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Local structure around Mn atoms in the inclusions in the semiconductor matrices

Anna Wolska

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1. Name

Anna Wolska

2. Scientific degrees

M.Sc. eng.

Warsaw University of Technology, Faculty of Technical Physics and Applied Mathematics, 1997

master thesis *"The application of numeric methods of spatial filtering in the correction of some selected defects of photographic pictures"* supervised by Ph.D. eng. Maciej Sypek

Ph.D.

Warsaw University of Technology, Faculty of Physics, 2001

Ph.D. thesis *"Studies of the electronic structure of the semiconductor crystals in the Cu-In-Se system by the x-ray absorption method"* supervised by prof. dr hab. Rajmund Bacewicz

3. Employment and research experience

1997-2001	Ph.D. studies at Faculty of Physics, Warsaw University of Technology
1998 - present	beamtimes (average 2-3 times a year) in the synchrotron laboratories in Germany, Sweden, France
1999 February-July	Erazmus-Sokrates scholarship at the Laboratoire de Mineralogie-Cristallographie de Paris (university Paris VI) France
2002 - present	Institute of Physics PAS, Warsaw
2002 - 2005	post-doc at Advanced Light Source granted by University of Nevada, Las Vegas (*UNLV*), United States

4. Bibliometric indicators according to Web of Science database

9 - Hirsch index

48 - number of publications indexed in the Web of Science database

243 - number of citations according to Web of Science database (26 April 2013[1])

98 - total *impact factor* of the publications[2]

[1] Current information can be found at Researcher ID: http:/www.researcherid.com/rid/A-5818-2012

[2] Index values are taken from the publication year except the papers from 2012 and 2013 where the values from 2011 were used.

5. Main scientific achievement

The main scientific achievement according to the provisions (*art.16 ust. 2 ustawy z dnia 14 marca 2003 r. o stopniach naukowych i tytule naukowym oraz o stopniach i tytule w zakresie sztuki - Dz. U. nr 65, poz. 595 ze zm.*) consists of 9 publications under a title:

Local structure around Mn atoms in the inclusions in the semiconductor matrices

Publications with the declarations of co-authorship and described habilitant's input are gathered in zał. 4.

H-1. **A. Wolska**, K. Lawniczak-Jablonska, M.T. Klepka, M.S. Walczak, A. Misiuk, *"Local structure around Mn atoms in Si crystals implanted with Mn^+ studied using x-ray absorption spectroscopy techniques"* Phys. Rev. B 75 (2007) 113201

H-2. **A. Wolska**, K. Lawniczak-Jablonska, S. Kret, P.Dłużewski, A. Szczepańska, M.T. Klepka, M.S. Walczak, Y. Lefrais, M. J. Hÿtch, A. Misiuk, *"Atomic order in magnetic inclusion of Mn in Si crystal: XAS and TEM studies"* J. Non-Cryst. Solids 354 (2008) 4189

H-3. **A. Wolska**, M.T. Klepka, K. Lawniczak-Jablonska, D. Arvanitis, A. Misiuk *"Structural and magnetic properties of Mn^+ implanted silicon crystals studied using X-ray absorption spectroscopy techniques"* Radiat. Phys. Chem. 80 (2011) 1119

H-4. **A. Wolska**, K. Lawniczak-Jablonska, M.T. Klepka, R. Jakiela, J. Sadowski, I.N. Demchenko, E. Holub-Krappe, A. Persson, D. Arvanitis *"XANES studies of Mn K and $L_{3,2}$ edges in the (Ga,Mn)As layers modified by high temperature annealing"* Acta Phys. Pol. A 114 (2008) 357

H-5. K. Lawniczak-Jablonska, **A. Wolska**, J. Bak-Misiuk, E. Dynowska, P. Romanowski, J. Z. Domagała, R. Minikayev, D. Wasik, M. T. Klepka, J. Sadowski, A. Barcz, P. Dluzewski, S. Kret, A. Twardowski, M. Kamińska, A. Persson, D. Arvanitis, E. Holub-Krappe, A. Kwiatkowski, "*Structural and magnetic properties of MBE grown MnSb layers on GaAs substrates"* J. Appl. Phys. 106 (2009) 083524

H-6. **A. Wolska**, M.T. Klepka, K. Lawniczak-Jablonska, J. Sadowski, A. Reszka, B.J. Kowalski *"MnSb inclusions in the GaSb matrix studied by X-ray absorption spectroscopy"* Radiat. Phys. Chem. 80 (2011) 1026

H-7. K. Lawniczak-Jablonska, **A. Wolska**, M.T. Klepka, S. Kret, J. Gosk, A. Twardowski, D. Wasik, A. Kwiatkowski, B. Kurowska, B. J. Kowalski, J. Sadowski *"Magnetic Properties of MnSb Nano-inclusions Formed in GaSb Matrix Directly During MBE Process"* J. Appl. Phys. 109 (2011) 074308

H-8. **A. Wolska**, K. Lawniczak-Jablonska, M.T. Klepka, A. Barcz, A. Hallen, D. Arvanitis, *"Study of the local environment of Mn ions implanted in GaSb"* Acta Phys. Pol. A 117 (2010) 286

H-9. **A. Wolska** in "Ion Implantation", edited by M. Goorsky, InTech (2012) p. 105, http://www.intechopen.com/books/ion-implantation

The second half of the twentieth century can be called the era of electronics. Electronic devices are getting smaller and faster. According to the empirical Moore's law the number of transistors in integrated circuits doubles approximately every 1.5 years. However, the classical electronics fast approaches the boundary set by nature itself. Further miniaturization of the transistors and memory cells will meet no only technical problems in the manufacturing but also the physical limits caused by the quantum effects emerging with the stepping down to the nanometric scale.[3] Further development requires a qualitative change in the methods of the processing and storing information.

It is expected that the alternative would be the spin electronics (spintronics) where beside a charge also a spin of electron would be used. It is predicted that such devices not only will be faster but also more energy-efficient. However, the main key to the success lays in finding an appropriate material to construct spintronic elements. In such materials band structure should strongly depend on the spin polarization of the electrons, an injection of the spin polarized electrons should be considerably easy, moreover, they should be easily incorporated into typical integrated circuits. However, above all, if they are planned for commercial use, they have to possess these properties at room temperature. Despite years of research on different types of compounds, this kind of material is not found yet. Nevertheless, the diluted magnetic semiconductors (DMS) are seen as promising materials for such task. Research on the DMS have been conducted at IP PAS already in late 1970s and 1980s.[4,5] In the next decade ferromagnetic properties of the GaAs doped with manganese[6] were discovered which resulted in still existing interest in this material.

In 2000 Dietl et al.[7] theoretically determined expected values of Curie temperature (T_C) for semiconductors doped with 5% of manganese. It appeared that for some of them T_C can reach above 300 K. This report stimulated growth of interest and increased attempts leading to the synthesis of new DMS materials with manganese.

