appropriately selected low temperature by ALD technique. The insulating properties of these thin amorphous layers have been presented [105]. As a result of the combination of two MBE and ALD growth methods ZnO:N/Al₂O₃/GaN junctions with good electrical parameters have been obtained. Published data [H9] were preceded by long and extended studies on GaN substrate preparation and growth parameters both of the ALD insulator layer as well as MBE ZnO layer.

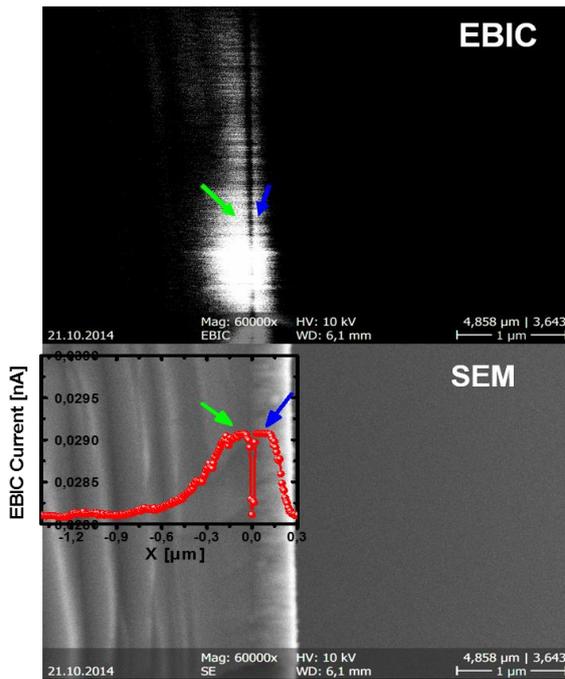


Fig. 9 (a) E-BIC scan across the ZnO:N/Al₂O₃/GaN junction (b) and the secondary electron image.

In the cross-sectional image of the heterostructures in secondary electrons (SE), the E-BIC line scan is added (red line) and superimposed with the SE image.

Although the charge is separated along the isolating layer, the two peaks, which are not symmetric in their profiles, represent the two prime locations of the spatially separated charges in the device: the *p-i* (indicated by a blue arrow) and *i-n* junctions (green arrow).

Obtained as a result of the combination of two MBE and ALD growth methods, ZnO:N/Al₂O₃/GaN junctions have good electrical performance. Based on current-voltage characteristics, we found that forward to reverse current ratios were $\sim 10^6$. Dark current for this types of structures was very low at the level of 10^{-11} A. However, the ideality factor for junctions with a spacers were higher than in the case of junctions without spacers and values larger than 2 were extracted from the analysis of the current vs. voltage characteristics. Furthermore, breakdown voltages higher than 10V and open voltages ~ 4 V were observed in such structures.

It is known, that the presence of the insulating layer, can modify the depletion region of the junction as well as introduce other types of defects into the layers/structures. Modification of the depleted area and creation of new types of defects might be the cause of observed changes in detection with respect to junctions without a spacer. This has been experimentally proven to be the case in our structures: when the spacer were present an additional detection peak at 400 nm was observed (Fig. 10). On the contrary, due to the thin insulation layer between the oxide and nitride layers, unlike structures without spacers, radiation detection is possible when small external voltage is applied to the structure, because The Al₂O₃ layer separates carriers between n-GaN/Al₂O₃ and Al₂O₃/p-ZnO junctions. Under electric field, carriers either tunnel through the barrier or hop over the Al₂O₃ barrier. Moreover, the presence of the insulator layer at the interface also increases the response time of the structures that are, in this case, at the level of tens of ms.

Such structures have not been investigated previously as UV detectors. The presence of the insulating Al₂O₃ layer in the heterostructure has been confirmed by E-BIC, (Fig. 9). The EBIC line profile presented in Fig 9 (b) as a red line is characteristic of a *p-i-n* device. It is evident that the junction exists on the ZnO/GaN interface and is continuous. Observation of the insulating spacer by E-BIC at the ZnO/GaN interface is a unique result confirming both the location of the junction as well as its modification by the insertion of the insulating spacer.

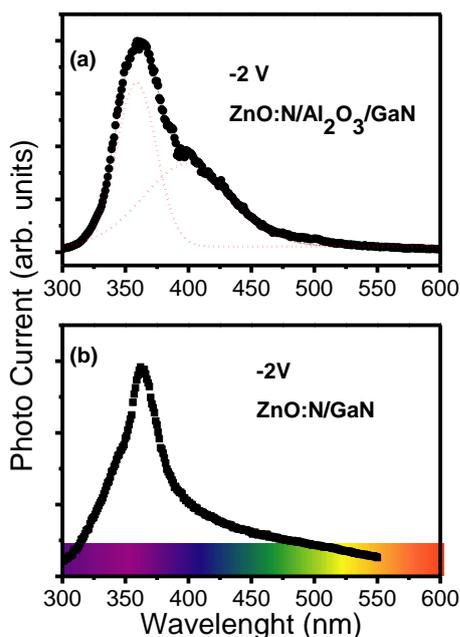


Fig. 10 Comparison between the diode structures:

(a) ZnO:N/Al₂O₃/n-GaN reverse voltage -2 V,

(b) ZnO:N/n-GaN reverse voltage -2 V.

By interface modification by adding insulating separators in heterojunctions it is possible to change their detection range [H9], [106]. Part of the research results for structures with spacers has also been patented, patent No.: P.403520, title: *Structure of p-i-n detector UV and method of realization of this structure* and the work on the use of other spacers is continued.

4.4.6 Summary of achievements presented in [H1-H9]

The ability to control the physical properties of modern materials, by examining their crystallographic structure, the arrangement of atoms in the sample volume and on the surface, taking into account point defects, including those resulting from doping, is essential both for the sciences and for future applications. In order to understand the mechanisms of change of material properties resulting from the introduction of dopant atoms, we need to know the local environment of these elements on the atomic scale. The conductivity of intentionally doped ZnO layers strongly depends on the dopant state. The local surroundings of the dopant atom may depend on growth conditions, annealing or additional doping, which justifies the purpose of carrying out comprehensive research in this direction. In the case of hard to achieve p-type ZnO, this general statement is of particular importance because of the considerable variety of models of the construction of acceptor centers that may be responsible for the p-type conductivity. Better experimental evidence for these models, at least some of them, will contribute to the better organization of at least some of the knowledge about effective and repeatable p-type doping. This will be very important for realizing p-n junction with a good electrical parameters. Designing, fabricating and testing diodes containing ZnO layers is essential for their future applications. One of such applications is the search for zero power detector structures working in the narrow spectral range in the UV region and ways to control the detection range of these structures. In this case, the use of heterojunctions based on wide-bandgap materials is highly recommended. The research I undertook has made an important contribution to the reproducible and well-controlled realization of high quality diode detector structures for the UV range, and for the understanding of the incorporation of V (N, As, Sb) dopants into the ZnO lattice.

- **Demonstration of chemical change / localization of the arsenic dopants in to ZnO crystal lattice as a result of a change in the annealing atmosphere by effective use of high resolution X-ray photoelectron spectroscopy (XPS) [H1].**

Observation of the change in the dopant state along with the change of the atmosphere of annealing explains, found in many works concerning the doping of ZnO, necessity of activating the As dopant by applying the annealing of ZnO layers after growth. The use of the high resolution XPS method to observe the local environment of arsenic atoms has allowed us to observe several contributions in the As3d spectrum coming from different arsenic centers. Specifically, it has been shown that, in the case of MBE layers, some arsenic atoms are incorporated into the zinc sites, some as $As_{Zn}-2V_{Zn}$ complex, and only a small fraction (a few percent) occupy oxygen sites. In addition, it was found that the intensity of each component depends on the annealing atmosphere. This result shows that the doping of arsenic in the ZnO matrix is very complicated, and so far none of the theoretical models fully describes how arsenic builds into the oxide matrix. Showing the complicated nature of the doping of arsenic atoms in ZnO through high-resolution XPS studies is a very important result for the scope of research of p-type doping.

