Summary of professional accomplishments

1. Name and surname: Jacek Zakrzewski

2. Diplomas, degrees - with the name,
place and year of acquisition, title of doctoral dissertation.

- 1991 MSc., experimental physics: Uniwersytet Mikołaja Kopernika w Toruniu (Nicolas Copernicus University in Toruń)
- 2001 PhD., Nicolas Copernicus University in Toruń
„Zjawiska fotoakustyczne w kryształach mieszanych A2B6" („Photoacoustic Phenomena of A2B6 Mixed Crystals")

Promoter: prof. dr hab. Hanna Męczyńska
Reviewers: prof. dr hab. Franciszek Rozpłoch
dr hab. Marek Grinberg prof. of Gdansk University

3. Information on employment in scientific institutions:

- 1991-1995 PhD. studies, Wydział Fizyki, Astronomii i Informatyki Stosowanej, UMK w Toruniu (Department of Physics, Astronomy and Applied Informatics, NCU Toruń)
- 1995-2002 assistant, Zakład Fizyki Półprzewodników, UMK w Toruniu (Semiconductor Physics Group, NCU in Toruń)
- od 2002 adjunct (associated professor), Zakład Fizyki Półprzewodników i Fizyki Węgla, UMK w Toruniu (Department of Semiconductor and Carbon Physics, NCU in Toruń)
- 9 October 2007 – 10 October 2008 – postdosctoral position funded be Centre National de la Recherche Scientifique (CNRS), Laboratoire d'Acoustique de l'Universite du Maine, France

4. Indication of achievements under Paragraph 16. 2 of the Act from 14 March 2003 on Academic Degrees, Titles and Titles in Art (Journal of Laws No. 65, item. 595, as amended):

A, B) As an achievement I report monograph:

„Piezoelektryczna spektroskopia fototermiczna w objętości i na powierzchni półprzewodników A2B6",

(„Piezoelectric Photothermal Spectroscopy in Volume and at the Surfaces of A2B6 Semiconductors")

Wydawnictwo Naukowe UMK, ISBN 978-83-231-2972-1, Toruń 2013

C) Description of the scientific work and results along with a discussion of their possible applications.

Photothermics is a branch of the science which investigates the phenomena appearing after the absorption of radiation and its transfer into the heat in the investigated sample. It can be applied to measurements of absorption spectra, exited states life times, thermal and elastic parameters of the materials.

Photothermal signal arises as a result of absorption of light. The part of radiation energy, which is transmitted through or scattered in the sample, doesn't affect the generation of photothermal signal. Photothermal methods could be applied to the investigations of materials, which cannot be measured by the conventional ones: materials strongly scattering the light such as powders and gels. The other "difficult" materials are opaque ones or these of the dimensions much more exceed the penetrations depth of the radiations. In the first case optical signal depends on the intensity of reflected and transmitted light and it is hard to be interpreted while in the second case the measurements are even more difficult because of small number of photons transmitted through the sample. "Difficult" materials are also pure, transparent ones of very small absorption.

Photothermics allows to determine thermal, optical and mechanical properties of material – it is both a kind of calorimetry and optical spectroscopy. Photothermal methods can be applied to the investigations of all kinds of organic, nonorganic, biological materials in three physical states: solid, liquid and gas.

Three types of detector can be used in photothermal measurements: microphone, piezoelectric or pyroelectric elements. In the first case, the method is called photoacoustics. Photoacoustic effect, which started the development of photothermal methods was discovered by Bell in 1881 [1], but until the article of Rosencwaig and Gersho in 1976 r. [2] it was not widely used. Theory for piezoelectric detection was published in the article of Jackson and Amer [3] and Blonskij [4], however they were not applied for photothermal spectroscopy. The model proposed at these articles don't allow to analyze the changes observed in phase and amplitude spectra in the case of not ideal materials (containing defect on the surfaces or in the volume of sample). The basis of interpretation in all these methods is the knowledge of temperature distribution but because of different way of detections the next analysis of is not the same. In microphone method one measures the changes of pressure in the chamber containing the sample (photoacoustic effect), in piezoelectric detection – strains and stress produced in the sample, in pyroelectric detection –temperature changes in the sample. In all cases the sample is illuminated by radiation periodically chopped. If the absorption of energy takes place, the sample becomes excited - it transits to the higher energy state. This energy is wholly or partially forwarded to the heat in non-radiative processes. In gases it is associated with kinetic energy of gas molecules, while in solids and liquids with vibration energy of ions and molecules.