However, production of the material with the ferromagnetic properties is only the first step. It is also important to determine their source, check if it does not originate from the precipitations or contaminations by the ferromagnetic metals. The material properties depend on its structure; therefore, it is extremely important to fully characterize new material. A perfect tool allowing to determine the local structure around the dopants is a synchrotron radiation absorption. The main advantage of this technique is an elemental selectivity. It means that even in the very complex compounds, by tuning the energy to the given absorption edge, one can obtain information about

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[3] H. Akinaga, H. Ohno *"Semiconductor Spintronics"* IEEE Transactions on Nanotechnology 1 (2002) 19

[4] R.R. Galazka *"Semimagnetic semiconductors Proc. 14th Int. Conf. on Physics of Semiconductors" (Edinburgh, 1978)* ed B L H Wilson (Bristol: Institute of Physics Publishing) 43 (1979) 133

[5] T. Story, R.R. Galazka, R.B. Frankel P.A. Wolff *"Carrier-Concentration-Induced Ferromagnetism in PbSnMnTe* Phys. Rev. Lett. 56 (1986) 777

[6] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, Y. Iye *"(Ga,Mn)As: A new diluted magnetic semiconductor based on GaAs"* Appl. Phys. Lett. 69 (1996) 363

[7] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand *"Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors"* Science 287 (2000) 1019

the local surrounding of a chosen element. This technique is not destructive and can be used to the samples with crystalline, microcrystalline or amorphous structure. What's more, modern detectors allow to gather signal even for the low concentration of the investigated element. Due to this reason, X-ray absorption has been widely applied to the study of the doped and diluted compounds. Data analysis allows to obtain the information about the local surrounding around the absorbing atom even up to radius of 10 Å for well ordered materials, however, usually the fitting is performed in the range up to 6 Å. In case of the materials with high disorder or amorphous the fitting range is getting smaller and very often it is limited to the first sphere only, but it still delivers unique information about the coordination of the given element. During the measurements the data are gathered for all atoms of the investigated element excited by the synchrotron radiation, therefore, it delivers the average information for a given area of the sample. Obtained information is usually representative for whole sample. If the atoms are in several chemical states, proper analysis still can deliver information about the percentage of each crystallographic phase in the compound.

The X-ray absorption spectrum is being usually divided into two regions: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). As a theoretical border between the ranges ~50eV above the edge is usually given, however in practice it depends on the investigated material and the edge type. In case of EXAFS, especially for the K edge, the tools for analysis are quite well developed. By using one of many programs and fitting the realistic model one can obtain information on the type and number of the nearest neighbors, their distances to the absorbing atom and their local disorder. However, the information about the angles between the atoms cannot be resolved. The main challenge in the EXAFS analysis is a determination of the right model and interpretation of the fitting parameters.

XANES region also contains information about number, type and the distances to the neighboring atoms, but it is also very sensitive to the spatial arrangements of the atoms. However, resolving this information is usually very complicated. There is no simple recipe telling how to analyze XANES spectra. The way depends on the investigated material, amount of information available and searched. For example by comparing the edge position for a given element in an investigated compound with the edge positions for its oxides one can determine its oxidation level. By using the linear combination analysis it is also possible to find out the percentage of the reference phases in the mixed compound. Another analysis strategy is to assume structure of the investigated material, build appropriate cluster, calculate the absorption spectrum and compare it with the experimental one. This strategy is not yet commonly used but it is under growing attention and several groups are working on the development of the calculation methods. Like in EXAFS, also here the main challenges are to select and built the realistic model and to make the interpretation of the results which requires experience and skills.

Another useful technique is X-ray Magnetic Circular Dichroism (XMCD). The measurements are conducted by change in the direction of the radiation circular polarization or change of the magnetic field direction. Presence of the external magnetic field activates the spin selection rules which leads to the differences in the absorption spectra gathered for both field

directions, visible for the elements with magnetic moment. XMCD is the only experimental method allowing to detect whether investigated element is a source of magnetic properties.

Described above unique methods using the absorption of the synchrotron radiation were utilized by me in order to determine a local structure around manganese atoms in selected semiconductors.

Silicon implanted with manganese ions

Investigations on the silicon crystals implanted with the 3d metals and rare earth ions have been developed already in 1990s. However, the Mn ions induced more interest only in 2005 when Bolduc et al.[8] reported that silicon crystals implanted with manganese can be ferromagnetic with Curie temperature above 400 K. What's more, this property seemed do not depend on the manganese concentration or the annealing processes. The authors, based on the magnetization measurements, proposed model with ferromagnetic exchange mediated by holes, however, they also underlined the necessity of structural investigations in order to check the possibility of the crystallites or other phase formation. On the other hand, Dubroca et al.[9] showed that the implantation of the silicon crystals with other nonmagnetic ions, like silicon or argon, can also lead to the production of the materials with ferromagnetic properties. These papers stimulated also my interest in this material.

I started my research on the silicon implanted with manganese ions from the samples implanted on the warm substrate (silicon wafer grown by floating zone method) and cold substrate (silicon wafer grown by Czochralski method).[10] I published the results in H-1 which is the first paper where, for this kind of samples, the local neighborhood around the Mn atoms was investigated directly by the X-ray absorption method.

Analysis of the XANES spectra for new compounds requires choosing and checking different strategies appropriate for the gathered data. In the first step, by using the standard spectra of the manganese oxides and manganese foil, I excluded the presence of the oxides and metallic Mn. In the further analysis I used a program ab-initio calculating the XANES spectra with the real space multiple scattering method. Among the input data one should give the Cartesian coordinates of all atoms around the central atom in radius of 7 Å at least. In my calculations I used 10 Å radii clusters, consisting of 300-400 atoms, depending on the structure. First, I checked models with the ordered structures, i.e. manganese built into the silicon crystalline structure. By using structural data of silicon I created a cluster where central Mn atom was in the substitutional position and several clusters where central Mn atom was located in the

[8] M. Bolduc, C. Awo-Affouda, A. Stollenwerk, M.B. Huang, F.G. Ramos, G. Agnello, V.P. LaBella *"Above room temperature ferromagnetism in Mn-ion implanted Si"* Phys. Rev. B 71 (2005) 033302

[9] T. Dubroca, J. Hack, R. E. Hummel, A. Angerhofer *"Quasiferromagnetism in semiconductors"* Appl. Phys. Lett. 88 (2006) 182504

[10] The samples investigated by me were produced in ITE.

interstitial positions. I did not find out any correlation with the experiment, therefore in the next step, I tested the models of the silicon-manganese inclusions. The structural data of the Mn_xSi_y compounds found in the literature allowed me to create the clusters for them and perform the calculations. Simulations showed that the Mn atoms are not built into the silicon matrix in the substitutional nor interstitial way. I also excluded the presence of the regular Mn_xSi_y inclusions.

In the FT EXAFS spectra (Fourier transformed to the real space) clearly distinguished is only the first coordination sphere which confirmed a lack of the long range order around the Mn atoms implied by the XANES analysis. This conclusion was taken into account during the creation and testing of the fitting models. EXAFS analysis allowed to quantitatively determine local surrounding around the Mn atoms, which appeared to depend on the implantation procedure. In the sample implanted on the warm substrate in the closest Mn neighborhood among ~7 Si atoms I also discovered ~1.5 of Mn atoms[11]. In the samples implanted on the cold substrate the Mn atoms are surrounded only by ~6 to ~7 Si atoms. Magnetization measurements[12] showed that T_C of the sample implanted on warm substrate, where Mn atoms were observed in the central atom neighborhood, is above 300 K. Two other samples showed weak ferromagnetic ordering at the temperature close to 5 K.