The XPS as well as luminescence spectra are reflecting changes of the arsenic state due to annealing processes. In all measured samples, we have observed a strong emission, which we attribute to free electron recombination with acceptor holes, as well as donor-acceptor pair emissions. This suggests a high concentration of As acceptors in all samples. The detailed studies of As3d are an important contribution to the discussion about the incorporation of this dopant in ZnO.

- **Demonstration of the effect of different growth conditions of ZnO layers on the chemical state of As, based on the studies [H1, H2].**

Naturally occurring defects and unintentional impurities can have a significant impact on the way in which intrinsic dopants are embedded in the ZnO matrix. In the works [H1] and [H2] we investigated the state of the As dopant in layers made by MBE and ALD, respectively. Comparing XPS results to samples obtained by various methods, we observed clear differences in the mutual intensity of the As3d photoemission spectra coming from arsenic atoms differently embedded in the structure. For the ALD layers, the contribution from the arsenic atoms located in the oxygen site is comparable to that of the zinc site or to atoms located as the $As_{Zn}-2V_{Zn}$ complex, whereas, in the MBE samples, the contribution of the arsenic atoms in the oxygen site is only a few percent. This shows that the method of embedding the As dopant for these layers is distinctly different, and thus drawing general conclusions about the local environment of the As dopant in ZnO is very complex, since the surrounding of this dopant may also depend on the growth conditions of the matrix.

Based on the results of [H2] we also find that for ALD layers made at low temperatures and heated after growth in As, it is expedient to increase the annealing temperature as it increases the number of As elements which embed in the structure in the form of $As_{Zn}-2V_{Zn}$ complex. This complex seems to be the dominant acceptor responsible for p-type conductivity.

The change in arsenic state, seen in XPS studies, is also visible in low temperature luminescence as an appearance of an acceptor peak in samples annealed at higher temperatures.

- **Demonstration of the effect of additional doping with V atoms on the state of arsenic [H3].**

The XPS examination has been done on a dedicated, unique series of ZnO samples double- and triple-doped by V-group atoms. The direct change of arsenic state due to doping with other V-group atoms has not been reported so far. This unique result, showing the change in components intensities in the As3d photoemission spectrum with the addition of Sb and N, confirms that additional dopant can lead to stable and efficient p-type in ZnO. It is important that additional doping with V atoms increases the concentration of As atoms embedded in the $As_{Zn}-2V_{Zn}$ arsenic complex in both "as grown" and "annealed" samples. Considering the fact that the dopants (As, Sb, N), studied in [H3], do not embed into ZnO in a simple substitutional way, these are important results. This issue has not yet found a theoretical explanation. The results obtained provide direct evidence of the possibility of improving the efficiency of the "dual acceptor doping" and constitute a valuable contribution to the knowledge of double doping of ZnO by acceptors.

- **Obtaining of high quality diode structures containing ZnO layers, singly and doubly doped with V atoms, and investigation of their properties [H4-H7].**

The results of the studies presented in H1 and H3, concerning the ZnO MBE layers doped by V-group, have been used to produce high-quality heterojunctions with very high forward to reverse current ratios of 10^5 - 10^7 . The rectification ratios obtained are some of the highest reported in the literature for this type of structures. Achievement of this result was made possible by investigating the process and developing an annealing procedure of the doped layers. The knowledge concerning the annealing of the layers after growth [H1] was essential in this case. In the case of growth of doped ZnO layers on GaN layers, which are also n-type partners, we obtain junctions with values of open voltages from 1.5V to 3V and breakdown voltages greater than -10V. The structures obtained were characterized by a low dark current of $\sim 10^{-10}$ A, comparable to or lower than the reported values for commercially available diode detectors – based on GaN. Such a low dark current allows the detection of the light with very low intensity. In the case of tested diodes, I confirmed in [H7] the position of the ZnO: N / GaN depletion layer on the ZnO/GaN interface. Observing the position of the depleted layer by E-BIC tests was not yet reported for this type of heterostructures. This result confirms the existence of ZnO / GaN junction precisely on the interface.

- **Obtaining of highly selective detection of UV radiation on heterostructures containing ZnO layers.**

The use of two wide bandgap materials (ZnO, GaN or SiC) in the junctions, slightly differing in energy gap width, allowed to obtain spectrally selective UV detectors. The detection width of the peaks at levels of several nanometers is comparable to the best selective UV detectors based on wide band gaps materials. In addition, high detection selectivity was obtained without the use of additional filters, which is necessary in the case of silicon detectors, for example. The use of p-n junction structures allowed the detection without applying additional external voltage, and the resulting ratios of the light to dark currents were several orders of magnitude. It was significant in this case that the value of dark current was very low, at the level of $\sim 10^{-10}$ A. In order to obtain high quality heterojunctions it was important to properly prepare / define the interface so as to create as few defects as possible. The use of wide band gaps materials (ZnO and GaN or SiC) on both sides of the junctions allowed the radiation to be detected both from the bottom and from the top. The measured response times, for the structures obtained, to the incident UV were at the level of 1 ms, and these results are at the top of

the results for the ZnO-based detectors (Table 1 in [95]), with the resulting values being limited by the use of a continuous mechanically chopped light source.

Summing up this achievement: as a result of the work we have been able to obtain and characterize highly selective and fast detector structures containing ZnO layers. Taking into account the fact that ZnO, in comparison with Si, GaAs and GaN, is more resistant to radiation, these detectors can be used in high altitude and in space applications.

- **Demonstration of the possibility of changing the detection range of the diode structures by modifying the interface by adding an insulating spacer [H9].**

In the case of highly selective UV detection, the situation where ZnO is coupled with another wide band gap semiconductor acting as an additional “filter”, as it has been already reported in the case of ZnO/GaN and ZnO/SiC heterojunctions structures, is very promising. However, in such structures, the band alignment represents a crucial issue. In the case of ZnO/GaN, as an example, the reported conduction band misalignment, ΔE_c , is ~ 0.73 eV. Band mismatch reduction, beneficial for reduction of the recombination at the interface, as well as for interfacial states passivation, can be obtained by introduction of an intermediate layer. The utilization of high band gap energy interlayers does not affect the devices possibility of being used both, for the front and for the back side UV detection. The ZnO/GaN heterojunctions structures containing Al₂O₃ spacers have not previously been characterized for their potential use in UV radiation detection. As a result of the research and the combination of the two growth methods of MBE and ALD, the p-i-n junctions containing ZnO layers, doped by V group atoms, with very good electrical parameters, were obtained. The presence of a thin continuous insulation Al₂O₃ layer has been confirmed in E-BIC studies, which is an extremely important and unique result, unreported so far for p-i-n heterostructures. We have observed a change in the detection range of these junctions with respect to junctions without insulating spacers, which also was not previously described. Detailed interlayer investigations and its impact on structural parameters make a significant contribution to the planning of diode detector structures that may find commercial applications.

Finally, I would like to emphasize my significant contribution to publications from the series H1-H9, which are presented here as the habilitation achievement.

In works [H1, H3], my leading contribution concerns the planning and the fabrication of a dedicated series of MBE samples as well as the planning of a series of annealings and experiments, including XPS examination. I interpreted XPS and PL results and prepared the publications.

In H2 I have actively participated in the interpretation of the XPS results and I had a major contribution to the description and interpretation of PL results, and also had a significant part in the preparation of the publication.

The XPS examination has been done at the Institute of Physical Chemistry of the Polish Academy of Sciences as part of the planned collaboration with the ICHF PAS in my NCN grant entitled: “*Study of V -group acceptor dopants and their mutual influence on each other in Zn(Mg)O/GaN heterostructures*”.

In the works H4 - H9, my leading contribution was to make and plan all the photocurrent examination, starting with the planning and construction of the measurement system, the execution and the planning of a series of experiments, and the analysis and description of the measurement results.

In the works H1, H3 - H7, H9 I headed the work, from the ideas for experiments, planning of the type of structures, planning their thermal processing and interpretation of much of the experimental results to the preparation of publications.