Piezoelectric detection can be applied to the investigations of crystals, but it is not useful for powders, greases and gels. For these materials it is much better to use photoacoustic detection with microphone placed in the chamber filled with gas. Periodic heating of the sample as a result of absorption leads to transfer of energy from the sample to non-absorbing gas. The changes of pressure are produced and they are detected by microphone.

In my work I concentrated on piezoelectric method and additionally on one of its kind – piezoelectric spectroscopy. The aim was to show the possibilities of this method in the investigations of thermal and optical properties of semiconducting materials of A2B6 group. The research of influence of surface preparation processes on the character of phase and amplitude spectra was also done.

Wide band-gap A2B6 compounds have lately intensively studied [5-8] and the main reason is their potential application for the production on miniaturized lasers emitting blue-green and green light, high-quality photodetectors of blue an UV region, Bragg mirrors and in spintronics. For these compounds, the change of energy gap value allows to obtain the materials of strictly defined optical properties, the change of lattice constant – the materials ideally fitted to the substrate used in epitaxial growth. Very promising material for application in spintronics is quaternary $Zn_{1-x-y}Be_xMn_ySe$ mixed compound. Manganese in $Zn_{1-x-y}Be_xMn_ySe$ is an isoelectronic admixture i.e. it functions as II's group element of the periodic table. Though Mn^{++} ion has five unpaired electrons at 3d shell, it behaves similar to ion of the shell closed. It causes that unlike the compounds of III-VI group, the II-VI materials can be additionally admixed to obtain *n* or *p* type conductivity, which is undoubted advantage. Mixed ternary semimagnetic compounds have been investigated for long time, but quaternary compound $Zn_{1-x-y}Be_xMn_ySe$ is a new one in this area. Introduction of beryllium causes decrease of lattice constant and increase of the value of energy gap and microhardness. The reason of bigger hardness is the change of the type of bonding – from ionic to covalent. The production of "hard" wide band gap A2B6 semiconductors is very important for the process of construction "green" laser. Hardening of the compound decreases the propagation of dislocations in the active layer of laser diode and degradation of this layer in time.

In the case of another investigated material, $Zn_{1-x-y}Be_xMg_ySe$, the proper combinations of components allows to fit the lattice constant to silicon - at the same time the value of energy gap remains high and could be over 4 eV. Thanks to those advantages this material is a candidate for the production of devices based on well developed silicon technology, but working in the blue and UV energy regions.

All the compounds investigated in the frame of my work were obtained in Department of Semiconductor and Carbon Physics, Nicolas Copernicus University in Toruń. Quaternary compounds $Zn_{1-x-y}Be_xMn_ySe$ and $Zn_{1-x-y}Be_xMg_ySe$ and pure binary ZnSe, CdS i CdSe were studied. The surfaces of the samples were treated mechanically (grinding, polishing with paste in the mixture of water and oil or polishing with diamond paste in the oil suspension), chemical (etching in $K_2Cr_2O_7 : H_2SO_4 : H_2O$ solution and 50% NaOH or HCl) and thermal (annealing in zinc vapor in 1170 K). The aim was to obtain the best state of quality of the surface.

In my monograph, I presented the simulations of phase and amplitude piezoelectric photothermal signal for different values of thermal and optical parameters, typical for semiconductors: energy gap, thermal diffusivity, Urbach tail broadening and for different thicknesses and frequencies of radiation modulation. The character of phase and amplitude depends on the relative position of sample and detector. It was discussed, how thermal and optical parameters influence photothermal spectra for both of these configurations. I showed how the bases of theories, first concerning microphone detection (Rosencwaig-Gersho theory for one layer model and Fernelius theory for two layers), can be applied to the piezoelectric one. I presented full solution for temperature distribution in the sample (not showed in above mentioned models). The examples present simulations both for pure sample and the ones with defects at the volume or located at the surfaces.