Big advantage of the XANES and EXAFS techniques is an ability to resolve the local surrounding of the chosen element. However, they don't give the information whether the atoms are distributed homogeneously through the sample or form the inclusions. Therefore, I took into consideration microscopy methods as well. Thanks to the HRTEM (High Resolution Transmission Electron Microscopy) investigation and EELS (Electron Energy Loss Spectroscopy) mapping, it was confirmed that in the sample implanted on the warm substrate the Mn atoms are grouped in the inclusions of the 5 nm diameter.

EXAFS analysis pointed out that there exists local disorder around the Mn atoms, but it also delivered the information about type, distance and number of the closest neighbors. Using these data I wrote a program which allowed to modify the model (MnSi structure) accordingly. Obtained clusters with vacancies and repositioned Mn neighbors allowed to perform precise simulation of the XANES spectrum, which finally confirmed that in the sample implanted into warm substrate the Mn atoms tend to form Mn-Si clusters with low manganese content. [H-2]

I conducted more complex research on the dependence between technological processes and local structure around the Mn atoms on three series of samples which were implanted on the cold substrate (silicon wafer grown by Czochralski method) and warm substrate (two types of substrates - silicon wafers grown by floating zone and by Czochralski method). The samples were annealed at the temperatures from 275 to 1000 °C under atmospheric or high pressure. [H-3] I did not observe significant differences induced by the annealing time or the pressure. The key factor influencing the local Mn surrounding was the annealing temperature. EXAFS analysis showed

[11] This is the average value that can illustrate the case where e.g. half on the Mn atoms has 2 and the other half has 1 neighboring Mn atom. This in average gives 1.5 of Mn atom for each central Mn.

[12] A. Misiuk, J. Bak-Misiuk, B. Surma, W. Osinniy, M. Szot, T. Story,J. Jagielski *"Structure and magnetic properties of Si:Mn annealed under enhanced hydrostatic pressure"* J. Alloys Compd.423 (2006) 201

that in part of the investigated samples around the Mn atoms only first sphere consisting of the Si atoms is formed. In the samples annealed at higher temperatures also second shell consisting of the Mn atoms appears. Performed analysis revealed that the temperature of the Mn-Si inclusion formation depends not on the substrate type but on its temperature during the implantation. In the samples implanted on the cold substrate the second shell is already completely formed after annealing at 450 °C. In the samples implanted on the warm substrate the second shell is partly formed after annealing at 600 ºC, but the temperature of 800 ºC is needed for its full formation. The formed crystallites belong to the group of compounds called the Nowotny phases or HMS (higher manganese silicides). Their Si/Mn ratio is between 1.70 and 1.75. Their lattice constant *a* is close to 5.5 Å while *c* changes from 17 to 118 Å. In spite of these differences the average local surrounding around the Mn atoms is so close to each other that the absorption analysis cannot distinguish them.

TEM (Transmission Electron Microscopy) and diffraction (XRD - X-ray Diffraction) measurements, in detail described in the P. Romanowski Ph.D. thesis[13] also showed that the substrate temperature during the implantation and the annealing temperature are the main factors influencing material's structure. In the case of the samples implanted into cold substrate the TEM images didn't show any inclusions for the sample annealed at 340 ºC and its diffractogram didn't show any additional reflexes in respect to the "as-implanted" sample. For the sample annealed at 600 ºC in the TEM images there were weakly visible inclusions and equally weak reflex connected with the Mn_4Si_7 phase in the diffractogram. For the sample annealed at 800 ºC the inclusion with the size of 30 nm was clearly visible, where the interplanar distances correspond to the tetragonal Mn_4Si_7. The EDX (Energy-Dispersive X-ray Spectroscopy) microanalysis confirmed that in this inclusion the Mn atoms are located. EXAFS analysis, due to the high sensitivity of the method, clearly shows that in both samples (annealed at 600 ºC and 800 ºC) the HMS phases were formed.

In case of the samples implanted into warm substrates (prepared with both methods), in the TEM analysis very small inclusions were visible already for the samples annealed at 340 ºC, 7-15 nm inclusions for annealed at 600 ºC and 20-30 nm for these annealed at 800 ºC. Diffractograms for these sets of samples show that the Mn_4Si_7 phase was formed after annealing at 600 ºC, but the strongest reflexes were visible for the samples annealed at 800 ºC which is in agreement with the tendencies indicated by the EXAFS analysis.

Some of the papers points towards the connection between the ferromagnetic properties and presence of the HMS inclusions, Zhou et al. [14] report the highest ferromagnetism for the samples with the inclusions of 11 nm, but these properties become weaker for the 6 and 15 nm inclusions. The authors explain that for the smaller inclusions crystalline structure is getting worse, while for

[13] Przemysław Romanowski *"Wpływ warunków wygrzewania na strukturę defektową krzemu implantowanego jonami manganu"* Ph.D. thesis, Institute of Physics PAS, Warsaw 2012

[14] S. Zhou, K. Potzger, G. Zhang, A. Mücklich, F. Eichhorn, N. Schell, R. Grötzschel, B. Schmidt, W. Skorupa, M. Helm, J. Fassbender, D. Geiger *"Structural and magnetic properties of Mn-implanted Si"* Phys. Rev. B 75 (2007) 085203

the bigger inclusions the bulk-like properties dominate. On the other hand, Yabuuchi et al.[15] postulate the presence of at least two types of the ferromagnetism sources, saying that one of them may be the 5-10 nm inclusions and linking them with the HMS phases with c equal to 4.8 nm ($Mn_{11}Si_{19}$) and 6.5 nm ($Mn_{15}Si_{26}$). In both papers, the inclusions were observed with the electron microscopy, their content was assumed from the EDX or XRD methods, and the magnetic properties were measured with SQUID (Superconducting Quantum Interference Device).

Magnetization results of the Si crystals implanted with Mn^+ ions performed at the IP PAS indicated that the ferromagnetic properties are detected in the samples annealed at low temperatures, [16,17] i.e. the samples where the HMS phases are not present. In order to verify if the Mn atoms are the source of the magnetic properties, I used the XMCD method which allows to check it experimentally. I performed the measurements at the $L_{3,2}$-Mn edges on the samples annealed at 275 °C where the strongest ferromagnetic properties were observed. Results didn't confirm the presence of the magnetic moment on the Mn atoms within the range of accessible magnetic fields and temperatures. [18] There is a possibility that the accessible magnetic field was too weak to order spin directions at room temperature. However, similar results were also obtained by Orlov et al.[19] Their measurements conducted at the K-Mn edge for the sample annealed at 850 °C with the HMS inclusion, did not detect the presence of the magnetic moment on the Mn atoms.[20] The results of the XMCD experiment can be also found in the report of Chow et al.[21] for the silicon implanted with manganese for four types of samples: "as-implanted" and annealed at 300 °C, 700 °C and 1000 °C. In none of the cases the dichroic signal was detected.