The development of zinc oxide research has yielded a huge scientific literature with over 50,000 publications. Despite of this, one still finds in this topic relatively poorly researched areas. One of the important directions of research, both for physics and technology and applications of ZnO, is the way of incorporation of acceptor dopants into the structure. The relationship between the properties of the layers, resulting from the existing defects, or due to the doping, and the quality of the semiconductor structures containing the said ZnO layers, is also significant. The publications that are the subject of this habilitation contributed to the partial clarification and deepening of knowledge concerning the doping of ZnO layers with the acceptors towards their applications. This has been reflected in the acceptance of works in international scientific journals, invitations to lectures on an international conferences and in citations.

Another important aspect is the application of research of the layer properties as well as interlayers quality to obtain high-quality semiconductor junctions, essential for many electronic applications. The obtaining the high quality ZnO/GaN and ZnO/SiC junctions, which have very high rectification ratios, which enable them to be used in opto-electronic devices is a significant result. One of such applications are ultraviolet radiation detectors. The results obtained for the ZnO-based junctions have shown new possibilities in the design of diode radiation detectors, which are characterized by very narrow detection ranges.

Mastering the process of growth, doping and thermal processing of dedicated ZnO layers allowed to obtain structures in which parameters such as low dark current, high selectivity, large ratio of bright to dark current and high rectification ratio were much better than previously achieved for similar systems. As a result, it made it possible to produce high quality junctions that could work as efficient and fast UV detectors and lead to the development of this direction of research. The method of fabrication of the structures above has been patented and currently we have two patents for detector structures.

5. Discussion of other scientific and research achievements

5.1 Description of scientific achievements unrelated to the topic of habilitation

As a student at the Faculty of Physics, University of Warsaw, precisely, during the final experiments and writing of the thesis, I started an internship at the Institute of Electron Technology. During traineeship I worked in the laboratory of molecular beam epitaxy (MBE). Dr. hab. Kazimierz Regiński was my academic supervisor. At the same time I was doing a master's thesis. As part of the thesis I was responsible for photocurrent measurements in samples contains GaInAs/GaAs quantum dots. The results of the thesis were partially published in [N1]. After graduating from the Warsaw University with the thesis entitled: „*The influence of light on the conductivity of structures containing quantum dots*” supervised by Krzysztof Korona PhD. I started doctoral studies at the Institute of Physics, Polish Academy of Sciences. The topic of my dissertation was related to preparation of ZnO and ZnMnO by thermal annealing of Zn-based materials. Metallic zinc, zinc telluride (ZnTe), zinc telluride with manganese (ZnMnTe), zinc nitride (Zn₃N₂) and zinc antimonide (Zn₃Sb₂) were used as a base materials. Materials, mentioned below, were annealed by RTA method and as a

consequence ZnO layers were obtained on the surface. Doping of ZnO layers by N, N+As, As or by Sb were realized as a consequence of annealing of base materials as well as using chosen substrates. Part of the samples were obtained and all annealed proces were done in cooperation with Eliana Kamińska PhD from ITE. Quality of ZnO layers were analyzed by X-ray diffractions [N2, N3].

During my PhD study, in the first step, I achieved the ZnTe and ZnMnTe layers by MBE. I was looking for methods of obtaining a metastable ZnTe wurtzite phase, for this purpose I was growing ZnTe on MnTe buffer with NiAs structure. Growth and characterization of MnTe layer with hexagonal NiAs structure was a subject of some papers [N4-N6]. At present, this subject enjoys re-interest and the work [N4] was cited in Nature Communication [107].

During my PhD study, my scientific activity concerned in general the optical spectroscopy of ZnO layers obtained by thermal annealing. In luminescence measurements it was possible to observe several optical lines associated with the presence of dopants and estimate their activation energy [N7, N8]. In Particular, in the energy region at 3.31 eV, I observed two peaks that behave as a function of temperature, in contrast to most papers which reported one wide peak in this region.

I also investigated the magneto-optical properties of the diluted magnetic $Zn_{1-x}Mn_xO$ layers [N9, N10]. The exchange integrals obtained in my research were much lower than theoretically predicted [108]. These were the first reports of this kind in the world, they were later confirmed for other systems such as the ZnCoO, GaFeN [109, 110]. The values of exchange integrals obtained in my research are included in the monograph on diluted magnetic semiconductors [111]. After completing my doctoral thesis, I dealt with the research of ALD layers with special attention to their optical properties, which resulted in a series of works [N11-N16]. I also participated in the work on the growth and characterization of quantum wires and quantum wells [N17-N21]. In particular, I was involved in research of quantum structures grown by MBE method on the polar and non-polar directions of growth.

[N1] “*Dynamics of photoexcited carrier in GaInAs/GaAs quantum dots*” **E. Ilczuk**, K.P. Korona, A. Babiński, J. Kuhl Acta. Phys. Pol. A 100 (3); 379-386 (2001).

[N2] “*P-type conducting ZnO: fabrication and characterisation*” E. Kamińska, A. Piotrowska, J. Kossut, R. Łukasiewicz, A. Barcz, R. Jakiela, E. Dynowska, **E. Przeździecka**, M. Aleszkiewicz, P. Wojnar, E. Kowalczyk Physica Status Solidi C-Current Topics in Solid State Physics 2 , 1119-1124 (2005).

[N3] “*Transparent p-type ZnO films obtained by oxidation of sputter-deposited Zn_3N_2* ” E. Kamińska, A. Piotrowska, J. Kossut, A. Barcz, R. Butkute, W. Dobrowolski, E. Dynowska, R. Jakiela, **E. Przeździecka**, R. Łukasiewicz, M. Aleszkiewicz, P. Wojnar, E. Kowalczyk SOLID STATE COMMUNICATIONS 135 , 11-15 (2005).

[N4] “*MnTe and ZnTe grown on sapphire by molecular beam epitaxy*” **Przeździecka E.** , Dynowska E. , Paszkowicz W. , Dobrowolski W. , Kępa H. , Majkrzak C. , Giebulowicz T.M. , Janik E. , Kossut J. Thin Solid Films 516, 4813–4818 (2008).

[N5] “*The crystallographic structure of thin Mn-rich ZnMnTe layers grown by molecular beam epitaxy*” E. Dynowska, **E. Przeździecka** JOURNAL OF ALLOYS AND COMPOUNDS 401 , 265-271 (2005).

[N6] “*Structural properties of MnTe, ZnTe Structural properties of MnTe, ZnTe, and ZnMnTe, and ZnMnTe*” N.G. Szwacki, **E. Przeździecka**, E. Dynowska, P. Bogusławski, J. Kossut ACTA PHYSICA POLONICA A 106 , 233-238 (2004).

[N7] „*Photoluminescence study of p-type ZnO : Sb prepared by thermal oxidation of the Zn-Sb starting material*” **E. Przeździecka**, E. Kamińska, I. Pasternak, A. Piotrowska, J. Kossut PhysRevB.76, 193303 (2007)

[N8] “*Photoluminescence study and structural characterization of p-type ZnO doped by N and/or As acceptors*” **E. Przeździecka**, E. Kamińska, K. Korona, E. Dynowska, W. Dobrowolski, R. Jakiela, Ł. Kłopotowski, J. Kossut SEMICONDUCTOR SCIENCE AND TECHNOLOGY 22 , 10-14 (2007).

[N9] “*p-type ZnO and ZnMnO by oxidation of Zn(Mn)Te films*” **E. Przeździecka**, E. Kamińska, E. Dynowska, W. Dobrowolski, R. Jakiela, Ł. Kłopotowski, M. Sawicki, M. Kiecana, J. Kossut PHYSICA STATUS SOLIDI C - CURRENT TOPICS IN SOLID STATE PHYSICS, VOL 3, NO 4 , 988 (2006).

[N10] “*Magneto-optical properties of the diluted magnetic semiconductor p-type ZnMnO*” **E. Przeździecka**, E. Kamińska, M. Kiecana, M. Sawicki, Ł. Kłopotowski, W. Pacuski, J. Kossut SOLID STATE COMMUNICATIONS 139 , 541-544 (2006).

[N11] “*ZnO grown by atomic layer deposition: A material for transparent electronics and organic heterojunctions*” E. Guzewicz, M. Godlewski, T. Krajewski, L. Wachnicki, A. Szczepanik, K. Kopalko, A. Wójcik-Głodowska, **E. Przeździecka**, W. Paszkowicz, JOURNAL OF APPLIED PHYSICS ,105 , 122413 (2009).