In 2002 Maliński [9] stated the solution of temperature distribution along the thickness of the sample based on the thermal waves interference model which was the development of the idea of Bennet and Patty [10]. This distribution was used many times in analysis of experimental data obtained for A2B6 compounds thanks to modifications associated with the presence of surface defects (Maliński published the first results with me [11]). In 2012, together with co-workers [12] I proposed in interpretation of piezoelectic spectra - applying the temperature distribution of Blonskij. I introduced, analogous to interference model, the modifications allowing the interpretations of spectra for materials with surface or volume defects. In my monograph all the simulations are made for modified Blonskij model. I showed that both of these distributions give the same results for pure and for defected samples. Blonskij's model is more universal then Fernelius' [13], in which one assume only one layer on the bulk of the sample (illuminated or non illuminated). In Blonskij's and interference ones there can exist layers of different thermal properties on both sides of the bulk of the sample.

The procedure of sample surface preparation affects the course of piezoelectric phase and amplitude of the spectra. Depending of the state of the surface additional maxima and changes are observed in amplitude and phase spectra, respectively. They are not predicted in Jackson-Amer and Blonskij's theory. The proper preparation of the surface decreases the amplitude of additional maxima and reduces the changes in phase – the course of the spectra corresponds to the character of the spectra for good quality. Thanks to his feature, photothermal spectroscopy can be applied to prepare the procedure of monitoring the surface quality. The surface treatment, besides the modifications of itself, introduces the changes in subsurface layer of the sample. I showed how piezoelectric method can help in estimating its thickness. Two models were discussed: in the first one, the change of thermal conductivity in subsurface region was assumed, in the second one - the existence of inactive subsurface layer. I also showed the relationship between the quality of the crystal and the course of amplitude and phase of photothermal signal.

The surfaces of the sample and subsurface layers, despite the same procedure of treatment can not be identical – at different sides the defects of different energy can be localized. Modified Blonskij's model allows the evaluation whether the observed defects are localized in the volume or at the surfaces of the sample. In the case of surface defects one can identify the type of defect and the side it is situated at. The course of amplitude and phase show the changes depending on the type of defects: volume or surface ones. For the proper interpretations it is necessary to compare both spectra. Amplitude one can show similar features for the presence of volume and surface defects. Phase spectra, different for these two cases allows to indicate the proper localization of the defects.

The studies carried thanks to piezoelectric photothermal spectroscopy are the basis for further applications. The laser excitation will allow the use this detection in photothermal microscopy. The use of different wavelength of laser radiation is of the crucial importance, it will allow to obtain the images for low and high absorption regions. I the case of semiconductors, the increase the modulation frequency to the values more then 50 kHz leads to decrease of the thermal diffusion length below one micrometer. It can be applied in the investigations of the degradations of surfaces of semiconducting devices. Such kind of research has already be made thanks to electroluminescence, atomic force microscopy and gate current leakage [14-16]. Piezoelectric microscopy (of different wavelengths of laser radiation) could be the complementary or alternative for these methods.

[1] A.G. Bell, Philos. Mag. 11, 5, 510 (1881).
[2] A. Rosencwaig, A. Gersho, J. Appl. Phys. 47, 64 (1976).
[3] W. Jackson, N.M. Amer, J. Appl. Phys. 51, 3343 (1980).
[4] I.V. Blonskij, V.A. Tkhoryk, M.L. Shendeleva, J. Appl. Phys. 79, 7, 3512 (1996).
[5] K. Perzyńska, M. Biernacka, P. Zaleski, F. Rozpłoch, J. Patyk, F. Firszt, H. Męczyńska, W. Paszkowicz, M. Marczak, Phys. Stat. Sol. (b) 2, 701 (2002).
[6] F. Rozpłoch, J. Patyk, F. Firszt, H. Męczyńska, J. Zakrzewski, A. Marasek Phys. Stat. Sol. (b) 229, 707 (2002).
[7] F. Firszt, K. Strzałkowski, J. Zakrzewski, S. Łęgowski, H. Męczyńska, A. Marasek, Cryst. Res. Technol. 42 1352 (2007).