In view of frequently conflicting reports about properties of the silicon implanted with manganese ions, question on the observed ferromagnetism origin seems to be still open. My investigation showed that the differences in the local surrounding around the Mn atoms are not directly correlated with macroscopic magnetic properties. Also attempts of detection the presence of the magnetic moment on the Mn atoms by the XMCD method didn't succeed. Obtained results indicate that the ferromagnetic properties of the silicon implanted with manganese visible at room

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[15] S. Yabuuchi, Y. Ono, M. Nagase, H. Kageshima, A. Fujiwara, E. Ohta *"Ferromagnetism of Manganese–Silicide Nanopariticles in Silicon"* Jpn. J. Appl. Phys. 47 (2008) 4487

[16] A. Misiuk, a. Barcz, J. Bak-Misiuk, P. Romanowski, L. Chow, E. Choi *"Stress-mediated redistribution of Mn in annealed Si:Mn"* Mat. Science and Eng. B 159 (2009) 361

[17] V. Osinniy, A. Misiuk, M. Szot, K. Swiatek, J. Bak-Misiuk, A. Barcz, W. Jung, M. Prujszczyk, T. Story *"Magnetic properties of silicon crystals implanted with manganese"* Materials Science-Poland 26 (2008) 751

[18] I also conducted the XMCD measurements for the samples annealed at 450 ºC (Czochralski and floating zone) and 650 ºC (Czochralski) but the quality of the spectra was too low for drawing the conclusions.

[19] A.F. Orlov, A.B. Granovsky, L.A. Balagurov, et al. *"Structure, electrical and magnetic properties, and the origin of the room temperature ferromagnetism in Mn-implanted Si"* J. Exp. Theor. Phys. 109 (2009) 602

[20] The authors didn't describe the exact experimental conditions. However, they conducted it at the ID12 beamline (ESRF), where accessible magnetic field (6T) is much higher than at I-1011 beamline (MAX-lab) where I was doing my measurements (0.1T).

[21] L. Chow, A. Misiuk, C.W. Pao, D.C. Ling, W.F. Pong, J. Bak-Misiuk *"Synchrotron radiation study of Mn implanted silicon"* Synchrotron Radiation in Natural Science 8 (2009) 25

temperature do not originate from manganese ions. The analysis performed by Granowsky et al.[22] on their own data and the accessible reports leads to similar conclusions. The authors imply that the observed magnetic properties are caused by structural defects produced by the ion implantation. I also would like to underline that despite a literature search, I was not able to find any report showing the presence of the magnetic moment on the Mn atoms from the XMCD measurements for silicon crystals implanted with manganese ions.

MnAs inclusions

During the search for the compounds with potential use in spintronics, for a long time only the uniform materials such as $Ga_{1-x}Mn_xAs$[23,24] were investigated. However, despite considerable effort put into the elaboration of proper technology, this compound shows ferromagnetic properties only below room temperature - the highest reported Curie temperature is around 200 K.[25] Moreover, during the growth very often the ferromagnetic precipitations appears forming multiphase ferromagnetic material.[26] These precipitations were usually considered as a major drawback. However, this drawback can be used to prepare magnetic composite materials which consist of small ferromagnetic nanoparticles immersed into the semiconductor host lattice. Such a composite material can be considered as a good semiconductor filled with nanomagnets providing a built-in local magnetic field at room temperature.

Very important information about the $Ga_{1-x}Mn_xAs$ layers is to determine the localization of the Mn atoms since they influence the magnetic properties of the material. The Mn atoms subsituting the Ga atoms in the GaAs matrix act as acceptors and contribute to the ferromagnetic ordering. On the other hand, the Mn atoms located in the interstitial positions are donors and by a hole compensation reduce the ferromagnetic properties. EXAFS quite fast become the standard technique used for determining the local Mn surrounding in the $Ga_{1-x}Mn_xAs$ layers,[27] especially since it can distinguish substitutional and interstitial positions.[28] However, it cannot distinguish

[22] A. Granovsky, A. Orlov, N. Perov, E. Gan'shina, A. Semisalova, L. Balagurov, I. Kulemanov, A. Sapelkin, A. Rogalev, A. Smekhova *"Above Room Temperature Ferromagnetism in Si:Mn and $TiO_{2-\delta}$:Co"* Journal of Nanoscience and Nanotechnology 12 (2012) 1

[23] T. Hayashi, M. Tanaka, T. Nishinaga, H. Shimada *"Magnetic and magnetotransport properties of new III-V diluted magnetic semiconductors: GaMnAs"* J. Appl. Phys. 81 (1997) 4865

[24] J. Sadowski, J. Domagala, J. Bak-Misiuk, K. Swiatek, J. Kanski, L. Ilver, H. Oscarsson *"MBE growth and properties of GaMnAs(100) films"* Acta Phys. Pol. A 94 (1998) 509

[25] L. Chen, X. Yang, F. Yang, J. Zhao, J. Misuraca, P. Xiong, S. von Molnár *"Enhancing the Curie Temperature of Ferromagnetic Semiconductor (Ga,Mn)As to 200 K via Nanostructure Engineering"* Nano Lett. 11 (2011) 2584

[26] K.Ando, A. Chiba, H. Tanoue *"Uniaxial magnetic anisotropy of submicron MnAs ferromagnets in GaAs semiconductors"* Appl. Phys. Lett. 73 (1998) 387

[27] R. Shioda, K. Ando, T. Hayashi, M. Tanaka *"Local structures of III-V diluted magnetic semiconductors $Ga_{1-x}Mn_xAs$ studied using extended x-ray-absorption fine structure"* Phys. Rev. B **58** (1998) 1100

[28] R. Bacewicz, A. Twarog, A. Malinowska, T. Wojtowicz, X. Liu, J.K. Furdyna *"Local structure of Mn in (Ga,Mn)As probed by X-ray absorption spectroscopy"* J.Phys. Chem. Solids 66, 2004 (2005).

type of the interstitial position (i.e. the type of the nearest neighbors) because dispersion curves on the Ga and As atoms are very similar to each other.

In majority of papers presenting the X-ray absorption results, the XANES range is not analyzed too deeply or it is completely ignored. Therefore, I concentrated my attention on the XANES spectra analysis. I started my investigation of the MnAs inclusions in the GaAs matrix from the series of the $Ga_{1-x}Mn_xAs$ samples where the nominal Mn concentration was equal to 6% and 8%. [H-4] Each series was consisting of 3 samples: "as grown", the annealed at 500 °C and at 600 °C. The annealing was supposed to enforce forming of the MnAs inclusions, cubic at 500 °C and hexagonal at 600 °C.

Comparison of the XANES spectra shape for the annealed samples with the MnAs standard led to the conclusions that indeed the annealing procedure enabled forming of this kind of compound.[29] Then I focused my attention on the "as-grown" samples. I assumed 3 possible positions: Mn subsituting Ga, Mn in the intersitital position with the Ga or As surrounding. Comparison of the calculated and experimental XANES spectra didn't show clear similarities to any of them. It means that the Mn atoms are located at least in two crystallographic positions and the measured spectrum is a weighted sum of inputs from all positions. It is possible to unravel this by using the linear combination analysis. However, for this kind of analysis one should have spectra of the standards which are not possible to be grown in this case. Therefore, I proposed new solution, not applied so far in the literature. Instead of the experimental I used the calculated standard spectra for three manganese locations: (1) all Mn atoms located in the subtitutional position, (2) all Mn atoms located in the interstitial position with the Ga atoms as the first neighbors, (3) all Mn atoms located in the interstitial position with the As atoms as the first neighbors. Using such standards in the linear combination analysis, I determined that less than 50% of the Mn atoms substitute the Ga atoms, while the rest is located in the interstitial positions with the Ga atoms as the nearest neighbors. I confirmed the results of the K-Mn edge analysis by the analysis of the L_3-Mn edge, showing that not only weakly localized p-states but also strongly localized d-states are sensitive to the localization of the Mn atoms in the GaAs crystalline structure.