[N12] “*Vertically stacked non-volatile memory devices - material considerations*” M. Godlewski, E. Guzewicz, J. Szade, A. Wojcik-Głodowska, Ł. Wachnicki, T. Krajewski, K. Kopalko, R. Jakiela, S. Yatsunenko, **E. Przeździecka**, P. Kruszewski, N. Huby, G. Tallarida, S. Ferrari MICROELECTRONIC ENGINEERING , 85 , 2434-2438 (2008).

[N13] “*Characterization of ZnO Films Grown at Low Temperature*” **E. Przeździecka**, T. Krajewski, Ł. Wachnicki, A. Szczepanik, A. Wojcik-Głodowska, S. Yatusnenko, E. Łuskaowska, W. Paszkowicz, E. Guzewicz, M. Godlewski ACTA PHYSICA POLONICA A 114 , 1303-1310 (2008).

[N14] “*ZnO by ALD - Advantages of the Material Grown at Low Temperature*” E. Guzewicz, M. Godlewski, T.A. Krajewski, L. Wachnicki, G. Łuka, W. Paszkowicz, J.Z. Domagała, **E. Przeździecka**, E. Łuskaowska, B.S. Witkowski ACTA PHYSICA POLONICA A 116, 814-817 (2009).

[N15] “*Comparison of dimethylzinc and diethylzinc as precursors for monocrystalline zinc oxide grown by atomic layer deposition method,*” L. Wachnicki, M. Lukasiewicz, B. Witkowski, T. Krajewski, G. Łuka, K. Kopalko, R. Minikayev, **E. Przeździecka**, J.Z. Domagała, M. Godlewski, E. Guzewicz PHYSICA STATUS SOLIDI B-BASIC SOLID STATE PHYSICS 247 , 1699-1701 (2010).

[N16] “*Epitaxial ZnO Films Grown at Low Temperature for Novel Electronic Application*” L. Wachnicki, A. Duzynska, J.Z. Domagała, B.S. Witkowski, T.A. Krajewski,

E. Przeździecka, M. Guzewicz, A. Wierzbicka, K. Kopalko, S. Figge, D. Hommel, M. Godlewski, E. Guzewicz, ACTA PHYSICA POLONICA A 120 , A7-A10 (2011).

[N17] “*Electro-optical characterization of ZnO/ZnMgO structure grown on p-type Si (111) by PA-MBE method*” M.A. Pietrzyk, E. Zielony, M. Stachowicz, A. Reszka, E. Płaczek-Popko, A. Wierzbicka, **E. Przeździecka**, A. Droba, A. Kozanecki JOURNAL OF ALLOYS AND COMPOUNDS 587 , 724-728 (2014).

[N18] “*Growth conditions and structural properties of ZnMgO nanocolumns on Si(111)*” M. A. Pietrzyk, M. Stachowicz, A. Wierzbicka, P. Dłuzewski, D. Jarosz, **E. Przeździecka**, A. Kozanecki JOURNAL OF CRYSTAL GROWTH 408 ,102-106 (2014).

[N19] “*Photoluminescence Properties of ZnO Nanowires Grown on Ni Substrate*” W. Zaleszczyk, K. Fronc, **E. Przeździecka**, E. Janik, A. Presz, M. Czapkiewicz, J. Wróbel, W. Paszkowicz, Ł. Kłopotowski, G. Karczewski, T. Wojtowicz ACTA PHYSICA POLONICA A 114 ,1451-1456 (2008).

[N20] “*Properties of ZnO single quantum wells in ZnMgO nanocolumns grown on Si (111)*” M.A. Pietrzyk, M. Stachowicz, A. Wierzbicka, A. Reszka, **E. Przeździecka**, A. Kozanecki OPTICAL MATERIALS 42 , 406-410 (2015).

[N21] “*Asymmetric ZnO/ZnMgO double quantum well structures grown on m-plane ZnO substrates by MBE*” M. Stachowicz, M.A. Pietrzyk, J.M. Sajkowski, **E. Przeździecka**, H. Teisseyre, B. Witkowski, E. Alves, A. Kozanecki Journal of Luminescence 186, 262–267 (2017).

5.2 Scientific projects

Since 2014, I'm **Principal Investigator** of the grant awarded by the National Centre of Sciences (Poland) no: 2013/09/D/ST3/03750 entitled: “*Study of V -group acceptor dopants and their mutual influence on each other in Zn(Mg)O/GaN heterostructures*”

In years 2009-2013, I was partially employed in the Institute of Physics, Polish Academy of Sciences in the frame of NanoBiom Project POIG.01.01.02-00-008/08 entitled “*Semiconductor Nanostructures for Applications in Biology and Medicine –Development and Commercialization of new Generation Devices for Molecular Diagnostics on the Basis of New Polish Semiconductor Devices*” realized in the framework of the Operational Program Innovative Economy. My results were reported several times presented in the course of the project in the expert panels and conferences.

During my Ph.D. studies, I was investigator of the grant no. 1P03B 084 30; 0058/H03/2006/30 awarded by the Committee of Scientific Research (Poland) entitled “*Production and characterization of ZnO layers with p-type conductivity*”, lead by my advisor Prof. dr hab. Jacek Kossut.

I was investigator of the grant awarded by the National Centre of Sciences (Poland) no:no. DEC-2012/07B/ST3/03567 (2013-2017) entitled: “*Microstructural and chemical determinants of electrical conductivity of zinc oxide*”

I was investigator of the European grant, entitled: *Vertically stacked memory cells based on heterojunctions made of hybrid organic/inorganic materials* VERSATILE, **2006-2009** (project no. 026714)

I participated in the ERASMUS + project where I participated in a training trips:

- Under the 2013/2014 program, I visited University of Minho, Braga, Portugal, a Scientific contact person from Portugal: Dr Maria Fátima Guimarães Cerqueira
- Under the 2016/2017 program, I plan to visit Helmholtz-Zentrum Dresden-Rossendorf, a Scientific contact person from Germany: Dr Sławomi Prucnal

5.3 The list of invited papers presented at international or national thematic conferences

I gave a 4 invited lectures on the topic of habilitation at international and national conferences.

- I.1 „*Selective UV Photodetectors based on ZnO*” **E. Przeździecka**, R. Schifano, S. Chusnutidinow, E. Guziewicz, M. Guziewicz, A. Kozanecki E-MRS Warszawa, symposium Z, September 19, 2016, Poland
- I.2 “*ZnO doped by one, two or three acceptors (As, N, Sb)- electronic structure, optical and electrical properties*” **E. Przeździecka**, Modern techniques in photoelectron spectroscopy – experiments and data analysis; October 19-22, 2015 Leszno, Poland
- I.3 „*Selektywne detektory promieniowania UV na bazie heterozłączy ZnO/GaN*,” **E. Przeździecka**, M. Stachowicz, S. Chusnutidinow, D. Snigurenko, S. Gierałtowska, A. Kozanecki XIV KRAJOWA KONFERENCJA ELEKTRONIKI 08 – 12.06.2015 Darłówko Wschodnie, Poland
- I.4 “*Zinc oxide based heterostructures as highly selective UV detectors*” **E. Przeździecka**, R. Schifano, S. Chusnutidinow, M. Stachowicz, T. A. Krajewski, E. Guziewicz, M. Guziewicz, A. Kozanecki Energy Materials Nanotechnology Prague Meeting 2016 (**EMN 2016**), June 21-24, Prague, Czech Republic

Invited Lectures presented by co-authors:

- J.1 „*PA-MBE grown ZnMgO/ZnO/ZnMgO heterostructures on p-type Si (111) –optical properties*” M. Pietrzyk, A. Reszka, M. Satchowicz, A. Droba, A. Wierzbicka, **E. Przeździecka**, A. Kozanecki BIT’s 2nd Annual World Congress of Advanced materials (2013) Suzhou, China
- J.2 „*Struktury kwantowe ZnMgO/ZnO/ZnMgO wykonywane metodą MBE*” A. Kozanecki, J. Sajkowski, M. Stachowicz, **E. Przeździecka**, M. Syperek XIII KRAJOWA KONFERENCJA ELEKTRONIKI 9 – 13.06.2014 Darłówko Wschodnie, Poland