[8] A. Waag, Th. Litz, F. Fisher, H.J. Lugauer, T. Baron, K. Schül, U. Zehnder, T. Gerhard, U. Lunz, W. Ossau, M. Keim, G. Reuscher, G. Landwehr, J. Cryst. Growth 184/185, 1, (1997).
[9] M. Maliński, Archives of Acoustics, 27, 3, 217 (2002).
[10] C.A. Bennet Jr, R.R. Patty, Appl. Optics, 21, 1, 49 (1982).
[11] M. Maliński, J. Zakrzewski, K. Strzałkowski, Int. J. Thermophys. 28, 1, 299 (2007).
[12] J. Zakrzewski, M. Maliński, K. Strzałkowski, D. Madaj, F. Firszt, S. Łęgowski, H. Męczyńska, Int. J. Thermophys. 33, 4, 733 (2012).
[13] N. Fernelius, J. Appl. Phys. 51 (1), 650 (1980).
[14] M. Montes Bajo, C. Hodges, M.J. Uren, M. Kuball, Appl. Phys. Letters 101, 033508 (2012).
[15] P. Makaram, J. Joh, J.A. Del Alamo, T. Palacios, C.V. Thompson, Appl. Phys. Lett. 96, 233509 (2010).
[16] F. Gao, B. Lu, L. Li, S. Kaun, J.S. Speck, C.V. Thompson, T. Palacios, Appl. Phys. Lett. 99, 223506 (2011).

5. Discription of the other scientific achievements

Outline of Professional career

Before PhD. degree:

In 1991, after graduate in physics (MSc.) I began post-graduate studies at Department of Physics and Astronomy, Nicolas Copernicus University (NCU) in Toruń at Semiconductor Physics Group led by prof. dr. hab. Hanna Męczyńska. At this time new equipment was bought for the experiments which were to start – photothermal spectroscopy of A2B6 semiconductors. My task was to set together all the devices and write the software to control the experiments. I constructed and tested several photothermal cells for piezoelectric detection using detectors of different thickness and resonant frequencies. These experiments led to the construction of photothermal cell which could be used both in room temperature and also in liquid nitrogen and helium. Initially the experiments were done for thin layers of ZnSe/GaAs. The results were promising but lack of samples caused the termination of this research. In 1995 I spent five months in Physik Department E16 Technische Universitat Munchen, Germany in the frame of Tempus program. In Germany I gained the experience in photoluminescence measurements of semiconductors. The same year I get the position of assistant in Semiconductor Physics Group, NCU in Toruń and I started the research of A2B6 mixed crystals with photothermal methods. All the measured compounds were grown in my group. The possibility of changing the energy gap of these crystals allows to obtain the materials of strictly defined optical properties, the change of lattice constant allows to obtain the materials ideally fitted to the substrate. These advantages lead very often to take into account new multiple compounds. Theoretical predictions of their optical and thermal properties is impossible and that's why so called material must be based on experience and intuition.

In 1998 and 1999 I spent one month (each year), at the fellowships in the frame of the program for young researchers of NCU at Universita Degli Studi di Roma "La Sapienza", Dipartamento di Energetica in the group of prof. T. Papa. I performed there, the measurements of optical and thermal parameters of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ using photoacoustic spectroscopy. At this technique, very popular in photothermics, it is microphone which is used as a detector. These stays allowed me to compare the results of other photothermal technique but also to get an experience to construct the microphone cell for use in my lab in Toruń.

In my research before PhD. thesis I focused on the experiments concerning the influence of composition of the compounds on its optical and thermal properties, both in room liquid nitrogen and helium temperatures. As-grown and annealed samples were under the investigations and I observed for the first time, the influence of preparation processes on the character of amplitude and phase spectra. The nature of research was pioneering, the method not very popular, but there were very promising results. For the investigated crystals I determined the dependence of the energy gap value on the composition of magnesium and beryllium. The method proposed by Zegadi [1] and theory of Jackson-Amer [2] were used. I also proposed the method to determine the energy gap value from the phase photothermal spectra. I determined the values of thermal diffusivity for different concentrations of Be in $Zn_{1-x}Be_xSe$ and $Zn_{1-x}Be_xTe$ mixed crystals. Thermal diffusivity is an important parameter which characterizes semiconductors. Its value is proportional to thermal conductivity and similarly to energy gap it clearly defines the material. Reciprocal of thermal diffusivity is a coefficient of temperature equalizing and has a great importance in constructing of semiconducting devices. Determination of optical and thermal parameters of these semiconductors is very important as they are new materials of unknown properties. I examined the dependence of the construction of piezoelectric photothermal cell on the course of amplitude and phase spectra and the influence of thermal treatment (annealing) for $Zn_{1-x}Mg_xSe$,$Zn_{1-x}Be_xSe$ and $Zn_{1-x}Be_xTe$. The subjects of my research were also CdSe, Cde and $Cd_{1-x}Mg_xSe$.