Information about manganese position in the "as-grown" samples is very important since, according to our further research, it influences the type of inclusions appearing after the annealing.[30,31] Subsequent investigations on the MnAs inclusions in the GaAs matrix (not included into the habilitation) allowed to determine that they crystallize in the hexagonal and cubical Z-B structure and usually both types of inclusions are present simultaneously. As a result,

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[29] More detailed analysis of the annealed samples is shown in the later papers which are not included in the habilitation.

[30] K. Lawniczak-Jablonska, J. Bak-Misiuk, E. Dynowska, P. Romanowski, J.Z. Domagala, J. Libera, **A. Wolska**, M.T. Klepka, P. Dluzewski, J. Sadowski, A. Barcz, D. Wasik, A. Twardowski, A. Kwiatkowski *"Structural and magnetic properties of nanoclusters in GaMnAs granular layers"* Journal of Solid State Chemistry 184 (2011) 1530

[31] K. Lawniczak-Jablonska, J. Libera, **A. Wolska**, M.T. Klepka, P. Dluzewski, J. Bak-Misiuk, E. Dynowska, P. Romanowski, J.Z. Domagala, J. Sadowski, A. Barcz, D. Wasik, A. Twardowski, A. Kwiatkowski *"Structural and magnetic properties of GaAs:(Mn,Ga)As granular layers"* Phys. Stat. Sol. B 248 (2011) 1609

at room temperature the GaAs:(Mn,Ga)As materials tend to show magnetic properties from ferromagnetic to superparamagnetic depending on the size, structure and the Mn concentration in the inclusions.[32] It introduces significant problems to the controlling of the material parameters.

In H-4 I showed for the first time in the literature that the XANES spectra analysis delivers additional information about the Mn atoms' surrounding which allows to distinguish the interstitial position with the Ga or the As atoms as the nearest neighbors and make the EXAFS analysis complete. It also allowed to determine the percent of the Mn atoms in each crystallographic position. I calculated the XANES spectra utilizing the real space multiple scatterings method. Later simulation made by Goncharuk et al.[33] with the FLAPW (full potential linearized augmented plane wave) method in the k space confirmed that XANES spectrum is sensitive to the type of the interstitial position independently on the calculation method.

MnSb inclusions

While planning to obtain composite material, ferromagnetic at room temperature, using the compound with high T_C, e.g. MnSb, seems to be a good idea. It was shown that bulk MnSb has a T_C of 587 K[34] while for MnAs it is only 318 K. Moreover, the $Mn_{1-x}Sb_x$ layers grown on the GaAs substrate can reach a T_C of 620 K.[35]

We started our research from the reference material, i.e. the MnSb thin layers grown by the MBE (molecular beam epitaxy) method on the GaAs(111) and GaAs(100) substrates. I conducted XANES and EXAFS analysis at the K-Mn edge confirming that the layers' structures correspond to the structure of the standard MnSb powder. XMCD measurements were carried out at the $L_{3,2}$ - Mn and $M_{5,4}$ -Sb edges. They showed the presence of the magnetic moment on the Mn and Sb atoms at low (~100 K) as well as at room (~300 K) temperature. Application of the spin sum rule allowed me to calculate the values for spin and orbital moments on the Mn atoms at both temperatures. Obtained values were subsequently corrected to account for the overlap of the Mn $2p_{1/2}$ and Mn $2p_{3/2}$ levels. The next correction compensated the influence of too low magnetic field which made impossible to reach full saturation. Finally, it appeared that the value of orbital moment found from experiment (0.45 μ_B/atom) was strongly increased versus the theoretical predictions (0.1 μ_B/atom). It seems quite important because an enhanced orbital moment often

[32] K. Lawniczak-Jablonska, J. Libera, **A. Wolska**, M.T. Klepka, P. Dluzewski, J. Bak-Misiuk, E. Dynowska, P. Romanowski, J. Sadowski, A. Barcz, D. Wasik, A. Twardowski, A. Kwiatkowski, K. Sato *"The source of room temperature ferromagnetism in granular layers with cubic (Mn,Ga)As clusters"* Phys. Status Solidi RRL 5 (2011) 62

[33] N.A. Goncharuk, J. Kučera, L. Smrčka *"Pre-edge XANES structure of Mn in (Ga,Mn)As from first principles"* Chem. Met. Alloys 2 (2009) 34

[34] A.F. Panchula, C. Kaiser, A. Kellock, S.S. Parkin *"Spin polarization and magnetotransport of Mn–Sb alloys in magnetic tunnel junctions"* Appl. Phys. Lett. 83 (2003) 1812

[35] H. Akinaga, K. Tanaka, K. Ando, T. Katayama *"Fabrication and magneto-optical properties of epitaxial ferromagnetic $Mn_{1-x}Sb$ thin films grown on GaAs and sapphire"* J. Cryst. Grow. 150 (1995) 1144

creates increased opportunities for magnetic applications in the low dimensional limit, as it is often linked with an enhanced magnetic anisotropy in surfaces and interfaces.

SEM (scanning electron microscopy) and AFM (atomic force microscopy) imagining showed that even in a pure MBE layer, MnSb doesn't form a uniform surface but it tends to form big pseudo-islands and columns. This indicated towards the natural tendency of the material to form the inclusions. [H-5]

Attempts to obtain the inclusions, in the same way as in the GaMnAs, i.e. through the annealing of the layers didn't bring the expected results. After many tests, finally the hexagonal MnSb inclusions were formed directly during the growth without a necessity for additional annealing. [H-6] EDX mapping (not shown in the paper) confirmed that the Mn atoms are located in the inclusions. Careful analysis of the SEM images of the MnSb inclusions grown on the GaSb(100) and GaAs(111)A substrates at 450 ºC and 520 ºC showed that their size becomes slightly bigger with the higher substrate temperature while their shape strongly depend on the type of the substrate. The inclusions on the GaAs(111)A substrates are long and thin while on the GaSb(100) substrates are shorted and thicker, square or rectangular. The percentage of the Mn atoms strongly influences inclusions' density but not their size. XANES and EXAFS analysis showed that the Mn atoms form hexagonal MnSb compound and do not have tendency to build into the GaSb matrix forming cubic GaMnSb alloy.

Further research on the magnetic properties showed that according to the predictions the inclusions are ferromagnetic at room temperature. Moreover, we observed very interesting behavior, i.e. dependence of the easy magnetization axis direction on the used substrate type. In case of the GaSb(100) substrates the direction of the easy magnetization axis is close to 30° (to the sample surface) while for the GaAs(111)A substrate it is close to 70°. [H-7] Such anisotropy we had observed in the XMCD as well as in the MFM (magnetic force microscopy) experiment.