- J.3 “*p-type Doping in ZnO*” E. Kamińska, **E. Przeździecka**, A. Piotrowska, J. Kossut, E. Dynowska, A. Barcz, W. Dobrowolski, I. Pasternak, P. Bogusławski XXXV Int. School on the Physics of Semiconducting Componds (Ustroń-Jaszowiec) (2006) Poland
- J.4 „*ZnO quantum wells in ZnMgO nanocolumns grown on Si (111) by MBE-optical and structural properties*” M. Pietrzyk, M. Satchowicz, D. Jarosz, **E. Przeździecka**, A. Reszka, A. Kozanecki BIT’s 3rd Annual World Congress of Advanced materials (2014) Suzhou, China
- J.5 “*p-type ZnO and nanostructured ZnO-based homojunction grown at low temperature*” E. Guziewicz, D. Snigurenko, T.A. Krajewski, **E. Przeździecka**, D. Jarosz, M. Pietrzyk, B.S. Witkowski Energy Materials Nanotechnology Prague Meeting 2016 (**EMN 2016**), June 21-24, 2016, Prague, Czech Republic
- J.6 “*ZnO by ALD-advantages of the material grown at low temperature*” E. Guziewicz, M. Godlewski, T. Krajewski, G. Łuka, W. Paszkowicz, J.Z. Domagała, **E. Przeździecka**, E. Łusakowska, B.S. Witkowski XXXVIII International School and Conference on the Physic of Semiconductors, Jaszowiec 2009, Poland
- J.7 “*Functionalizing ZnO*” E. Kamińska, A. Piotrowska, **E. Przeździecka**, I. Pasternak, E. Guziewicz, E. Dynowska, P. Bogusławski, J. Kossut First Polish-American Symposium: new low dimensional structures of wide gap semiconductors for spintronics and new functional materials (2007) Poland
- J.8 “*Growth of p-type znO by oxidation Zn-based compounds*” E. Kamińska, **E. Przeździecka**, A. Piotrowska, I. Pasternak, P. Bogusławski, J. Kossut 13th Int. Conf. on II-VI Compounds (2007) Jeju, South Korea

5.4 Other lectures presented personally at national and international conferences

- O.1 **E. Przeździecka**, R. Schifano, S. Chusnutidinow, T. A. Krajewski, E. Guziewicz, M. Guziewicz, M. Stachowicz, A. Kozanecki,
“*Characterization and photoresponse of ZnO based heterostructures*”
9th International Workshop on Zinc Oxide and Related Materials (IW ZnO 2016), Taipei, Taiwan, October 30 – November 2nd (2016), Taiwan
- O.2 **E. Przeździecka**, S. Chusnutidinow, M. Stachowicz, E. Guziewicz, D. Snigurenko, K. Kopalko, R. Jakiela, A. Kozanecki
„*Electrical properties, and Optical properties of p-n and p-i-n heterostructures based on p-ZnO, n-GaN and i-Al₂O₃*”
17th International Conference on II-VI Compounds and Related Materials PARIS 13-18 September (2015) France
- O.3 **E. Przezdziecka**, W. Lisowski, M. Stachowicz, A. Wierzbička, A. Reszka, R. Jakiela, M. A. Pietrzyk, J. W. Sobczak, A. Jablonski, A. Kozanecki

„PA-MBE Zn(Mg)O samples doped by one, two or three acceptors (As, N, Sb)-electronic structure, optical and electrical properties.” 8th International Workshop on Zinc Oxide and Related Materials (IW ZnO 2014) Kanada

- O.4 **E. Przeździecka**, W. Lisowski, M. Stachowicz, A. Reszka, R. Jakiela, J. W. Sobczak, M. Krawczyk, A. Wierzbicka, M. A. Pietrzyk, A. Jablonski, A. Kozanecki *„As-N, As-Sb dual acceptor doping in PA-MBE ZnO samples – electronic structure, optical and electrical properties”* Warsaw, E-MRS (2014), Poland
- O.5 **E. Przeździecka**, M. Stachowicz, A. Wierzbicka, A. Reszka, K. Gościński, A. Droba, S. Gieraltowska, E. Guziewicz, R. Jakiela, J. M. Sajkowski, D. Jarosz, M. A. Pietrzyk, P. Dłużewski, T. Wojciechowski, A. Kozanecki;
“Highly selective UV detectors bases on PA-MBE grown p-n (p-ZnO:(As-Sb)/n-GaN) and p-i-n (p-ZnO:As/HfO₂/n-GaN) heterojunctions”; E-MRS (2013) Fall Meeting; Poland
- O.6 **E. Przeździecka**, E. Guziewicz, R. Jakiela, D. Snigurenko, M. Stachowicz, A. Barcz, A. Kozanecki, W. Lisowski, J. W. Sobczak, M. Krawczyk, A. Jablonski
„XPS study of arsenic doped ZnO”; E-MRS (2013) Fall Meeting; Poland
- O.7 **E. Przeździecka**, K. Gościński, A. Wierzbicka, A. Droba, A. Reszka, R. Jakiela, D. Dobosz, K. Kopalko, M. Stachowicz, J.M. Sajkowski, M.A. Pietrzyk, S. Gieraltowska, M. Godlewski, A. Kozanecki *„MBE grown p-ZnO:As/n-GaN diodes as selective UV detectors”* 41 "Jaszowiec" International School and Conference on the Physics of Semiconductors (2012), Poland
- O.8 **E. Przeździecka**, E. Kamińska, K. Korona, E. Dynowska, W. Dobrowolski, R. Jakiela, W. Pacuski, Ł. Kłopotowski, J. Kossut *“Optical properties of p-type ZnO and ZnMnO doped by N and/or As acceptors”* 28th Int. Conf. on the Physics of Semiconductors (2006) - Vienna, Austria,
- O.9 **E. Przeździecka**, E. Kamińska, I. Pasternak, E. Dynowska, W. Dobrowolski, R. Jakiela, A. Barcz, Ł. Kłopotowski, K. Korona, J. Kossut *“Optical properties of p-type ZnO:(N,As,Sb)”* E-MRS Fall Meeting (2006)- Warsaw, Poland.

Additionally, I was coauthor of 16 oral presentations presented by co-authors. The total number of all conference posters presentations in which I'm coauthor (including those which are not listed in Journal of Citation Reports) amounts to 80.

5.5 Presented seminars

I gave a 7 seminars on the topic of habilitation and 2 related to the topic of the doctorate.

S.1 **E. Przeździecka** *„Zinc oxide in heterojunctions - selective UV radiation detectors”* solid state physics seminar at the Warsaw University (Friday) May 20, 2016

S.2 **E. Przeździecka** *„Selective UV detektors based on ZnO/GaN diodes made by MBE method”* Vth Conference on Quantum Semiconductor Nanostructures for Applications in Biology and Medicine 17 - 18 April 2013

S.3 **E. Przeździecka** *„Selective UV detektors based on ZnO/GaN diodes for sensor application made by MBE method”* VIth Conference on Quantum Semiconductor Nanostructures for Applications in Biology and Medicine 7 - 8 May 2014

S.4 **E. Przeździecka** „*Selective UV detectors based on ZnO/GaN diodes made by MBE method*” Seminar in Physics of Condensed Matter IP PAS, March 12th 2013

S.5 **E. Przeździecka** „*Diode structures based on MBE for sensor applications. (Task 6)*” Presentation on the Panel of Experts of the Key Project: Quantum Semiconductor Nanostructures for Applications in Biology and Medicine - Development and Commercialization of new Generation Devices for Molecular Diagnostics on the Basis of New Polish Semiconductor Devices, 2012 IP PAS

S.6 **E. Przeździecka** “*MBE grown p-ZnO: As / n-GaN diodes as selective UV detectors*”, ON4 Seminar, 5 June 2012

S.7 **E. Przeździecka** „*Heterostructures based on wide-beam materials - as UV detectors*” Report on the institute's activities for 2015