In 2001 I completed my PhD. thesis "Photoacoustic phenomena in A2B6 mixed crystals".

Afer PhD. :

In 2002 I get the position of adjunct (associated professor) at Department of Semiconductor and Carbon Physics, NCU in Toruń. I develop and continue my research on photothermal methods of A2B6 semiconductors.

In 2003 was coordinator of KBN-DAAD program of common support of personal exchange connected with the realization of research projects: "Correlation of local thermal and electronic transport properties with local optical spectroscopic parameters of semiconductor materials with defect structures". In the frame of this program me and my colleagues visited the group of prof. J Pelzl in Ruhr-Universität in Bochum, German scientists were our guest in Toruń. One of the aims of our cooperation was to use infrared photothermal radiometry (PRT) for the investigation of optical and thermal parameters of A2B6 semiconductors. PRT offers the simple, contactless method of sample temperature determination. Simultaneous measurements made by classic photoacoustic detection (with microphone) and infrared radiometry conducted in the conditions, where the excitation takes place form the opposite side then the detection – they allow determination both thermal diffusivity and thermal effusivity. The comparison of photothermal and radiometric signals gives the information about thermal emissivity of the material.

In the further investigations in Toruń I focused on the interpretation of the obtained piezoelectric spectra. It was strengthened by the cooperation with dr. Mirosław Maliński (now dr. hab. prof TUK) of from Technical University in Koszalin. New models, proposed thanks to the cooperation allowed new interpretations of the experimental results for various materials and composition of components. We began experiments with new construction of piezoelectric cell giving possibility to carry the measurements in *front* and *reverse* configurations, the construction without the drawback of the previous ones and giving new possibilities. New experiments also concerned the influence of surface preparation processes for the course of amplitude and phase of photothermal spectra.

In years 2007/2008 I got a one your postdoctoral position funded by Centre National de la Recherche Scientifique in Laboratoire d'Acoustique de l'Universite du Maine, Le Mans, France in the group of prof. Vitalij Gusev. The subject of my stay was the imaging and characterization of the surface defects of metals with nonlinear acoustics and photoacoustics. In my research I applied the technique of mixed frequencies based on the generation of acoustic and thermal waves thanks to two light sources (two laser of the same wavelength) which intensity is modulated with two different frequencies. Thanks to it, in the imaging of the sample surface (scanning of the surface in plane *XY*) one can apply the linear or nonlinear component. The method could be used as an optic one when interferometry or deflectometry is used for detection. The vibrations of the defect can also be excited by high power piezoelectric element. It could be applied for every light absorbing materials covering surface defect or like in the case of metals – prepared artificially cracks or fractures.

After my return to Poland I continued of A2B6 mixed crystals investigations, mainly $Zn_{1-x-y}Be_xMg_xSe$ and $Zn_{1-x-y}Be_xMn_xSe$. The goal was to investigate and interpret the experiment results for the samples after the mechanical (grinding, polishing), chemical (etching) and thermal (annealing) treatment. Besides the interpretations usually used, based on modified Jackson-Amer and interference models, I proposed applying new model based on Blonskij's [3] and Frenelius' [4] models, not used in photothermal spectroscopy yet. The last investigations were the base to write the monograph, which I present as my main achievement in habilitation process. In point 4, I described and indicated the results associated with it.

I'm the author of 56 articles in reviewed journal and 4 in conference materials, the result of my research were presented in 33 scientific conferences and 3 educational ones. I was the head of two KBN grants and four grands of NCU. Between 2002 and 2011 I was the member of program committee of Workshop on Photoacoustic and Photothermics, my scientific activity was six times awarded be rector of NCU (group awards). I was the promoter of four thesis (two MSc. and two bachelor).

The list of my articles and information about educational achievements, international cooperation and science popularization are enclosed in the attached list.

[1] A. Zegadi, M. A. Slifkin, D. Djamin, A. E. Hill and R. D. Tomlinson Phys. Stat. Sol (a) 133, 533 (1992)
[2] W. Jackson, N.M. Amer, J. Appl. Phys. 51, 3343 (1980).
[3] I.V. Blonskij, V.A. Tkhoryk, M.L. Shendeleva, J. Appl. Phys. 79, 7, 3512 (1996).
[4] N. Fernelius, J. Appl. Phys. 51 (1), 650 (1980).