Despite of many attempts, formation of considerably smaller inclusion was not achieved with the MBE method. Therefore, we decided to test the implantation method in order to obtain the MnSb nanoinclusion in the GaSb matrix. While we were starting research, there were only few papers concerning the Mn ions implantation into GaSb crystals. [36] It caused the necessity to try many procedures of producing these materials. We started from low ion doses and energies. Already first tests allowed to draw some conclusions. Detailed analysis of the EXAFS results showed that the nearest neighbors of the Mn atoms are the Ga atoms. It appeared that the implantation process removed the Sb atoms from the matrix in the Mn surrounding and as a result the distances to the subsequent Ga spheres became shorter. The areas formed in this way consist of the Ga-Mn compound in the F-43m cubic structure characteristic for GaSb but not common for the Ga-Mn alloy. [H-8] Magnetic measurements revealed that these samples are showing weak ferromagnetic properties independent on the temperature in the range of 30 - 300 K. Our analysis

[36] Ch. Chen, N. Chen, L. Liu, J. Wu, Z. Liu, S. Yang, Ch. Chai *"$Ga_{1-x}Mn_xSb$ grown on GaSb with mass-analyzed low-energy dual ion beam deposition"* J. Cryst. Growth 279 (2005) 272 and the next reference

can explain the results of Zhang et al.[37] for the samples implanted with low-energy Mn ions. With the MFM they observed ferromagnetic nanoclusters, while the XRD didn't show the existence of the other phase, which means that their structure was close to that of GaSb. With high probability it can be assumed that they observed the inclusions of the type described by me in the paper H-8.

In the next tests higher energies and ion doses were applied together with the post-implantation processes like annealing at the Ar atmosphere or antimony vapors. In the latter case, together with antimony, oxygen was introduced which caused formation of the manganese oxides. The results indicated that more sophisticated procedures should be applied. Therefore, the co-implantation with noble gases was used. The aim was to make the matrix amorphous which was supposed to prevent the Sb atoms escape. Substrate temperature during the implantation was kept at 80 K. In additional tests in some of the samples beside the Mn^+ also the Sb^+ ions were implanted. Secondary ion mass spectrometry (SIMS) revealed that the new procedures indeed prevented the escape of the Sb atoms and the implantation of additional Sb^+ ions changed the profiles of the element distribution in the samples. However, these processes also introduced high amount of oxygen. Analysis of the X-ray absorption spectra revealed that the oxygen reacted with manganese forming the manganese oxides. It confirmed that the high vacuum free of oxygen is extremely important in the implantation process. Therefore, in the next tests we made an attempt to protect the surface of the implanted crystal with the Si_3N_4 layer. It didn't work in the expected way but it helped to outline the next step. Next experiments led to the conclusions that more promising is the implantation on the warm substrate because higher temperature help in the matrix recrystallization and close the diffusion channels for oxygen. [H-9]

The X-ray absorption measurements which I conducted for all the samples obtained from the test procedures clearly pointed out that manganese show higher chemical affinity towards gallium than antimony and formation of the MnSb inclusions through the implantation into the GaSb matrix can be very complicated if not impossible. Moreover, the SIMS depth profiles analyzed by me together with the X-ray absorption results revealed that the conclusions about the chemical state of an element drawn only from the similarity of the profiles are not valid. The confirmation of the phase formation should be made by different method, e.g. the analysis of the X-ray absorption spectra. I demonstrated that the X-ray absorption methods give the final proof on the bonding way of the dopants in the investigated material.

Analysis of the MnSb inclusions in the GaSb matrix showed that it is a good material to obtain the inclusions ferromagnetic at room temperature. It can be grown by the MBE method without a necessity for additional annealing. Moreover, this material shows magnetic anisotropy with the direction depending on the substrate type. The substrate type influences the shape of the inclusions as well, which was showed for the first time in the H-6. We also showed that the size of the inclusions can be, to some extent, controlled by changing the growth temperature.

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[37] F. Zhang, N. Chen, Z. Liu, Ch. Chai, S. Yang, J. Yang, J. Wu, L. Lin, F.D. Callaghan, T. Li, C.T. Foxon, C.A. Bates *"The Micro-Magnetic Structures of M^+ Ion-Implanted GaSb"* Jpn. J. Appl. Phys. 42 (2003) 3389

Research on the Mn based inclusions in different matrices conducted by me showed that it is possible to obtain semiconducting composite material ferromagnetic at room temperature. We confirmed that utilization of the compound with high Curie temperature, i.e. MnSb, is a right choice. X-ray absorption analysis allowed to connect the changes in the local structure around the Mn atoms with macroscopic properties of the investigated materials.

After many years of work on the new DMS materials, growing number of researchers starts to be aware of the fact that it is necessary to find out the real information about the dopants' bonding and locations since they are very often completely different from those predicted theoretically. This leads to wider appreciation of the novel methods of the material characterization, especially synchrotron based methods.[38] My publications are the examples of the application of the modern methods in determining location of the Mn atoms in the semiconductor matrices, using not only already classical EXAFS method, but also unconventional XANES analysis.

Results of my work are available in form of publications. I was also invited to write a book's chapter concerning the implantation. Moreover, I presented the results of my research on the inclusions with manganese in the form of seminars (3), conference lectures (4) posters (13) and in the scientific reports from the synchrotron experiments (12).

[38] T. Dietl *"A ten-year perspective on dilute magnetic semiconductors and oxides"* Nature Mater. 9 (2010) 965

6. Other scientific achievements

I defended my master thesis *"The application of numeric methods of spatial filtering in the correction of some selected defects of photographic pictures"* in January 1997 at the Faculty of Technical Physics and Applied Mathematics (Warsaw University of Technology). In March 1997 I started my Ph. D. study on the same faculty. At the same time I directed my interests towards solid state physics. During my first year I was working on the photoluminescence and optical absorption measurements on the Cu-In-Se materials. In 1998, for the first time, I was introduced to the synchrotron techniques due to the collaboration with Professor Krystyna Jabłońska from the Institute of Physics, PAS. At the same time, thanks to her, I was able to join the X-ray absorption experiments at the DCI and Super-ACO synchrotrons (LURE, Orsay). The power and versatility of this technique made such impression on me that few months later I applied for and obtained a Sokrates-Erazmus scholarship (February - July 1999) at the Laboratoire de Mineralogie-Cristallographie de Paris (Paris VI). I was under the supervision of Dr. Philippe Sainctavit who was also a beamline scientist at the beamline SU-23 (Super-ACO) and who helped me to learn about the everyday work at the synchrotron laboratory and introduced me into new techniques based on the absorption of the synchrotron radiation. After my return to Warsaw I didn't abandon synchrotron experiments. In 1999, 2000 and 2001 I participated in three beamtimes at the DORIS synchrotron ring (HASYLAB, Germany).

I defended my Ph. D. thesis *"Studies of the electronic structure of the semiconductor crystals in the Cu-In-Se system by the x-ray absorption method"* in December 2001. It obtained a distinction granted by the Scientific Council. Research included in the thesis were based on the measurements I conducted for low $L_{3,2}$-Se, $L_{3,2}$-Cu (beamline SU-22, Super-ACO) and high L_3-In, L_1-In, K-Se, K-Cu (A1 station, DORIS) energy edges.