S.8 **E. Przeździecka**, K. Gościński, D. Dobosz, K. Kopalko, A. Wierzbička, A. Droba, R. Jakiela, A. Reszka, M. Stachowicz, J. Sajkowski, T. Krajewski, M. Pietrzyk, A. Kozanecki. „*Diode structures based on MBE for sensor applications. (Task 6)*” – Presentation on the Panel of Experts of the Key Project: Quantum Semiconductor Nanostructures for Applications in Biology and Medicine - Development and Commercialization of new Generation Devices for Molecular Diagnostics on the Basis of New Polish Semiconductor Devices, 2011 IP PAS

S.9 **E. Przeździecka** „*ZnO - work on a p- type of conductivity*” X-ray seminar Tuesday, November 3, 2009

S.10 **E. Przeździecka** „*Properties of p-type ZnO and ZnMnO obtained by oxidation of Zn (Mn) layers*” Seminar in Physics of Condensed Matter IP PAS, February 28, 2006

5.6 Building of unique research equipment

I constructed and modified the photocurrent and photocurrent transients measurement systems. The photocurrent measurement system allows performing photocurrent investigations as a function of the wavelength of the incident radiation by using a white light source followed by a monochromator. Photocurrent measurements can be performed either in the absence of applied voltage or with applied voltage to the sample. The use of argon laser allows them to measure photocurrent as a function of power of incident radiation. Mechanical light chopper used on the laser beam allows us to measure the kinetics of photocurrent for a given wavelength of incident radiation. The measuring system allows to illuminate the sample both from the top and from the bottom. Execution and significant modification of this measuring system allowed obtaining the results described in the papers [H4-H9]. All of the photocurrent studies included in [H4-H9] were done by me on described above measurement system. Moreover, such equipped laboratory is used for teaching II/III years students of faculty of Physics University of Warsaw “Detectors”.

I took an active part in the installation, assembly and commissioning of the MBE Compact 21 machine. It is a unique epitaxial growth machine that allows, among other things, doping of ZnO layers by using arsenic, antimony and nitrogen sources. On the above mentioned system I made the ZnO samples themselves, which are the basis of research presented in papers H1, H3, H4, H5, H6, H7, H9.

I participated in the purchase, modification and extension of the DLTS measurement system for lower frequencies.

Preparation of specifications for the purchase of MBE machines for CEZAMAT Center for Advanced Materials and Technology.

5.7 Organization of conferences, reviewer and editorial activities

I prepared a part of the presentation in the endeavor for organization of the International Workshop of ZnO, this presentation was positively evaluated and in 2018 the conference will take place in Warsaw.

I was reviewer of about 20 publications in various scientific journals:

Sensors and Actuators, Appl. Phys. Lett., phys. stat. solidi (c) and (b), Acta Phys. Pol. A, Material Science – Poland, Journal of Crystal Growth, Applied Physics A, Applied Materials and Interfaces, Central European Journal of Physics, Thin Solid Films, Journal of Chemistry C.

5.8 Teaching and popular science activity

I gave classes for second year students of Nanostructure Engineering from University of Warsaw in the frame of laboratory: "Technology and Design of New Materials". The supervisor of the whole laboratory is Prof. Maria Kamińska from University of Warsaw (2016 summer semester). My subject was "Detectors". In 2017, this subject will continue to be taught by me.

I co-supervise also PhD studies of MSc Karolina Paradowska - Wroclaw University of Technology, Department of Quantum Technologies, entitled: „*Electro optic properties of ZnO and ZnMgO-based heterostructures produced by PA-MBE* ". Opening date: 05.05.2016. Supervisor: Prof. Ewa Płaczek-Popko.

I supervised 3 students during their practice in the Institute of Physics, PAS:

- Magdalena Tyrakowska student of the Physics Department of Warsaw University of Technology
- Justyna Pokrzywnicka student of the Cardinal Wyszyński University in Warsaw
- Michał Solecki vel Szymański student of the Physics Department of the University of Warsaw

I was a chairman at session of Energy Materials Nanotechnology Prague Meeting 2016 (EMN 2016), June 21-24, Prague, Czech Republic

Popular science activity:

I am supervisor of the action *Popular science classes* at the Institute of Physics (2015-2017).

I've given several popular science lessons For students from secondary and high schools in the laboratory for molecular beam epitaxy. The lessons are part of the popular science offer for schools of the Institute of Physics, PAS.

5.9 Participation and awards at the fair

T.1 International Exhibition of Economic and Scientific Innovations *INTARG silver medal* for „ *Innovative, highly selective UV detectors*” – I prepared the poster, the presentation and the demonstrator.

T. 2 The word exhibitions on inventions, research and new technologies Brussels Innova 17-19.11.2016 Brussels - **gold medal** for “*Innovative UV detectors based on wide gap semiconductors*”, I prepared the poster, the presentation and the demonstrator.

5.10 Patents and Patent Applications

Patents:

PL 220515 30.11.2015 *The structure of a UV detector and the method of manufacturing of the structure of a UV detector;*
authors: **E. Przeździecka** A. Kozanecki

P.403520 *The structure of a p-i-n UV detector and the method of manufacturing of this structure;*
authors: **E. Przeździecka**, S. Gierałtowska, E. Guziewicz, M. Godlewski, A. Kozanecki

Patent Applications:

P.412613 *The structure of a transparent ultraviolet detector and the method of manufacturing of a structure of a transparent ultraviolet detector;* authors: M. Guziewicz, W. Jung, E. Guziewicz, **E. Przeździecka**, R. Schifano, T. Krajewski

P.416263 *Electrical junction based on zinc oxide and a method of manufacturing of this junction;* authors: M. Pietrzyk, **E. Przeździecka**, E. Guziewicz, D. Snigurenko



Ewa Przeździecka

6. References

- [1] Jagadish C, Pearton SJ. **2006**. Zinc Oxide Bulk, Thin Films and Nanostructures Oxford: Elsevier.
- [2] Ozgur U, Alivov YI, Liu C, Reshchikov MA, Dogan S, Avrutin V, Cho SJ, Morkoc H. **2005**. *Journal of Applied Physics* **98** 041301
- [3] Fan MM, Liu KW, Zhang ZZ, Li BH, Chen X, Zhao DX, Shan CX, Shen DZ. **2014**. *Applied Physics Letters* **105** 011117
- [4] Coskun C, Look DC, Farlow GC, Sizelove JR. **2004**. *Semiconductor Science and Technology* **19** 752
- [5] Kohan AF, Ceder G, Morgan D, Van de Walle CG. **2000**. *Phys. Rev. B* **61** 15019-27
- [6] Wang LG, Zunger A. **2003**. *Phys. Rev. Lett.* **90** 256401
- [7] Van de Walle CG. **2000**. *Phys. Rev. Lett.* **85** 1012-5
- [8] Cox SFJ, Davis EA, Cottrell SP, King PJC, Lord JS, Gil JM, Alberto HV, Vilao RC, Pirotto Duarte J, yres de Campos N, Weidinger A, Lichti RL, Irvine SJC. **2001**. *Phys. Rev. Lett.* **86** 2601-4
- [9] Park CH, Zhang SB, Wei SH. **2002**. *Phys. Rev. B* **66** 073202
- [10] Limpijumnong S, Zhang SB, Wei SH, Park CH. **2004**. *Phys. Rev. Lett.* **92** 155504
- [11] Puchala B, Morgan D. **2012**. *Phys. Rev. B* **85** 195207
- [12] Liu L, Xu J, Wang D, Jiang M, Wang S, Li B, Zhang Z, Zhao D, Shan C-X, Yao B, Shen DZ. **2014**. *Phys. Rev. Lett.* **108** 215501
- [13] Reynolds JG, Reynolds Jr CL, Mohanta A, Muth JF, Rowel JE, Everitt HO, Aspnes DE. **2013**. *Appl. Phys. Lett.* **102** 152114
- [14] Kewei Liu, Makoto Sakurai, Masakazu Aono. **2010**. *Sensors* **10** 8604-34
- [15] Ćwirko R, Bielecki Z, Ćwirko J, Dobrzański L. **2006**. *Opto-Electronics Review* **14** 149–154
- [16] Wagner C, Harned N. **2010**. *Nat Photon* **4** 24-6
- [17] Razeghi M, Rogalski A. **1996**. *Journal of Applied Physics* **79** 7433-73
- [18] Chih-Han Chen, Shouou-Jinn Chang, Sheng-Po Chang, Meng-Ju Li, I-Cherng Chen, Ting-Jen Hsueh, Cheng-Liang Hsu. **2009**. *Chemical Physics Letters* **476** 69
- [19] Ching-Ting Lee, Tzu-Shun Lin, Hsin-Ying Lee. **2010**. *IEEE Photonic Technology Letters* **22** 1117
- [20] Johnsn MAL, Shizuo Fujita, Rwoiland Jr.W.H, Hughes WC, Cook JW, Schetzina JF. **1996**. *Journal of Electronic Materials* **25** 855
- [21] Almamun Ashrafi ABM, Nguyen Thanh Binh, Bao-Ping Zhang, Yusaburo Segawa. **2004**. *Appl. Phys. Lett.* **84** 2014
- [22] Alivov YaI, Ozgur U, Dogan S, Johnstone D, Avrutin V, Onojima N, Liu C, Xie J, Fan Q, Morkoc H. **2005**. *Applied Physics Letters* **86** 241108
- [23] Yuen C, Yu SF, Lau SP, Rusli, Chen TP. **2005**. *Applied Physics Letters* **86** 241111
- [24] Jeong IS, Kim JH, Im S. **2003**. *Applied Physics Letters* **83** 2946-8
- [25] Jeong IS, Kim JH, Park HH, Im S. **2004**. *Thin Solid Films* **447-448** 111-4
- [26] Huang H, Fang G, Mo X, Yuan L, Zhou H, Wang M, Xiao H, Zhao X. **2009**. *Applied Physics Letters* **94** 063512
- [27] Placzek-Popko E, Paradowska KM, Pietrzyk MA, Gumienny Z, Bieganski P, Kozanecki A. **2015**. *Journal of Applied Physics* **118** 074501
- [28] Zhang D, Uchida K, Nozaki S. **2015**. *Journal of Applied Physics* **118** 094502
- [29] Sandvik P, Mi K, Shahedipour F, McClintock R, Yasan A, Kung P, Razeghi M. **2001**. *Journal of Crystal Growth* **231** 366-70