In February 2002 I started work at the Institute of Physics PAS in Warsaw. From August 2002 till July 2005 I worked as a post-doc at the Advanced Light Source, Berkeley sponsored by University of Nevada, Las Vegas (USA). My main task was to supervise the construction and tests of the new soft X-ray emission spectrometer. I also joined into the projects carried out by my new group, i.e. photofragmentation[39] and non-dipole experiments.[40] However, I was still able to spend some time on conducting the X-ray absorption measurements for my group at IP PAS

[39] (a) MN Piancastelli, WC Stolte, R Guillemin, **A Wolska**, SW Yu, MM Sant'Anna, DW Lindle *"Anion and cation-yield spectroscopy of core-excited SF_6"* J. Chem. Phys. 122 (2005) 094312; (b) M. N. Piancastelli, W. C. Stolte, R. Guillemin, **A. Wolska**, D. W. Lindle, *"Photofragmentation of SiF4 upon Si 2p and F 1s core excitation: Cation and anion yield spectroscopy"* J. Chem. Phys. 128 (2008) 134309

[40] (a) O. Hemmers, R. Guillemin, D. Rolles, **A. Wolska**, D.W. Lindle, K.T. Cheng, W.R. Johnson, H.L. Zhou, S.T. Manson *"Nondipole effects in the photoionization of Xe 4d(5/2) and 4d(3/2): Evidence for quadrupole satellites"* Phys. Rev. Lett. 93 (2004) 113001; (b) O. Hemmers, R. Guillemin, D. Rolles, **A. Wolska**, D.W. Lindle, E.P. Kanter, B. Krassig, S.H. Southworth, R. Wehlitz, B. Zimmermann, V. McKoy, P.W. Langhoff, *"Low-energy nondipole effects in molecular nitrogen valence-shell photoionization"* Phys.Rev. Lett. 97 (2006) 103006

and coworkers from University of Alberta, Edmonton, Canada. I also worked as a beamline scientist during beamtimes reserved for the students from UNLV and IP PAS. Some of the results were published in the papers[41,42] and master thesis.[43]

After my return to IP PAS I focused on the X-ray absorption techniques and started research on the subject connected with ferromagnetism in the Mn doped materials. However, I didn't confine to these projects only. I have broadened my competences by taking part in the research on the other materials, e.g. $In_xAl_{1-x}N$ thin layers[44], hydrogen storage in Laves phases[45], chitosans[46] or metal-organic complexes[47].

I am a member of Polish Society of Synchrotron Radiation (PSSR) since 1998. In 2005 I had created and started maintaining a PSSR website and I was continuously doing it till October 2011. In 2010 I had prepared and was also working on the English version of the website.[48] During 2008-2011 I was working for the Society as a PSSR Board Member. In 2010 I also become a member of the International X-ray Absorption Society (IXAS) - the organization gathering the scientists from all over the world, interested in the X-ray absorption methods.

I was a secretary of the international conference *9th International School and Symposium on Synchrotron Radiation in Natural Science (ISSRNS)*, Ameliówka, 15-20 June 2008. The conference gathered more than 100 scientists and students from Poland and abroad.

I was a member of the Programme Committees in the conferences:

* VIII National Meeting of Synchrotron Radiation Users, Podlesice, 24-26 September 2009.

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[41] M. Klepka, K. Lawniczak-Jablonska, M. Jablonski, **A. Wolska**, R. Minikayev, W. Paszkowicz, A. Przepiera, Z. Spolnik, R. Van Grieken *"Combined XRD, EPMA and X-ray absorption study of mineral ilmenite used in pigments production"* Journal of Alloys And Compounds, 401 (2005) 281

[42] E. Piskorska, K. Lawniczak-Jablonska, R. Minikayev, **A. Wolska**, W. Paszkowicz, P. Klimczyk, E. Benko, *"Quantitative phase analysis of cubic boron nitride based composites by X-ray absorption near edge structure"* Spectrochim. Acta, Part B 62 (2007) 461

[43] Chirantha Prageeth Rodrigo *"Synthesis and characterization of strontium fluorapatite"* M.Sc. thesis, University of Nevada, Las Vegas 2005

[44] S. Kret, **A. Wolska**, M.T. Klepka, A. Letrouit, F. Ivaldi, A.Szczepańska, J-F. Carlin, N.A.K. Kaufmann, N. Grandjean *"TEM and XANES study of MOVPE grown InAlN layers with different indium content"* Journal of Physics: Conference Series 326 (2011) 012013

[45] M.T. Klepka, **A. Wolska**, K. Lawniczak-Jablonska, S. Filipek, R. Sato, V.Paul-Boncour, I. Marchuk *"EXAFS and XRD investigation of crystal structure in Cr doped YMn_2 deuterides"* Radiat. Phys. Chem. 80 (2011) 1019

[46] M.T. Klepka, K. Lawniczak-Jablonska, **A. Wolska**, A. Slawska-Waniewska, C.A. Rodrigues, A. Debrassi, C. Bordini *"Iron location in O-carboxymethyl chitosans determined by X-ray Absorption Spectroscopy"* Chem. Phys. Lett. 501 (2011) 523

[47] A. Drzewiecka, A.E. Koziol, M.T. Klepka, **A. Wolska**, H. Przybylinska, S.B. Jimenez-Pulido, K. Ostrowska, M. Struga, J. Kossakowski, T. Lis *"Synthesis and structural studies of novel Cu(II) complexes with hydroxy derivatives of benzo[b]furan and coumarin"* Polyhedron 43 (2012) 71

[48] Currently the website created by me can be seen on the new one in the "old_version" bookmark.

* 10th International Symposium and School on Synchrotron Radiation in Natural Science – ISSRNS-10, June 6-11, Szklarska Poręba, 2010.

* "IX National Meeting of Synchrotron Radiation Users", Warszawa, September 2011.

* "11th International School and Symposium on Synchrotron Radiation in Natural Science" Kraków - Tyniec, maj 2012.

In order to popularize the X-ray absorption techniques I took part in organization of the scientific workshop: *"Application of X-ray Absorption Technique for Determination of the Local Atomic and Electronic Structures of the Materials"* (13-15 November 2006, Warsaw). Judging that my lectures *"Basics of the X-ray absorption"* and *"FEFF code - modeling of XANES spectra"* can be useful for people wanting to start working on the data analysis I put them on my website.[49] I am also a coauthor of the chapter *"Absorption Spectroscopy of the X-ray Radiation"* in the script *"Synchrotron Radiation in the spectroscopy and structural research"* edited by B.J. Kowalski, W. Paszkowicz and E.A. Görlich. The main task of this book is to popularize synchrotron techniques among Polish scientists and students which became very important since the Polish synchrotron (SOLARIS) is being built. In my part of the script (also available on my website) I described and showed some examples on how to start XANES and EXAFS data analysis.

To the didactics and popularization of the absorption techniques I can add also a training of a student who was learning how to analyze EXAFS spectra by working on the enamel and dentine data gathered at the K-Ca edge. It resulted in a report: *"Synchrotron radiation absorption as a tool in determining local structure around the Ca atoms in the enamel and dentine"*. In 2011 I created and guided the exercise *"The world from atom's perspective - looking for local atomic surrounding by using synchrotron radiation"* in the workshop for gifted young students organized by the Polish Children's Fund (Krajowy Fundusz na Rzecz Dzieci).