- [30] Van Hove JM, Hickman R, Klaassen JJ, Chow PP, Ruden PP. **1997**. *Applied Physics Letters* **70** 2282-4
- [31] Chen X, Zhu H, Cai J, Wu Z. **2007**. *Journal of Applied Physics* **102** 024505
- [32] Ćwirko J, Ćwirko R, Mikołajczyk J. **2015**. *Metrol. Meas. Syst.* , **22** 119
- [33] Li J, Wei S-H, Li S-S, Xia J-B. **2006**. *Phys. Rev. B* **74** 081201(R)
- [34] Pearnton SJ, Norton DP, Ip K, Heo YW, Steiner T. **2004**. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **22** 932-48
- [35] Wahl U, Rita E, Correia JG, Marques AC, Alves E, Soares JC, ISOLDE C. **2005**. *Phys. Rev. Lett.* **95** 215503
- [36] Boonchun A, Lambrecht WRL. **2013**. *physica status solidi (b)* **250** 2091
- [37] Bang J, Sun YY, West D, Meyer BK, Zhang S. **2015**. *J. Mater. Chem. C* **3** 339-44
- [38] Lee EC, Kim Y, Jin Y, Chang K. **2001**. *Phys. Rev. B* **64** 085120
- [39] Lautenschlaeger S, Hofmann M, Eisermann S, Haas G, Pinnisch M, Laufer A, Meyer BK. **2011**. *physica status solidi (b)* **248** 1217
- [40] Duan XY, Yao RH, Zhao YJ. **2008**. *Applied Physics A* **91** 467-72
- [41] Lu JG, Zhang YZ, Ye ZZ, Zhu LP, Wang L, Zhao BH, Liang QL. **2006**. *Applied Physics Letters* **88** 222114
- [42] Bin W, Yue Z, Jiahua M, Wenbin S. **2009**. *Applied Physics A* **94** 715-8
- [43] Fan JC, Sreekanth KM, Xie Z, Chang SL, Rao KV. **2013**. *Progress in Materials Science* **58** 874-985
- [44] Look DC, Farlow GC, Reunchan P, Limpijumngong S, Zhang SB, Nordlund K. **2005**. *Phys. Rev. Lett.* **95** 225502
- [45] Ryu YR, Lee TS, White HW. **2003**. *Applied Physics Letters* **83** 87-9
- [46] Kang HS, Kim GH, Kim DL, Chang HW, Ahn BD, Lee SY. **2006**. *Applied Physics Letters* **89** 181103
- [47] Vaithianathan V, Lee BT, Kim SS. **2005**. *Applied Physics Letters* **86** 062101-3
- [48] Przeździecka E, Kaminska E, Korona K P, Dynowska E, Dobrowolski W, Jakiela R, Kłopotowski L, Kossut J. **2007**. *Semiconductor Science and Technology* **22** 10
- [49] Przeździecka E, Kaminska E, Pasternak I, Piotrowska A, Kossut J. **2007**. *Phys. Rev. B* **76** 193303
- [50] Shen Y, Hu W, Zhang T, Xu X, Sun J, Wu J, Ying Z, Xu N. **2008**. *Materials Science and Engineering: A* **473** 201-5
- [51] Wang P, Chen N, Yin Z, Yang F, Peng C, Dai R, Bai Y. **2006**. *Journal of Applied Physics* **100** 043704
- [52] Wang SP, Shan CX, Li BH, Zhang JY, Yao B, Shen DZ, Fan XW. **2009**. *Journal of Crystal Growth* **311** 3577-80
- [53] Volbers N, Lautenschlager S, Leichtweiss T, Laufer A, Graubner S, Meyer BK, Potzger K, Zhou S. **2008**. *Journal of Applied Physics* **103** 123106
- [54] Pan X, Ye Z, Li J, Gu X, Zeng Y, He H, Zhu L, Che Y. **2007**. *Applied Surface Science* **253** 5067-9
- [55] Zhao JZ, Liang HW, Sun JC, Bian JM, Feng QJ, Hu LZ, Zhang HQ, Liang XP, Luo YM, Du GT. **2008**. *Journal of Physics D: Applied Physics* **41** 195110
- [56] Zeng DW, Xie CS, Zhu BL, Song WL, Wang AH. **2003**. *Materials Science and Engineering: B* **104** 68-72
- [57] Zang CH, Su JF, Wang B, Zhang DM, Zhang YS. **2011**. *Journal of Luminescence* **131** 1817-20
- [58] Qin JM, Yao B, Yan Y, Zhang JY, Jia XP, Zhang ZZ, Li BH, Shan CX, Shen DZ. **2009**. *Applied Physics Letters* **95** 022101
- [59] Wardle MG, Goss JP, Briddon PR. **2006**. *Phys. Rev. Lett.* **96** 205504
- [60] Cox SFJ, Davis EA, Cottrell SP, King PJC, Lord JS, Gil JM, Alberto HV, Vilao RC, Pirotto Duarte J, yres de Campos N, Weidinger A, Lichti RL, Irvine SJC. **2001**. *Phys. Rev. Lett.* **86** 2601-4
- [61] Kim KK, Kim HS, Hwang DK, Lim JH, Park SJ. **2003**. *Applied Physics Letters* **83** 63-5

- [62] Kim KK, Niki S, Oh JY, Song JO, Seong TY, Park SJ, Fujita S, Kim SW. **2005.** *Journal of Applied Physics* **97** 066103
- [63] Fan JC, Zhu CY, Fung S, Zhong YC, Wong KS, Xie Z, Brauer G, Anwand W, Skorupa W, To CK, Yang B, Beling CD, Ling CC. **2009.** *Journal of Applied Physics* **106** 073709-6
- [64] Hesong Guan, Xiaochuan Xia, Yuantao Zang, Fubin Gao, Wancheng Li, Guoguang Wu, Xiangping Li, Guotong Du. **2008.** *Journal of Physics: Condensed Matter* **20** 292202
- [65] Ding M, de Jong BHWS, Roosendaal SJ, Vredenberg A. **2000.** *Geochimica et Cosmochimica Acta* **64** 1209-19
- [66] Xu N, Xu Y, Li L, Shen Y, Zhang T, Wu J, Sun J, Ying Z. **2006.** *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films* **24** 517
- [67] Janotti A, Van de Walle CG. **2007.** *Phys. Rev. B* **76** 165202
- [68] Fan JC, Xie Z, Wan Q, Wang YG. **2007.** *Journal of Crystal Growth* **307** 66-9
- [69] Snigurenko D, Jakiela R, Guziewicz E, Przeździecka E, Stachowicz M, Kopalko K, Barcz A, Lisowski W, Sobczak JW, Krawczyk M, Jablonski A. **2014.** *Journal of Alloys and Compounds* **582** 594-7
- [70] Zhao W, Zhao L, Shi Z, Xia X, Li X, Dong X, Chang Y, Zhang B, Du G. **2011.** *Applied Surface Science* **257** 4685-8
- [71] Kumar A, Kumar M, Singh BP. **2010.** *Applied Surface Science* **256** 7200-3
- [72] Volnianska O, Boguslawski P, Kaminska E. **2012.** *Phys. Rev. B* **85** 165212
- [73] Vlasenflin TH, Tanaka M. **2007.** *Solid State Communications* **142** 292-4
- [74] Liang JK, Su HL, Chuang PY, Kuo CL, Huang SY, Chan TS, Wul YC, Huang JCA. **2015.** *Appl. Phys. Lett.* **106** 212101
- [75] Hsieh PT, Chen YC, Kao KS, Wang CM. **2008.** *Applied Physics A* **90** 317-21
- [76] Wei XQ, Man BY, Liu M, Xue CS, Zhuang HZ, Yang C. **2007.** *Physica B: Condensed Matter* **388** 145-52
- [77] Snigurenko D, Guziewicz E, Krajewski T, Jakiela R, Syryanyy Y, Kopalko K, Paszkowicz W. **2016.** *Mater. Res. Express* **3** 125907
- [78] Joseph M, Tabata H, Kawai T. **1999.** *Japanese Journal of Applied Physics* **38** L1205
- [79] Bian JM, Li XM, Gao XD, Yu WD, Chen LD. **2004.** *Applied Physics Letters* **84** 541-3
- [80] Zhang BY, Yao B, Li YF, Zhang ZZ, Li BH, Shan CX, Zhao DX, Shen DZ. **2010.** *Applied Physics Letters* **97** 222101-3
- [81] Duan L, Wang P, Yu X, Han X, Chen Y, Zhao P, Li D, Yao R. **2014.** *Phys. Chem. Chem. Phys.* **16** 4092-7
- [82] Li W, Kong C, Qin G, Ruan H, Fang L. **2014.** *Journal of Alloys and Compounds* **609** 173-7
- [83] Sun J, Liang H, Zhao J, Feng Q, Bian J, Zhao Z, Zhang H, Luo Y, Hu L, Du G. **2008.** *Applied Surface Science* **254** 7482-5
- [84] Huang YC, Weng LW, Uen WY, Lan SM, Li ZY, Liao SM, Lin TY, Yang TN. **2011.** *Journal of Alloys and Compounds* **509** 1980-3
- [85] Hong SK, Ko HJ, Chen Y, Hanada T, Yao T. **2000.** *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **18** 2313-21
- [86] Hyung-Kyu Choi and Jang-Ho Park and Sang-Hun Jeong and Byung-Teak Lee. **2009.** *Semiconductor Science and Technology* **24** 105003
- [87] Look DC, Reynolds DC, Litton CW, Jones RL, Eason DB, Cantwell G. **2002.** *Applied Physics Letters* **81** 1830-2
- [88] Liang HW, Lu YM, Shen DZ, Liu YC, Yan JF, Shan CX, Li BH, Zhang ZZ, Fan XW. **2005.** *physica status solidi (a)* **202** 1060
- [89] Zeuner A, Alves H, Hofmann DM, Meyer BK, Hoffmann A, Haboek U, Strassburg M, Dworzak M. **2002.** *physica status solidi (b)* **234** R7
- [90] Look DC, Claflin B, Alivov YI, Park SJ. **2004.** *physica status solidi (a)* **201** 2203
- [91] Tsukazaki A, Akasaka S, Najahara K, Ohno Y, Ohno H, Maryenko D, Ohtomo A, Kawaski M. **2010.** *Nat Mater* **9** 889-893
- [92] Guziewicz E, Godlewski M, Wachnicki L, Krajewski TA, Luka G, Gieraltowska S, Jakiela R, Stonert A, Lisowski W, Krawczyk M, Sobczak JW, Jablonski A. **2012.** *Semiconductor Science and Technology* **27** 074011

- [93] Korona KP, Drabinska A, Caban P, Strupinski W. **2009**. *Journal of Applied Physics* **105** 083712
- [94] Witkowski BS, Wachnicki L, Gieraltowska S, Sybilski P, Kopalko K, Stachowicz M, Godlewski M. **2014**. *physica status solidi (c)* **11** 1447
- [95] Kind H, Yan H, Messer B, Law M, Yang P. **2002**. *Advanced Materials* **14** 158-60
- [96] Look DC. **2001**. *Materials Science and Engineering: B* **80** 383-7
- [97] Kramm B, Laufer A, Reppin D, Kronenberger A, Hering P, Polity A, Meyer BK. **2012**. *Appl. Phys. Lett.* 094102
- [98] Li S, Fang G, Huang H, Long H, Wang H, Mo X, Dong B, Zhao X. **2012**. *Appl. Phys. B* **107** 497-502
- [99] Zhu GY, Li JT, Shi ZL, Lin Y, Chen GF, Ding T, Tian ZS, Xu CX. **2012**. *Appl. Phys. B* **109** 195-9
- [100] Liu WZ, Xu HY, Zhang LX, Zhang C, Ma JG, Wang JN, Liu YC. **2012**. *Applied Physics Letters* **101** 142101
- [101] Wang T, Wu H, Zheng H, Wang JB, Wang Z, Chen C, Xu Y, Liu C. **2013**. *Applied Physics Letters* **102** 141912
- [102] Przeździecka E, Chusnutdinow S, Guziewicz E, Snigurenko D, Stachowicz M, Kopalko K, Reszka A, Kozanecki A. **2015**. *Journal of Physics D: Applied Physics* **48** 325105
- [103] Xu HY, Liu YC, Liu YX, Xu CS, Shao CL, Mu R. **2005**. *Appl. Phys. B* **80** 871-4
- [104] Taube A, Gieraltowska S, Guut T, Malachowski T, Pasternak I, Wojciechowski T, Rzodkiewicz W, Sawicki M, Piotrowska A. **2011**. *Acta Phys Pol A* **119** 696
- [105] Przeździecka E, Gościński K, Gieraltowska S, Guziewicz E, Jakiela R, Kozanecki A. **2014**. *Key Engineering Materials* **605** 310
- [106] Vikas LS, Vanaja KA, Subha PP, Jayaraj MK. **2016**. *Sensors and Actuators A: Physical* **242** 116-22
- [107] Kriegner D, Vyborny K, Olejnik K, Reichlova H, Novak V, Marti X, Gazquez J, Saidl V, Nemeč P, Volobuev VV, Springholz G, Holy V, Jungwirth T. **2016**. *Nature Communications* **7** 11623
- [108] Dietl T, Ohno H, Matsukura F, Cibert J, Ferrand D. **2000**. *Science* **287** 1019
- [109] Pacuski W, Kossacki P, Ferrand D, Golnik A, Clibert J, Wegscheider M, Navarro-Quezada A, Bonanni A, Kiceana M, Sawicki M, Dietl T. **2008**. *Phys. Rev. Lett.* **100** 037204
- [110] Pacuski W, Ferrand D, Clibert J, Deparis C, Gaj JA, Kossacki P, Morhain C. **2006**. *Phys. Rev. B* **73** 035214
- [111] Dietl T, Awschalom D, Kaminska M, Ohno H. Spintronics. **2008**. Semiconductors and Semimetals.