Work at the Institute of Physics doesn't give many opportunities to work with students. However, the X-ray absorption methods deliver very important information which raises interests also among the Ph.D. students. Thanks to this my expertise completed the Ph. D. theses of Mieczysław Pietrzyk[50], Andreas Persson[51] and Przemysław Romanowski.[52]

I also served as a reviewer for subsequent journals: *Radiat. Phys. Chem. (3), Acta Phys. Pol. A (5), Phys. Rev. Lett. (2), J. Electron. Spectr. (1), Physica Status Solidi (1), Archives of Metallurgy and Materials (1).*

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[49] http://info.ifpan.edu.pl/~wolska/ bookmark "books"

[50] Mieczysław Pietrzyk *"Wkład otwartych powłok 3d i 4f do struktury elektronowej wybranych półprzewodników IV-VI z Mn, Gd i Eu"* Ph.D. thesis, Instytut Fizyki Polskiej Akademii Nauk, Warszawa 2009

[51] Andreas Persson *"X-ray Absorption Spectroscopy on Nano-Magnet Arrays and Thin Films"* Ph.D. thesis, Uppsala Universitet, Uppsala 2010

[52] Przemysław Romanowski *"Wpływ warunków wygrzewania na strukturę defektową krzemu implantowanego jonami manganu"* Ph.D. thesis, Instytut Fizyki Polskiej Akademii Nauk, Warszawa 2012

From beginning of 2009 till end of 2011 I was the head of the Group of X-ray spectroscopy and microanalysis at the Laboratory of X-ray and Electron Microscopy Research at the Institute of Physics PAS.

I was a main participant in a grant *"Magnetic composites based on MnSb for the future of nanoelectronics"* (2007-2010). List of the grants where I was a participant is gathered in enclosure 6 (zał. 6). From 2002 till 2012 I was a main proposer and a project leader of 7 synchrotron projects at the HASYLAB and MAX-lab laboratories. I was also leading the research in a 3-year project at HASYLAB and I was a participant in 11 projects leading by my coworkers (zał. 6). Having granted a beamtime and its financial support from EU is connected with the reporting duty which resulted in 33 scientific reports (3 during my Ph.D. studies) where I am a coauthor (zał. 5).

Obtained data and its analysis were presented by me or by my coworkers on the international conferences in Poland and abroad which resulted in 130 conference presentations in the form of orals and posters (10 during my Ph.D. studies). I am coauthor of 48 publications indexed in the Web of Science database and a coauthor of 8 publications in the papers not indexed in this database. I was also invited to write a chapter in a book *"Ion Implantation"* edited by Mark Goorsky which is a part of my habilitation.

As I mentioned before I have been taking part in the projects connected not only with the manganese inclusions. Many different subjects can be found in the list of papers and conference presentations (zał. 5). As the examples I will describe few cases showing versatility of the X-ray absorption technique.

Lithium-based conducting glasses are promising candidates for electrolyte materials of the thin-film batteries. However, at room temperature most of them exhibit relatively low ionic conductivity values. The increase of the conductivity can be achieved by adding some dopants. Since the properties of material depend on its structure, it is important to learn where the dopants are located. XANES measurements of the $Li_2Si_2O_5$ doped with vanadium were conducted at the K edge of vanadium. Pre-peak and edge analysis supported by empiric rules gathered in the paper of Chaurand et al.[53] determined the vanadium ionicity as equal to +4, +5 or intermediate which indicates that vanadium subsitutes silicon atoms. Theoretical XANES calculations confirmed that

[53] P. Chaurand, J. Rose, V. Briois, M. Salome, O. Proux, V. Nassif, L. Olivi, J. Susini, J.-L. Hazemann, J.-Y. Bottero *"New Methodological Approach for the Vanadium K-Edge X-ray Absorption Near-Edge Structure Interpretation: Application to the Speciation of Vanadium in Oxide Phases from Steel Slag"* J. Phys. Chem. B 111 (2007) 5101

the V atoms prefer the Si sites.[54]

During the X-ray absorption measurements we can tune energy to a specific absorption edge of a chosen element. If this element is in different chemical phases the obtained spectrum is a weighted sum of all of them. EXAFS analysis allows to determine these phases and their percentage. As an example, the ZnCoO layers grown by the atomic layer deposition method can be taken. The Co atoms were introduced into ZnO in order to obtain ferromagnetic material. Indeed, magnetic properties of the layer differ between themselves which is in correlation with the X-ray absorption results. The samples where the Co atoms substitute the Zn atoms forming a uniform layer don't exhibit ferromagnetic properties. In case of the samples with such properties, between two coordination spheres characteristic for ZnO, another peak appears which was identified as metallic Co input. EXAFS analysis revealed that in these samples around 1/4 of the Co atoms formed metallic inclusions changing magnetic properties of the samples. We didn't observe dependence between the inclusion formation and concentration of Co in the layer. [55,56]

The application, that seems the most interesting to me now, is to use full potential of XANES and EXAFS methods in order to determine the geometry of metal-ligand interaction in biological complexes. The binding mechanism of the ligands to metallic cation can influence the biological activity of the complexes. EXAFS analysis determines distances, type and number of the nearest neighbors which limits the quantity of the possible structural models. XANES region, in contrast to EXAFS, is very sensitive to the spacial arrangement of the neighboring atoms. Therefore, XANES calculations for the models pointed out by EXAFS help to choose the most probable among them. Conclusions drawn due to a correlation of the methods from the boundary of chemistry and physics allow to describe full structure of the investigated compound.

Together with my coworkers from the Institute we created a research team investigating such scientific problems. One of our publications[57] is a perfect example of the potential of this type of analysis. We presented three Cu(II) complexes with derivatives of phenoxyacetic or benzoic acid and thanks to the EXAFS and XANES analysis we showed that for each of them the local surrounding differs forming polyhedra with the planar square, tetragonal pyramid and tetragonal bipyramid geometry.

Part of the work on the synthesis of new compounds we perform at the Institute of Physics.

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[54] W. Paszkowicz, **A. Wolska**, M.T. Klepka, S. abd el All, and F.M. Ezz-Eldin, *"Combined x-ray diffraction and absorption study of crystalline vanadium-doped lithium disilicate"* Acta Physica Polonica A 117 (2010) 315

[55] **A. Wolska**, M.T. Klepka, B.S. Witkowski, M.I. Łukasiewicz, E. Guziewicz, M. Godlewski *"X-ray absorption fine structure investigation of the low temperature grown ZnCoO films"* Acta Phys. Pol. A 121 (2012) 883

[56] M.I. Łukasiewicz, A. Wójcik-Głodowska, E. Guziewicz, **A. Wolska**, M.T. Klepka, P. Dłużewski, R. Jakieła, E. Łusakowska, K. Kopalko, W. Paszkowicz, Ł. Wachnicki, B.S. Witkowski, W Lisowski, M Krawczyk, J W Sobczak, A Jabłoński, M. Godlewski *"ZnO, ZnMnO and ZnCoO films grown by atomic layer deposition"* Semiconductor Science and Technology 27 (2012) 074009

[57] M.T. Klepka, A. Drzewiecka, **A. Wolska**, W. Ferenc "*XAS studies on Cu(II) complexes with derivatives of phenoxyacetic and benzoic acids"* Chem. Phys. Lett. 553 (2012) 59

Results which we presented so far induced enormous interest and we got propositions of collaboration with laboratories in Lublin, Poznań and Wrocław. Now we are applying for the grants which enable us to develop our chemistry laboratory and create dedicated scientific workshop.

Using the X-ray absorption in the metal-organic research is a new application of this method, perfectly presents its versatility. Together with widening the field of application, the data analysis methods are also being under consideration. There had been created and are being developed programs which allow to fit the XANES spectra. This opens much more possibilities, which I am planning to use during the continuation of my work.